High Mobility Single-Crystalline-Like Si and Ge Thin Films on Flexible Substrates by Roll-to-Roll Vapor Deposition Processes

A Dissertation

Presented to

the Faculty of the Department of Mechanical Engineering

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in Materials Science and Engineering

by

Ying Gao

May 2016

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Acknowledgements

It is a great honor for me to thank those who made this dissertation possible.

Firstly, I would like to express my sincere gratitude to my supervisor - Prof. Venkat Selvamanickam, for generously granting me the opportunity to join his research group, providing me the strong support and invaluable guidance throughout my research, and creating many opportunities to attend conferences and get scholarships. I have been extremely lucky to have a supervisor who cared so much about students. With his incredible support and encouragement, I not only finished the dissertation, but also developed a personality which I used to be short of – persistence.

I also appreciate Dr. Jae-Hyun Ryou and Mojitaba Asadirad for their efforts in achieving high performance devices based on our optimized materials, which make my dissertation more systematically. I want to thank Dr. Pavel Dutta for his knowledge and insights in semiconductors which helped me go through a myriad of difficulties. Furthermore, I would like to thank Sicong Sun for equipment drawings and some assistant work, Yao Yao (female) for buffer layers supply, Dr. Eduard Galstyan for the TEM work and George Pope for system maintenance. Without their assistance, it is difficult for me to finish this dissertation.

I would also like to thank to my colleagues and friends in our group for their help and support in a number of ways: Dr. Goran Majkic, Dr. Xiaofen Li, Dr. Monika Rathi, Dr. Soumen Kar, Jian Cao, Yongkuan Li, Xinwei Cai, Haichao Guo, LJ Saldana, Rudra Pratap, Wenbo Luo, Yao Yao (male), Mei Yang, Aarthi Sundaram, Renjie Wang, Louis Delgado and Joanna Taormina.

I also want to address my thanks to my committee members, Dr. Jae-Hyun Ryou, Dr. James K. Meen, Dr. Jiming Bao, and Dr. Haleh Ardebili, for their insightful comments and questions.

My cordial gratefulness also goes to my important friends in my life, Dr. Narayan Das Khatri, Dr. Aixia Xu, Dr. Likun Li, Wei Zhang, Yun Liu, and Xiaonan Hu. Their care and support gave me courage to finish Ph.D. I would like to give very special thanks to my son, Noah Wu, for his very innocent smile and warm hugs, which melted my heart even I was tired of work sometime and reminded me to be a good mother for him. I am also indebted to my husband, Dr. Jingjie Wu, for his continuous love and strong support on both my life and work. It would never have been possible for me to take this work to completion without his incredible support and encouragement. At last, I owe my deepest gratitude to my beloved parents Meixian Cao and Yaming Gao, for their selfless love and support. To them I dedicate this dissertation.

Last but not the least, I acknowledge the funding for this project partly from U.S. Department of Energy SunShot Initiative and Texas Center for Superconductivity at University of Houston. High Mobility Single-Crystalline-Like Si and Ge Thin Films on Flexible Substrates by Roll-to-Roll Vapor Deposition Processes

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Abstract

The widespread use of high efficiency III–V multi-junction solar cells is limited by the cost and brittleness of Ge wafers that are used as templates for epitaxial growth. In order to provide an affordable and scalable bottom template, this work aims to achieve epitaxial growth of Ge and Si films on inexpensive and flexible substrates by roll-to-roll continuous deposition. These singlecrystalline-like Si and Ge thin films on metal substrates can also be utilized in high mobility thin film transistors (TFTs) well beyond the realm of present-day TFTs based on amorphous Si and organic materials.

The strategy of "seed and epitaxy" was employed for epitaxial growth of Ge and Si films. It consists of an initial growth of biaxially-textured seed layer on a flexible non-crystalline substrate by ion beam assisted deposition (IBAD) followed by a deposition of lattice and thermally-matched epitaxial layers. In epi-Ge growth, the epitaxial buffer stack of "CeO₂/LaMnO₃/MgO" was grown on IBAD MgO seed template by roll-to-roll magnetron sputtering. Single-crystalline-like Ge films was epitaxially grown on the CeO₂-buffered templates by medium frequency magnetron sputtering or plasma enhanced chemical vapor deposition with carrier mobility values as high as $1100 \text{ cm}^2/\text{V} \cdot \text{s}$, which is about 1000 times higher than that of amorphous Ge. These epi-Ge templates were successfully utilized to grown n- or p-type single-crystalline GaAs thin films by metal organic chemical vapor deposition which have been used to fabricate solar cells. Moreover, the epi-Si thin films were also grown on this Ge template. The resulting n-type Si film is highly oriented along (004) direction with an electron mobility of 230 cm²/V-s.

High performance TFTs fabricated on both single-crystalline-like n-Si channel on flexible metal substrate, and p-Ge on flexible glass substrate confirm the superior electronic quality of the grown films. The flexible TFT of n-Si (p-Ge) exhibits an on/off ratio of ~ 10^6 (10^6), a field-effect mobility of ~ $200 (105) \text{ cm}^2/\text{V-s}$, and a threshold voltage of -0.7 (1.0) V. These devices with superior performance open up a new era toward the next-generation flexible electronics and optoelectronics.

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List of Abbreviations

AFM	atomic force microscopy
ALD	atomic layer deposition
AR	air mass
BCC	body centered cubic
CeO ₂	cerium oxide
CIGS	copper indium gallium diselenide
CMOS	complementary metal oxide semiconductor
CVD	chemical vapor deposition
CW	continuous wave
DC	direct current
DL	diffusion length
EBSD	electron back scattered diffraction
EDX	energy-dispersive X-ray spectroscopy
FCC	face centered cubic
FF	fill factor
FIB	focused ion beam
FWHM	full-width at half-maximum
GaAs	gallium arsenide
GADDS	general area detector diffraction system
HRXRD	high resolution X-ray diffraction
HTS	high temperature superconductor
HWCVD	hot wire chemical vapor deposition
IBAD	ion beam assisted deposition

IBSD	ion beam sputtering deposition				
IGZO	indium gallium zinc oxide				
IPA	isopropylalcohol				
LCD	liquid-crystal-display				
LMO (LaMnO ₃)	lanthanum manganese oxide				
LPE	liquid phase epitaxy				
MBE	molecular beam epitaxy				
MgO	magnesium oxide				
MJ	multi-junction				
MOCVD	metal organic chemical vapor deposition				
NIR	near-infrared				
PB	parallel beam				
PECVD	plasma-enhanced chemical vapor deposition				
PF	pole figure				
PLD	pulsed laser deposition				
PV	photovoltaic				
PVD	physical vapor deposition				
RB	research buffer				
RF	radio frequency				
RF-MCS	radio frequency magnetron co-sputtering				
RFMS	radio frequency magnetron sputtering				
RHEED	reflection high-energy electron diffraction				
RMS	root mean square				
SAED	selected area electron diffraction				

SEM	scanning electron microscopy				
SIMS	secondary ion mass spectrometry				
SK	Stranski-Krastanov				
SOG	spin-on-glass				
SOI	semiconductor on insulator				
TDD	threading dislocation density				
TEM	transmission electron microscopy				
TFT	thin film transistor				
TiN	titanium nitride				
TLM	transmission line method				
ТО	transverse optical				
UHV	ultra-high vacuum				
UHV-CVD	ultra-high vacuum chemical vapor deposition				
V _{OC}	open circuit voltage				
VPE	vapor phase epitaxy				
XRD	x-ray diffraction				
YBCO	yttrium barium copper oxide				
YSZ	yttria-stabilized-zirconia				

Chapter 1 Introduction

1.1 Flexible electronic and optoelectronic devices

Flexible electronic and optoelectronic devices have been intensively studied for a decade due to the increased demand for flexible, lightweight, and mobile electronics that can be used in real-time healthcare monitoring (I), wearable displays (2), morphing touch screens (3), biometric devices (4), and solar cells (5). Among all the applications, most flexible electronics are built on polymers because of its good elasticity, flexibility, transparency and light weight. However, the limited process temperature and fast degradation rate of polymer in moisture and oxygen result in low performance and poor stability (6). Flexible glass is a good alternative due to its enhanced thermal stability and to the fact that it is an efficient barrier to moisture and oxygen. Flexible steel foil, with high mechanical strength, flexibility, light weight and high thermal stability, is another promising candidate for high performance flexible electronic and optoelectronic devices (7). In this dissertation, both flexible glass and flexible Hastelloy substrates are applied to grow high quality semiconductor thin films for solar cell and thin film transistors (TFTs) applications.

1.1.1 Flexible solar cells

A solar cell or photovoltaic (PV) cell is a device to convert solar energy into electrical energy in the form of current and voltage. Among different types of commercialized solar cells, the most widely applied one is the silicon (Si)-based single junction solar cell, while the most efficient one is the III–V compound multi-junction (MJ) tandem solar cell typically made on germanium (Ge) wafers.

(1) Si-based solar cells

Si-based solar cells are dominant and constitute almost 90% of the PV market (8). Up to now, the highest efficiencies Si solar cells can reach is up to 25% (9). The high performance, however, only comes with single-crystal Si (c-Si) and high processing cost. Moreover, wafer-based cells are limited in their size and lack of flexibility. Although a thicker crystalline Si (20-40 μ m) is

needed to be the absorption layer to permit sufficient optical absorption and electron-hole pair generation in the device because of its indirect bandgap, a good design of light trapping could enable sufficient collection to reach an efficiency of 15% with 4 μ m heteroepitaxial c-Si thin film (*10, 11*). Hence, the Si solar cell market will be more attractive if high crystalline quality Si thin films can be fabricated on inexpensive flexible substrates (flexible glass or metal foil), which will not only reduce the cost by eliminating the active layer thickness from few hundreds micrometers to few micrometers while maintain the high efficiency, but substitute the rigid and brittle c-Si wafer with flexible and robust substrates.

(2) III-V compound multi-junction tandem solar cell on Ge

A MJ solar cell employs multiple p-n junctions made of different semiconductor materials. Each junction is tuned to the absorption of a specific wavelength range of the light to produce electric current. The different materials with different bandgaps in multi-junctions absorb a broader range of wavelengths. As seen from Figure 1.1 (b), the bandgaps for InGaP, GaAs, and Ge cover most of the wavelengths from 300 nm to 1700 nm. The choices of materials for each junction are determined by the requirements for lattice matching, bandgap matching and current matching. Lattice matching means the layer materials have close lattice constants in order to reduce the growth imperfections and crystal defects which cause degradation in electrical properties. The bandgap matching indicates the materials are ordered with decreasing bandgaps, Eg, allowing sub-bandgap light $(hc/\lambda \le e \cdot E_g)$ to transmit to the lower sub-cells. Therefore, suitable bandgaps must be chosen such that the design spectrum will balance the current generation in each of the sub-cells, achieving current matching (12). The most popular structure for the MJ is: InGaP for the top sub-cell ($E_g =$ 1.8 - 1.9 eV), GaAs for the middle sub-cell ($E_g = 1.4 \text{ eV}$), and Ge for the bottom sub-cell ($E_g = 0.67$ eV). Figure 1.1 (a) shows the three materials with a perfect lattice matching and bandgap matching from each other, which enables the demonstrated MJ cells performance over 43.5% (13), where the theoretical limiting efficiency can reach 86.8% under highly concentrated sunlight with an infinite number of junctions (14).



Figure 1.1 (a) Combinations of bandgap and lattice constant for various materials used in III-V solar cells; (b) quantum efficiency of triple-junction solar cell [15].

Because the high cost of the Ge single crystal wafers limits the III-V MJ solar cell application, researchers have worked on developing GaAs solar cells on significantly lower-cost substrates (15, 16). With the same diamond cubic structure as Ge, Si serves as an ideal alternative substrate for GaAs. There are three approaches to realize III-V/Si tandem solar cells. (1) Mechanical stacking: the Si sub-cell is fabricated separately and then joined to the GaAs sub-cell by intermediate conductive layer and metal grids, which normally cause optical losses. The efficiency can reach 29.6% with the structure of GaAs/Si tandem solar cell under 350 suns (17). (2) Direct wafer-bonding: same as mechanical stacking but without including a conductive intermediate layer. A mirror-polished clean surface is required. The highest efficiency reached 30% with the structure of GaInP/GaAs/Si under 112 suns (18). However, both approaches require liftoff process and re-use of substrates, which are not suitable for the mass production. (3) Epitaxial growth of GaAs: a promising alternative choice having a few process steps and simple module integration, leads to the lowest cost compared with the previous two approaches. The problem is the large threading dislocation densities (around 1×10^9 cm⁻²) and defects in top cell because of 4% lattice mismatch between the GaAs (5.65 Å) and Si (5.43 Å), and 50% thermal expansion coefficient difference (5.5 µm·m⁻¹K⁻¹ for GaAs and 2.6 µm·m⁻¹K⁻¹ for Si), as shown in Table 1.1 (19). In order to control and confine the misfit dislocations between GaAs and Si, many methods

have been investigated such as thermally-cycled growth of the III-V intermediate layers, insertion of different types of III-V buffer layers, and Si-Ge graded buffer to reduce the stress caused by the lattice mismatch (20-23). After tremendous efforts, the GaAs threading dislocation density has been decreased to 3×10^6 cm⁻² by suppression of three-dimensional Volmer–Weber island formation during initial deposition using molecular beam epitaxy (MBE) (24). However, modeling results show that the dislocation density of the GaAs active layer should be in the order of ~ 10^5 cm⁻² to obtain high efficiency (~18%) on Si substrate (25). Also, the use of MBE limits the scalability to the commercial fabrication of GaAs solar cells.

Material	Lattice constant (nm)	Band gap at 300K (eV)	Density (g/cm ³)	Thermal expansion coefficient (K ⁻¹)	Electron mobility (cm²/V.s)	Hole mobility (cm²/V.s)
Si	0.543	1.124 (i)	2.329	2.6×10 ⁻⁶	1450	500
Ge	0.566	0.664 (i)	5.323	5.5×10 ⁻⁶	3900	1800
GaAs	0.565	1.424 (d)	5.318	5.5×10 ⁻⁶	9200	400

Table 1-1 Material properties of bulk Si, Ge and GaAs.

Therefore, Ge is still the best suitable substrate for GaAs heteroepitaxial growth because of the close lattice constant and thermal expansion coefficient, as shown in Table 1.1. However, single crystal Ge wafer is more brittle and expensive, heavier and thicker than Si wafer, and its market is limited mainly to space application. A promising approach is to grow high-quality Ge on low-cost substrates, such as ceramics, glass, flexible metal foils or other materials, which will have great potential to replace the single crystal Ge wafers. In this dissertation, the high quality singlecrystalline-like Ge is fabricated on both flexible glass and Hastelloy to serve as templates for the biaxial-textured GaAs thin film growth.

1.1.2 Thin film transistors (TFTs)

TFT is a special kind of field-effect transistor fabricated by deposited thin films, including active semiconductor layer, metallic contact and dielectric layer, on a supporting substrate (e.g. glass), to control the current (e.g. amplify analog or digital signals) by utilizing a small voltage. The best application of TFTs is in the liquid-crystal-display (LCD). Currently the most popular TFTs are developed based on amorphous Si (a-Si) (26-28), nanocrystalline Si (nano-Si) (29, 30), polycrystalline Si (poly-Si) (7, 31), organic semiconductors (32, 33), and oxide semiconductors (34, 35).

Material	Deposition technique	Mobility (cm²/V.s)	I_/I_ on off	Spatial uniformity	Stability	Ref.
Amorphous Si	PECVD	1	10 ⁵ -10 ⁷	High	Low	(26-28)
Nanocrystalline Si	PECVD	10	10 ⁶ -10 ⁸	Medium	Medium	(29, 30)
Polycrystalline Si	Excimer laser (or high temperature annealing	300	10 ⁵ -10 ⁷	Low	High	(7, 31)
Organics	Printing or vacuum evaporation	1	10 ² -10 ⁴	Low	Low	(32, 33)
Oxide semiconductors	Sputtering but printing also emerging	10	> 10 ⁵	High	High	(34, 35)
$\begin{array}{l} Monolayer \\ MoS_2 \end{array}$	CVD	10	107-108	High	Low	(36)

Table 1-2 Performance of flexible TFTs based on different materials.

As shown from Table 1.2, the TFTs fabricated by different materials have a problem with either poor spatial uniformity or low device stability, except those made by oxide semiconductors (eg. indium gallium zinc oxide (IGZO)). Although the TFTs fabricated by IGZO have high stability, the field effect mobility (μ) remains low ~10 cm²/V-s, which is significantly lower than the typical

values of single-crystalline Si with $\mu > 400 \text{ cm}^2/\text{V-s}$. The low mobility values limit the device applications to only switches of individual pixels in display systems. Although poly-Si TFTs exhibit mobility values up to ~300 cm²/V-s (7, 31), issues such as non-uniformity of the mobilities and threshold voltages because of grain boundaries are still unresolved. TFTs based on singlecrystalline Si with mechanical flexibility have been developed by a layer transfer technique, but are limited by high cost and difficult scalability (37). Therefore, a biaxial-textured semiconductor layer with mechanical flexibility, extraordinary performance characteristics, high reliability, and low processing cost would be very valuable for advanced flexible electronics technologies.

1.2 Si and Ge

Among all the electronic and optoelectronic devices applications mentioned above, group-IV Si and Ge semiconductors have been widely explored and developed. Even in the same group with the same diamond structure, different semiconductor materials differ in their properties and applications. For example, Si dominates the worldwide photovoltaic (PV) market with conventional c-Si solar cells (*38*) and a-Si thin film solar cells (*39*). More applications, such as field effect transistors (FETs) (*40*) and photodiodes (*41*), are mostly fabricated by Si thanks to its abundance in nature, environmental benignity, temperature stability, excellent carrier transport characteristics, and good compatibility with oxide materials. As for Ge, the major applications are focused on infrared optics (*42*), fiber-optic systems (*43*), and high efficiency MJ solar cells (*44*). SiGe alloy is also widely used in integrated circuits for heterojunction bipolar transistors or as a strain-inducing layer for complementary metal oxide semiconductor (CMOS) transistors (*45*). Both Si- and Ge-based optoelectronic devices and circuits dominate around 95% of the semiconductor market (*46*).

In both Si and Ge applications, the materials are further classified into single crystalline, polycrystalline, and amorphous materials, depending on their crystallinity. The performance of amorphous semiconductors are not accepted as high-performance and low-power-consumption

devices mainly due to their low mobility values. Poly-semiconductor thin films exhibit reasonable electrical properties, however, major technical challenges still remain unresolved, including nonuniformity in the mobilities and threshold voltages caused by the different grain sizes and grain boundaries, which makes their application in devices impractical (7). Moreover, grain boundaries in solar cells provide electron traps that act as recombination centers to reduce minority carrier lifetimes thus reducing their performance (47). Single crystalline Si (or Ge) is the best choice in electronic devices application due to its highest performance characteristics, as it is free of major crystalline defects of dislocations and grain boundaries that act as carrier traps, scattering source, provide leakage paths, etc. (48). However, single crystalline Si (or Ge) technology requires rigid, brittle and bulky single-crystal wafers to be used as active layers in devices, limiting scalable large area processing. Compared with Si, single-crystalline Ge wafer is even more expensive because of Ge refining and Ge crystal growth process (49). In addition, both Si and Ge single crystalline wafers lack mechanical flexibility and are easy to break during the transportation and installation. Therefore, if high-quality single crystalline-like semiconductor Si/Ge thin films with suitable electrical properties can be developed on inexpensive flexible substrates, it will not only further reduce cost and weight of electronic devices by eliminating the single crystalline wafers, but also open up opportunities for mass production of high performance flexible electrical and optoelectronic devices

1.3 Approaches of biaxial textured thin film growth on low-cost substrates

In thin film technology, deposited materials can be divided into three types: amorphous, polycrystalline, and textured. There are two types of preferred textures. (1) Fiber texture: the orientation of a certain lattice plane is preferentially parallel to the substrate plane, but the azimuthal direction exhibits a random distribution of orientations, as is shown from Figure 1.2 (a). Typically, films growth with body centered cubic (BCC) structure have a (110) preferred out-of-plane orientation.

However, in this structure, many arrays of dislocations in grain boundaries caused by grain boundary misorientations will deteriorate the material electrical performance. Normally grain boundary misorientations consist of tilt misorientation and twist misorientation. Both types of misorientations result in defects that lead to recombination, reducing carrier diffusion length (DL) and the solar cell open circuit voltage (V_{OC}) (50). In fiber texture, the twist misorientation mostly appears because the film lacks azimuthal ordering of in-plane *a* and *b* axes. (2) Biaxial texture: both out-of-plane and in-plane directions are well aligned with a preferred crystallographic orientation, as shown in Figure 1.2 (b).



Figure 1.2 Schematic of fiber texture and biaxial texture in thin film.

In the semiconductor field, biaxially-textured thin films are preferred since they normally provide better electrical performance because of small grain-to-grain misorientations. It helps to reduce the dislocation densities at the grain boundaries thus making the free carriers more easily transported (*51*). Normally, biaxial texture growth, also called epitaxial growth, is achieved by physical or chemical vapor deposition at elevated temperatures. However, both approaches require single crystal substrates that are often not available in large size or can be expensive in large-scale production. Two leading approaches, rolling-assisted biaxially-textured substrates (RABiTS) (*52*, *53*) and ion beam assisted deposition (IBAD) techniques (*54*), were developed to solve this crucial problem to achieve biaxial texture on low cost polycrystalline or amorphous substrates. Both approaches have been successfully demonstrated for the template fabrication for the 2^{nd} generation high temperature superconductor (HTS) wire (*55*).

1.3.1 Rolling-assisted biaxially-textured substrates



Figure 1.3 Schematic of the RABiTS process.

RABiTS, developed by Oak Ridge National Laboratory (53), utilizes thermomechanical processing of base metals to obtain a very sharp, well-developed cube texture. Ni is an example of material used in the RABiTs process as seen from Figure 1.3 (56). Starting with a randomly-oriented Ni bar/plate, cold rolling is used to produce a distinct copper-type rolling texture, followed by recrystallization to a cube texture. Then, appropriate chemical and structure matched buffers are deposited on the cube-textured base metal to achieve biaxial textured thin films for HTS or other electronic devices application. However, the reported substrates are only limited to Ag, Ni, Cu and Ni-based alloys (56). Ag substrate has issues with high-angle grain boundaries, economy, and strength in long length application. Alternative FCC metals like pure Ni can achieve biaxial texture growth but are not ideal conductors and lack the tensile strength required for many applications. And uncontrolled oxide formation on the substrate can lead to cracking of buffer layers as well as

cracking of the superconductor or semiconductor top layer. Although Ni alloy with other elements, such as Cr, V, W and Cu, can help to increase the yield strength and resist to oxygen, the impurity elements do influence the recrystallization behavior and increase grain boundary grooving. Cu has even less resistance to oxidation than Ni, but Cu is not preferred for RABiTS process (*57*). Moreover, the RABiTS approach is limited the substrates in the FCC metal, which is not suitable for epitaxial growth of semiconductor on flexible insulator (SOI) substrates for the further applications such as wearable displays, electronic skin and other transparent flexible electronic devices. Therefore, a universal biaxial texture growth technique is required to satisfy the demands of flexible devices.

1.3.2 Ion beam assisted deposition (IBAD)

As a more promising technique for preparing highly textured templates on various substrates, IBAD takes advantage of controllability, reproducibility and flexibility. It normally combines a traditional thin film growth method (e-beam evaporation, DC/RF sputtering, laser ablation or ion sputtering) with the simultaneous bombardment of the sample surface by energetic ions from an ion source. The ions come from either inert gas, such as Ar, or reactive gas such as O₂. A schematic of our IBAD system is shown in Figure 1.4.

In our system, the biaxially-textured thin films are fabricated using reel-to-reel ion beam assisted deposition. The deposited atoms are produced by ion beam sputtering of a target. The assist ions impinge on the growing film at an optimized incident angle to maximize the degree of in-plane alignment of the film. Without the assist beam, the film normally shows a polycrystalline or fiber texture, in which all grains share a crystallographic axis parallel to the normal direction (c axes) of the substrate surface, but lack azimuthal ordering of in-plane a and b axes. The fundamental mechanisms of controlling thin film crystallographic orientation by assist ion beam are not very clear, but the most popular understandings include (1) nucleation-based control process and (2) growth-based selection process.



Figure 1.4 Schematic of IBAD process.

(1) Nucleation-based control process: This model is using the lowest surface energy to explain the tendency to form the preferred orientation of IBAD films. Normally, the deposited atoms are self-arranged into the crystalline planes with lowest surface energy during the ion assisted deposition. If we take the TiN as an example, the surface energy per unit area of the hkl plane γ_{hkl} is given by the following equation:

$$\gamma_{hkl} = \frac{1}{2} \alpha N_{hkl} / A_{hkl}, \qquad (equ. 1.1)$$

where α is the bond strength, N_{hkl} is the broken bonds per atom, and A_{hkl} is the surface area occupied by every surface atom. For TiN structure, N₁₁₁ = 3, N₂₂₀ = 2, N₂₀₀ = 1, A₁₁₁ = $\sqrt{3a^2/4}$, A₂₂₀ = $\sqrt{2a^2/4}$, and A₂₀₀ = $a^2/4$, where a is the lattice constant. Then the ratio of the surface energies in different planes of the TiN can be estimated as (58):

$$\gamma_{200} < \gamma_{220} < \gamma_{111},$$
 (equ. 1.2)

which means TiN (200) plane is a preferred growth orientation during the nucleation stage with the help of ion beam assisted deposition due to lower the surface energy.

However, as the TiN film thickness keeps increasing, the preferred orientation changes from $\{001\}$ to $\{111\}$ if the ion energy is less than 500 eV. Therefore, the predominant factor for the preferred orientation is not only determined by the surface energy in the nucleation stage. Pelleg et al. proposed that the film growth orientation is determined by the surface energy at small film thickness, but with film thickness increase the strain starts increasing, corresponding to the in-plane compression (*59*). Finally, the strain energy competes with the surface energy to dominate the preferred growth orientation. It has been calculated that the strain energy in different planes of TiN is (*58*)

$$U_{111} < U_{220} < U_{200}$$
, (equ. 1.3)

therefore, a change of the {001} texture to the {111} texture happens at low ion beam energy in order to minimize the elastic deformation energy. However it is hard to explain that if the ion energy increases to higher than 500 eV, the TiN preferred growth orientation is changed from the {111} to {001} orientation. The model of growth-based slection process can well explain the development of biaxial alignment during IBAD.

(2) Growth-based selection process: This model combines the channeling effect and shadowing effect based on the columnar structure film to explain the biaxially alignment during IBAD process, as seen from Figure 1.5 (60, 61). The channeling effect means that, during the assist ion beam bombardment of the surface, the grains whose unit lattice has a plane parallel to the ion beam direction would effectively survive due to the planar ion channeling between the planes without suffering significant sputtering yield. The shadowing effect means that, under bombardment of the ion beam, grains with channeling direction parallel to the ion beam direction experience the lowest etching rate and hence have the fastest growth direction. Figure 1.5 shows

<200> biaxial alignment of YSZ by IBAD due to shadowing of misoriented grains (60). In this process, low energy ions etch back the pre-deposited and misoriented grains in the films leaving crystallites with preferred orientation that will shadow other grains upon continued deposition, eventually extending to form the surface. Sonnenberg et al. argued that this in-plane alignment is produced by a growth process rather than a nucleation phenomenon. Because the biaxial alignment of the YSZ induced by simultaneous ion beam bombardment develops during the late stages of film growth, a thick YSZ film (> 0.5 μ m) is normally required to achieve good in-plane alignment (60). The mechanism can also explain the biaxial alignment of IBAD MgO film, in which nucleating crystallites oriented to the ion beam channeling direction continue to grow while all other crystallites are etched away by the assist ion beam (62-64). Substrates with rougher surface (> 1 nm) cannot yield good biaxial alignment films using IBAD, which also proves this growth-based model from the other side. Therefore, the growth-based selection process due to shadowing explains well the biaxial alignment during the IBAD process.



Figure 1.5 <200> biaxial alignment by IBAD due to shadowing of misoriented YSZ grains.
The most popular biaxial-textured thin films grown by IBAD include titanium nitride (TiN) (65-68), magnesium oxide (MgO) (69-73), yttria-stablized zirconia (YSZ) (64), calcium fluoride (CaF_2) (74, 75) and cerium oxide (CeO_2) (76-83). YSZ was selected to be the earliest material as the biaxially-textured template for YBCO growth on Ni substrates in 1991 by lijima et al (84). YSZ has a cubic fluorite structure with lattice constant 5.14 Å. In the IBAD process, the ion beam incident angle was set as 55° , corresponding to the easiest channeling direction (<111> axis) of 54.7° from the substrate normal. However, the biaxial texture evolution occurs very slowly for YSZ, requiring around 1 µm thickness to achieve the optimum in-plane texture and thus, several hours' long time process is needed (64). An alternative material, CeO₂, with the same fluorite crystal structure, required a low deposition temperature, low assist beam energy, and low ion to atom (I/A) ratios to form biaxial (100) texture by IBAD. If it is processed at higher energy, atom mobility on the growing surface is enhanced thus favoring the preferred (111) direction growth. However, because of the low energy ion beam, the incident ions have difficulties in removing misarranged atoms from the channel, therefore, a broader in-plane alignment of 16° was achieved even with film thicknesses up to 4000 nm (82). With another type of fluorite structure material, IBAD-CaF₂, a porous buffer structure is formed. Such a structure is not desirable for further growth of semiconductor films, and requires an additional thick capping layer with very slow deposition rate (75). Therefore, the fluorite structure materials such as YSZ, CeO_2 and CaF_2 are not suitable for the fast IBAD process with both good in-plane and out-of-plane texture, which limit their application as a template material for the epitaxial semiconductor thin film growth.

Compared to IBAD fluorite structure materials, the rock salt materials, such as TiN (68), MgO (71), NbN and ZrN (85), were also demonstrated as the IBAD templates for high quality YBCO thin film growth. The films were found to have a (100) out-of-plane and (220) in-plane orientation aligning parallel to the ion beam direction (45° with respect to the substrate normal) according to the <110> channeling direction. But one of the major differences between IBAD rock salt crystals and fluorite crystals is the critical thickness to achieve the biaxial texture. The IBAD

rock salt materials required only 10 nm to achieve biaxial texture during the nucleation stage, which is more than 100 times less than that for IBAD YSZ (72). The rapid texture formation translates to a processing time of less than a minute, significantly lowering the cost. The reason for the fast process is due to the preferred out-of-plane alignment of the (100) direction for the IBAD rock salt material; then the ion beam needs to align only the in-plane orientation, which simplifies the texturing process and enables texture formation at an early stage (86). SuperPower produced kilometer lengths of IBAD-MgO template buffers with both good in-plane and out-of-plane routinely (87). For typical nitride rock salt materials, such as TiN, taking advantage of good electrical conductivity compared with MgO, enable the realization of a conductive buffer architecture within the IBAD approach (65-68). Although there are many reports on the optimization of IBAD MgO and TiN, most of them are focused on the application of superconductors. None of them cover texture revolution that impacts Si and Ge growth.

In this dissertation, biaxially-textured MgO was grown on Hastelloy with different ion assist beam current, beam voltage and exposure time to reach the optimum biaxial texture. Then the optimized condition was applied on the different substrates, such as flexible glass and ceramics, for the various Si and Ge-based electronic and optoelectronic applications.

1.4 Epitaxial growth of buffer layers and semiconductor layer

1.4.1 The structure of buffer layers



Figure 1.6 Schematic of the epitaxial buffer layers used in this work on growth of biaxially-textured semiconductor films on IBAD-MgO template.

SuperPower Inc. has successfully demonstrated high quality and long length YBCO growth on metal substrates by employing of a buffer stack of LaMnO₃/homoepitaxial-MgO on MgO template made by IBAD (87). It was shown that a CeO₂ layer is needed on this buffer stack for epitaxial growth of Ge because of the structural compatibility between CeO₂ and Ge (or Si). Since the CeO₂/Si interface is not chemically stable at the elevated high temperatures (~ 700-900 °C) required for epi-Si film growth (88), a thin Ge layer is normally used as a transition layer for the epitaxial Si growth. Crystal structures of the biaxially-textured buffer layers used for Si and Ge growth are shown in Figure 1.6.



Figure 1.7 (a-d) Schematic illustration and (e-h) projection of atom locations in the (001) basal plane of MgO, LaMnO₃, CeO₂, and Si (or Ge); (i) top view, (j) 3D side view and (k) illustration of in-plane rotation in the (001) basal plane between LaMnO₃ and CeO₂.

In this structure, LaMnO₃ plays a critical role as a transition layer for CeO₂ [100] epitaxial growth on MgO [100] buffer layer, even though there is a 28% lattice mismatch. As seen from the projection of atom locations in the (001) basal plane of MgO and LaMnO₃ in Figure 1.7 (e) and (f), the lattice parameters in the basal plane of orthorhombic perovskite structure LMO are a = 5.53 Å and b = 5.71 Å. The pseudocubic lattice parameter of 3.91 Å is closely matched to the lattice parameter of MgO (a = 4.22 Å). Domain epitaxy occurs in growth of LaMnO₃ on MgO, where 13 unit cells of LaMnO₃ match with 12 unit cells of MgO. Due to the large lattice mismatch between the LaMnO₃ (0.391 nm) and CeO₂ (0.540 nm), epitaxial CeO₂ has to be grown 45° rotated along the phi direction with respect to the LaMnO₃ unit cell, because of a better lattice match between the lattice parameter of LaMnO₃ and half of the diagonal distance of the CeO₂ unit cell (0.381 nm). It results in a epitaxial growth within only ~3% mismatch, where two corner Ce atoms match with the two center La atoms, as shown from the Figure 1.7 (i) top view and (j) side view. Then diamond structure of Ge (or afterwards Si) is biaxially-textured grown on fluorite structure of CeO₂, because the projection of the atomic locations in the basal plane of CeO₂ matches perfectly with those on the basal plane of Ge.

In order to confirm the rotation occurred in the CeO₂ layer, more analysis including reflection high energy electron diffraction (RHEED) patterns and (110) pole figures (PF) of relevant biaxially-textured buffer layers (MgO, LaMnO₃, and CeO₂) were performed as shown in Figure 1.8. RHEED patterns show a strong electron diffraction pattern of cubic structure MgO; then the pattern for CeO₂ displays 45° rotation with the assist of LaMnO₃ transition layer. The RHEED patterns of Si and Ge perfectly match with that of CeO₂, indicating no rotation between Si (or Ge) and CeO₂. PFs for the buffer layers offer additional strong evidence. The PF of CeO₂ displays four symmetric peaks which rotate about 45° along the Φ direction compared with LaMnO₃. But, the Si (110) PF duplicates the same phi angle as CeO₂, where LaMnO₃ maintains the same phi angle as the MgO. Both RHEED patterns and PF of buffer layers prove the previous epitaxial growth model where there is an in-plane rotation of 45° between CeO₂ layer and LaMnO₃ layer.



Figure 1.8 (a) - (d): RHEED patterns for epitaxial buffer layers (MgO, LaMnO₃, and CeO₂) and active semiconductor layer (Si). (e) - (h): Corresponding (110) and (220) pole figures (PF) of relevant biaxially-textured layers, indicating a clear four-fold symmetry.

1.4.2 Epitaxial growth of buffer layers

Physical vapor deposition (PVD) is widely used to produce the epitaxial thin films by condensation of a vaporized material onto various biaxially-textured templates. The common PVD techniques include thermal evaporation, e-beam evaporation, sputtering, molecular beam epitaxy (MBE), pulsed laser deposition (PLD), ion plating, etc. Among these techniques, sputtering is commonly employed for good film uniformity, reliable control over the film properties, deposition on large-area substrates, and cost efficiency (*89*).

Sputter deposition utilizes a glow plasma to bombard the surface of the target with energetic ions (such as Ar^+) to eject atoms, and then deposit them onto the substrate to form a thin

film. Secondary electrons are also emitted from the target surface as a result of the ion bombardment, and these electrons play an important role in maintaining the plasma. Sputter deposition is generally conducted using a magnetron source. Magnetron sputtering can be performed with direct current (DC), radio frequency (RF), or in a reactive mode to enhance the efficiency of the deposition rate and reduce the operating pressure. All the buffer layers in the multilayer architecture made in this work were grown epitaxially by reel-to-reel magnetron sputtering systems under various conditions.

For MgO deposition, twin Mg targets are used because metal targets yield higher deposition rate than oxide targets. By using the metal target, two operating modes of the reactive magnetron sputtering discharge can be achieved: metallic mode and compound mode. If the reactive gas is of low partial pressure, it normally results in a high sputtering rate, therefore, metallic mode for Mg deposition. When the reactive gas partial pressure increases, the MgO compound starts to form on both the substrate and the Mg target surface, which causes target poisoning. A fully-poisoned target allows for growth of stoichiometric MgO films, but the deposition rate is significantly lower than the Mg deposition. Therefore, a transition regime between the metallic and the compound mode is critical for the growth of stoichiometric MgO compound films with relatively high deposition rates. In this work, the metallic mode should be avoided because of two reasons: (1) deposited Mg contaminations will diffuse into the semiconductor active layer and severely reduce minority carrier lifetime thus deteriorate device performance; (2) high consumption rate of Mg target which can also damage the target assembly. During sputtering of MgO, the transition from the reactive mode to metallic mode is recognized by careful observation of the color change of the plasma and simultaneous monitoring of the O₂ partial pressure.

For further growth of the epitaxial buffer layer, LaMnO₃, a LaMn alloy target is preferred for the high deposition rate as well. However, for epitaxial CeO₂ thin film deposition, a CeO₂ oxide target is employed because the change in the oxidation state of Ce between Ce⁴⁺ and Ce³⁺ is normally happens at different O₂ partial pressure and process temperature with Ce target (90). The phase transition from cubic CeO_{2-x} to hexagonal Ce_2O_3 is not preferred for the epitaxial Si and Ge growth.

1.4.3 Other buffers used for the epitaxial Si and Ge growth

In addition to the previous mentioned template (CeO₂/LaMnO₃/MgO) used for Si and Ge growth, some other approaches were employed to fabricate epitaxial Si or Ge on unbuffered substrates. Such approaches normally need to meet the following requirements: (1) provide large grain size compared with the target active layer thickness; (2) present surface orientation that promotes good epitaxy; (3) incorporate a low density of intra-grain defects; and (4) contain low angle grain boundaries for a good in-plane texture (*11*).

Efforts to achieve Si and Ge epitaxy include excimer laser crystallization (91), metalinduced crystallization (92), and epitaxial lift-off and transfer (93). However, those techniques are limited from widespread use because of non-scalable and expensive process. Other demonstrated direct approaches for Si and Ge heteroepitaxy growth have been based on different IBAD templates. The first oriented Si film grown on metal substrates was developed by Findikoglu, et al, who empolyed γ -Al₂O₃ as a template layer for the biaxial-textured Si growth using e-beam evaporation. However, the Si film electrical performance was severely limited by a high density of misfit dislocations and stacking faults due to the large lattice mismatch of 45% between Si and γ -Al₂O₃ (94). CeO₂ (fluorite structure) has better structural compatibility and closer lattice match with Si. However, epitaxial growth of Si on CeO_2 was hindered by the formation of amorphous SiO₂ at the interface (88). CaF_2 (the same structure as CeO_2 without oxygen anion) can also be used as a template layer. The reported CaF_2 layer, however, is not well textured, resulting in poor performance in photovoltaic devices (74). Our group has successfully demonstrated growth of superior biaxially-textured Ge film (FWHM $< 1^{\circ}$) with (001) out-of-plane orientation on CeO₂ buffer stacks with high hall mobility (833 cm^2/Vs) (95-97), which can be an exceptional candidate for highly-oriented Si growth.

1.4.4 Growth of single crystal-like Si and Ge active layers

Based on the various seed layers for the Si and Ge growth, several growth techniques such as hot wire chemical vapor deposition (HWCVD), plasma-enhanced chemical vapor deposition (PECVD), e-beam evaporation, MBE, and sputter epitaxy have been applied to Si and Ge epitaxy (98). HWCVD was a choice for biaxially-textured Si growth on flexible substrates because of the high growth rate of the Si (110 Å/s) (11, 99-102); however, the grain size of Si made by this method is smaller than that of Si fabricated by PECVD (100). RF-PECVD was known as one of the most popular techniques to grow device-quality crystalline thin films at lower temperatures and often with improved electrical properties compared to HWCVD (103, 104). It takes advantage of low kinetic energy particle bombardment of a growing Si film surface, which enables epitaxy at low temperature and high growth rate (98). Sputtering is another approach to achieve the epitaxial growth of Si and Ge on seeded buffer layers, but the deposition rate is relatively low compared with both HWCVD and RF-PECVD (97, 105). Another drawback is the fixed dopant concentration in the target which restricts the Si or Ge thin film carrier concentration.

In this work, single-crystal-like Si and Ge films were developed on various flexible substrates. For Ge thin film growth, a CeO₂/LaMnO₃/homo-MgO/IBAD MgO buffer stack was employed on flexible Hastelloy. All the multiple-step deposition processes used for this buffer are compatible with continuous roll-to-roll manufacturing which is necessary for economical process and scale up of flexible electronic components. The Ge film texture, morphology and mobility were studied based on different process temperatures and film thicknesses. In order to reduce the diffusion issue, the IBAD CeO₂ buffer layer was directly fabricated on flexible glass for epitaxial Ge growth. For Si thin film fabrication, biaxially-textured Ge template was utilized to grow heteroepitaxial Si thin films on metal alloy tapes. Both magnetron sputtering and RF-PECVD approaches were utilized for epitaxial Ge and Si growth. Moreover, single-crystal-like flexible Si and Ge thin films have been, for the first time, developed for potential applications such as solar cells and TFTs.

1.5 Motivation and outline

This dissertation aims to develop high quality single-crystalline-like Ge and Si thin films on biaxially-textured templates overlaid on metal and glass substrates for flexible electronic and optoelectronic devices application. The IBAD templates, biaxially-textured MgO and CeO₂ were grown on both metal-based and glass substrates in a reel-to-reel IBAD system. Subsequently, the intermediate buffer layers (CeO₂/LaMnO₃/homo-MgO) were deposited by reel-to-reel RF magnetron sputtering under various conditions. This research focuses on optimizing process parameters for heteroepitaxial growth of Si and Ge thin films by both PECVD and magnetron sputtering approaches in order to achieve controllable carrier concentrations and high carrier mobility. Moreover, efforts were undertaken to establish the relationship between the film quality in terms of texture, crystallinity, dislocations, and surface roughness and electrical properties. The overall outline is as follows:

Chapter 2 will discuss IBAD templates including CeO₂ and MgO, which will be applied for the epitaxial Si and Ge growth. These IBAD templates were fabricated and optimized on different flexible substrates, such as metal (Hastelloy C-276) tape, flexible glass (NEG, OA-10G), and flexible ceramic (YSZ from ENRG Inc.). During the IBAD process, the main parameters (ion energy, ion to atom flux ratio, process time and ion incident angle) were modified to study their effects on the texture of films.

Chapter 3 will detail fabrication of single-crystalline-like Ge thin films on both IBAD CeO₂/flexible glass and IBAD MgO/flexible Hastelloy or glass. With the traditional buffer structure (CeO₂/LaMnO₃/homo-MgO/IBAD MgO) overlaid on flexible Hastelloy, the influence of deposition temperature as well as that of film thickness on grain size, texture, surface roughness, carrier mobility and concentration were studied. In order to eliminate diffusion of elements from the metal substrate into the active semiconductor layer, various approaches were studied including increasing the thickness of the Al₂O₃ diffusion barrier, using the low temperature process by RF-PECVD, replacing the substrate to the flexible glass, etc. Finally, a Ge p-n bottom junction and a

TFT based on (111) oriented Ge / flexible glass substrate were successfully fabricated using the optimized epitaxial Ge thin films.

Chapter 4 will cover fabrication of single-crystalline-like Si thin films on biaxially-textured Ge templates. Two approaches, radio frequency magnetron co-sputtering (RF-MCS) and RF-PECVD, were employed to grow Si films. The effects of deposition factors such as process temperature, film thickness, gas flow rate, etc. on the quality of biaxially-textured Si films were comprehensively studied. Moreover, controllable phosphorus (P) doping in Si films with different gas phase precursors was explored for future practical device application. Finally, a flexible Si TFT device based on this structure was successfully demonstrated.

In Chapter 5, the results of this dissertation are summarized, and possible future work based on them is proposed.

Chapter 2 Biaxially-textured templates growth by ion beam-assisted deposition

2.1 Introduction

Mechanically flexible electronics, such as wearable electronics, printed sensors, electronic skin, actuators, and flexible solar cells, have gained a lot of attention in recent years (*106, 107*). However, active layers in most of those devices are made of polycrystalline or amorphous thin films (*7, 34*). The carrier mobilities (< $10 \text{ cm}^2/\text{V.s}$) of these films are insufficient to be used in high performance optoelectronics devices (*34*). Single crystal wafers (Si, Ge, GaAs, etc.) possess high electrical performance, but their application in flexible electronics is restricted by their rigid, brittle and expensive nature. Therefore, it would be highly beneficial to develop high-quality epitaxial thin films with superior electrical properties on inexpensive flexible substrates to replace polycrystalline or amorphous thin films.

A promising strategy to grow epitaxial single-crystalline-like semiconductor thin films on flexible substrates is called the "seed and epitaxy" technique (88, 96). Two main "seed and epitaxy" approaches include the ion-beam assisted deposition (IBAD) (54) and rolling-assisted biaxially-textured-substrates (RABiTS) (52), as mentioned in Chapter 1. The IBAD technique takes advantages of the fact that both the assist ion source and sputter ion source can be operated independently which enables it to be a highly efficient, controllable, reproducible, and scalable process (72). In this chapter, biaxially-textured templates were designed and deposited on a flexible non-crystalline substrate using the IBAD technique. Then the lattice and thermal-matched epitaxial layers were grown on the IBAD layer for further semiconductor epilayer growth by standard deposition methods. A schematic of the IBAD template on a foreign flexible substrate for the subsequent biaxial-textured thin film growth is shown in Figure 2.1. The resulting biaxially-textured semiconductor thin films exhibit low-angle grain boundaries which are relatively less

detrimental to the electrical properties of the films (88), and so they are promising replacements for inferior quality amorphous and polycrystalline films as channels in flexible electronics devices.



Figure 2.1 Schematic of the IBAD template on foreign flexible substrate for subsequent biaxiallytextured thin film growth.

In this chapter, different amorphous substrates used to grow the IBAD templates are discussed. The criteria to select the substrates include high temperature stability, chemical inertness, suitable mechanical strength, cost effectiveness and good flexibility. Thin metal (Hastelloy C-276) tape, flexible glass (NEG, OA-10G), and flexible ceramic yttria-stabilized zirconia (YSZ) from ENRG were selected for the IBAD CeO₂ or MgO layer growth. These IBAD layers will be applied for the further epitaxial Si and Ge growth. The main IBAD parameters including ion energy, ion to atom flux ratio, process time and ion incident angle were manipulated to achieve the optimal quality of the textured films (*72*).

2.2 Experiments and characterization

2.2.1 System structure for IBAD

The biaxially-textured templates described in this work were fabricated by a reel-to-reel IBAD. The configuration of the IBAD system as shown in Figure 2.2 is composed of a sputtered ion source, an assist ion source, the target assembly, an in-situ monitor system, the reel-to-reel system, a vacuum system and a cooling system.

Sputter ion source: The ion beam sputter deposition (IBSD) employed in this work consisted of a 6 cm \times 22 cm ion source, capable of an accelerating voltage up to 1500 V and ion

beam current up to 1000 mA. The main components include a discharge chamber, an electron source, grids, and a neutralizer. During operation, a gas species such as Ar is introduced into the discharge chamber. A plasma is established by the ionized Ar^+ from the electron source. Then the ionized Ar^+ is accelerated to high velocities by the potential difference from the plasma generator to the grid electrode. The ion beam then exits through the extractor apertures and drifts in a direct line in vacuum to the target. A neutralizer is placed downstream from the source where it emits electrons to balance the positive ions of the beam, preventing charge built up in the target. The IBSD process is controlled by a VEECO RF 2001 source controller.

Assist ion source: The assist source is the same type of ion source as the sputter source, also controlled by the VEECO RF 2001 source controller, except that the assist source orientation is adjustable over an angle of 0° - 90°) with respect to the substrate normal.

Target assembly: Two targets with the same size, 40cm×30cm, are mounted on each side of the target holder using a high thermal and electrical conductivity paste for better cooling. The target holder can be flipped over in order to deposit two different materials in sequence without breaking vacuum, as shown in Figure 2.2. The sputtered atoms derived from collisions between incoming ions and the target are directly deposited onto the substrate.

In-situ monitor system: This includes three in-situ monitors: (1) Deposition rate is measured by a quartz crystal monitor located near the substrate holder. The piezoelectric quartz crystal generates voltage when it is set to vibrate at its resonant frequency. (2) Ion flux is a critical parameter to be measured at the substrate position during the ion source operation, since it is a function of the ion source parameter and background pressure. The Faraday cup is positioned near the substrate and faces the ion source to measure the ion current density at the substrate. (3) In-situ texture development is monitored by a refractive high energy electron diffraction (RHEED) system (STAIB Instruments, EK-35-R). It consists of an electron source, a CCD camera and a phosphor

screen. An electron source provides a well-collimated beam in an energy range up to 35 keV; then the beam is accelerated onto the substrate at a grazing angle with respect to the substrate planes. The phosphor screen located at the end of the chamber displays the diffraction pattern from the growing film. CCD camera captures the diffraction pattern. KSA RHEED control software is used to adjust the beam path and energy to the sample position and also for data acquisition. The crystal quality of the growing film can be monitored in real time by RHEED.

Reel-to-reel system: The substrates (polished flexible Hastelloy) are spot welded with bare Hastelloy tapes (leader tape) and loaded on the spools. For the other samples, such as flexible glass and YSZ, they are mounted on the bare leader tape using mechanical holder and then loaded on the spools. A certain tension between two spools is maintained using two motors to drive the tape and also keep the tape flat during deposition. One of the spools is connected to an encoder so that the movement rate of the tape can be controlled precisely. The tape moving speed is 0.1–100 cm/min.

Vacuum system: The vacuum system includes the pumping system and the pressure monitor system. The pumping system utilizes a mechanical rotary vane pump for reducing the pressure in the main chamber to low vacuum (5×10^{-2} Torr) and two cryogenic pumps (cryo-pump) which are driven by a helium compressor to further evacuate the chamber to high vacuum ($<10^{-6}$ Torr). The cryo-pumps are isolated from the vacuum chamber by an auto-controlled downstream throttle valve (320 mm) which can be closed when venting the chamber. Another chamber is for the RHEED electron gun control chamber, which utilizes a mechanical scroll pump for pumping to a low vacuum and a turbo pump to pump to high vacuum. The RHEED chamber is isolated from the main vacuum chamber by a manually controlled vacuum valve which is normally closed when film deposition is complete. The pressure monitor system is equipped with convectron gauges that function from 760 Torr to 10^{-3} Torr, and ion gauges for 10^{-2} Torr to 10^{-10} Torr. The convectron gauges are located at the chamber and mechanical pump foreline, and the ion gauges are located in the cryo-pump lines. **Cooling system**: A chilled closed liquid loop is used for cooling the chamber, substrate, ion sources, neutralizers, crystals, cryo-pump compressors, and water vapor cryo-pumps. Each of these coolant loops is monitored by a flow sensor and controlled by associated valves under control of the pneumatic valve manifold.



Figure 2.2 Schematic of IBAD system configuration

2.2.2 Growth of biaxially-textured MgO layer on amorphous flexible substrates

The metal substrate Hastelloy C-276 (12 mm wide×50 µm thick) was electropolished to a root mean square (RMS) surface roughness less than 1 nm. An amorphous film of alumina (~80 nm) was deposited on the polished Hastelloy substrate at room temperature by reactive magnetron sputtering to provide a diffusion barrier to cations from the metal substrate. The surface roughness of the Al₂O₃ diffusion barrier was one of the parameters that was studied in this work. Then a thin yttria layer (~7 nm) was deposited by IBSD in IBAD chamber to serve as a pristine surface for the nucleation of the MgO film. The sputtering ion beam current and ion beam voltage were set at 240 mA and 950 V for yttria deposition. The ion assist source incident angle on the substrate was another parameter that was studied. Afterwards, MgO films were synthesized by ion beam

sputtering of a Mg target to react with O_2 at room temperature with simultaneous bombardment of the substrate by an Ar⁺ ion beam with an incident angle of 45° to the substrate normal. Different parameters of assist beam current (70 – 90 mA), beam voltage (900 – 1300 V) and ion exposure time (40 – 110s) were optimized in the process. RHEED was used to monitor the crystallinity of MgO thin film in-situ during growth in order to obtain the best crystallographic texture. After the IBAD process, a thick homoepitaxial MgO (homo-MgO) was deposited onto the IBAD MgO samples by magnetron sputtering. Both in-plane and out-of-plane textures of the homo-epi MgO were measured.

The optimal beam voltage and beam current parameters for IBAD MgO growth on flexible Hastelloy were extended to flexible glass (50 mm × 10 mm × 50 μ m, length × width × thickness). The flexible glass is OA-10G from NEG with thickness 50 μ m, safe bending radius 40 mm and strain point 650 °C. Six glass substrates were mechanical mounted on bare Hastelloy tape to use them on a spool. Unlike Hastelloy, the glass substrate was first cleaned for five minutes by a presputtering treatment with ions having energies of 100 eV to enhance subsequent film adhesion, because the cleaning procedure can remove most contaminations on the glass surface including surface-bonded polymer chains, oil films and terminal oxide layers. Ion bombardment also made the glass substrate a little bit rough which could thus strengthen film-substrate interfaces. After the cleaning process, the optimized beam current and beam voltage parameters were applied to IBAD MgO on the glass substrates for 40 – 90 s to select the right process time.

Novel flexible ceramic substrate YSZ, ceraflex (3 mol% yttria of YSZ from ENRG), is another good alternative due to its good thermal stability and effective barrier to moisture and oxygen. However, the initial film surface roughness of YSZ is much higher (30 - 50 nm) than that for glass and polished Hastelloy substrates. In order to reduce the roughness, spin-on-glass (SOG) T14 (Honeywell Electronic Materials) was coated on ceraflex at 4000 rpm for 1 min and then baked at 450 °C to remove the chemical elements (*108*). Three layers of SOG coating were used to reduce the surface roughness further to less than 1 nm. Then, the same process for IBAD MgO on glass substrate was applied to the flexible YSZ.

2.2.3 Fabrication of biaxially-textured CeO₂ on flexible substrate

Both flexible glass and Hastelloy were applied as substrates to grow IBAD CeO₂. Prior to deposition, the substrates were cleaned by Ar^+ ions bombardment with energies of 100eV for five minutes to ensure cleanness. A mixture of Ar and O₂ was used as the assist source gases at an assist beam energy of 900 eV. The sputter ion beam energy was 950 eV with different ion exposure times from 20 to 70 s. After the IBAD CeO₂ process, homoepitaxial CeO₂ and heteroepitaxial Ge were grown on flexible Hastelloy and glass, respectively. By employing IBAD CeO₂, the number of buffer layers in the stack for epitaxial semiconductor growth can be reduced to one.

2.2.4 Characterization of biaxially-textured flexible thin films

<u>RHEED</u>

The IBAD layers are mainly characterized by RHEED, an in-situ surface crystal structure monitor system developed by STAIB Instruments. It consists of: (1) a RHEED gun that produces a high-brightness, small-size and low-divergence electron beam up to 35 keV, which is accelerated to the substrate at a grazing angel with respect to the substrate planes; (2) a power supply that is remotely controlled by a compact control box to adjust the beam intensity, focus and position; (3) a CCD camera together with a phosphor screen, located at the other side of the RHEED gun to collect the reflected diffraction pattern; (4) a KSA 400 imaging and analysis system for multiple function imaging.

<u>X-ray diffraction (XRD) measurements</u>

In order to study the crystallographic orientation of the epitaxial MgO, CeO₂, and Ge, high resolution XRD (HRXRD) theta-2theta and rocking curve scans were conducted using a triple-axis

Rigaku Smartlab diffractometer. The parallel beam (PB) mode was specially used. Scans were analyzed with EVA Software.

Detailed X-ray pole figure measurements of homo-MgO were conducted using a Bruker 2D General Area Detector Diffraction System (GADDS). A wide 2 θ and chi range scan were simultaneously conducted in GADDS in a very short measuring time. Phase identification was performed by integration over selected ranges of 2 θ and chi. Phi scans extracted from the pole figures were used to determine in-plane texture of the films.

Atomic force microscopy (AFM)

The substrate surface morphology and roughness were characterized using AFM dimension 3100 (tapping mode). The tap frequency was 300 kHz.

2.3 Results and discussion

2.3.1 Development of IBAD MgO biaxial texture

(1) Film texture as a function of Hastelloy surface roughness

Two Al₂O₃ thin films with different surface roughnesses (2.79 nm and 0.98 nm) were prepared as templates for IBAD MgO growth. AFM images from the two templates are shown in Figures 2.3 (a) and (b). It is observed from the RHEED patterns in Figures 2.3 (c) and (d) that the MgO grown on a rougher Al₂O₃ surface shows near polycrystalline rings, whereas the MgO grown on a smoother Al₂O₃ surface (< 1 nm) shows perfect cubic biaxial texture. It confirms that the substrate surface roughness has a significant effect on the initial nucleation texture of IBAD MgO films. As discussed in Chapter 1, the texture evolution of IBAD MgO is nucleation mediated, which requires only 10 nm thickness to induce optimal texture. If the surface is too rough, any asperities in the substrate at the order of magnitude of 10 nm or greater will prevent the coalescence of grains resulting in a discontinuous film growth(*72, 109*). Thus, the subsequent homo-MgO deposition forms a polycrystalline texture. As a result, the quality of substrate roughness is critical for optimal IBAD-MgO growth.



Figure 2.3 AFM surface profile of Al₂O₃ overlaid Hastelloy with different RMS roughness of (a) 2.79 nm and (b) 0.98 nm; (c) and (d) are real-time RHEED patterns from IBAD MgO deposited on the corresponding Al₂O₃ buffer layers (a) and (b), respectively.

(2) Film texture as a function of ion beam angle

Ion beam angle is critical in biaxial texture formation for the channeling and shadow effect. To examine the influence of ion beam angle on the IBAD MgO texture, the assist ion source was adjusted to different incident angles of 45° and 60° with respect to the substrate normal. IBAD MgO was then deposited with beam current of 80 mA and beam voltage of 900 V for 80 seconds. In order to confirm the in-plane and out-of-plane texture, a homo-MgO layer with 60 nm thickness was deposited on each sample at a substrate temperature of 820 °C. The films were then characterized using XRD phi and omega scans for in-plane and out-of-plane texture, respectively. The full width of half maximum (FWHM) of omega scan decreased from 3.1° to 2.3° when beam angle was adjusted from 60° to 45°. Moreover, the in-plane texture improves as evidenced by the transition of a near polycrystalline ring (fiber texture) to four sharp spots in the (110) and (111) pole figures of homo-MgO as shown in Figure 2.4 (a) and (c) respectively. It means that the ion beam angle primarily influences the in-plane film texture, while the out-of-plane texture is relatively constant. In addition, the small value of FWHM in phi scan at beam angle of 45° is consistent with MgO <220> channeling direction due to less sputtering yield (*57*).



Figure 2.4 Pole figure analysis of homo-MgO grown on IBAD-MgO which was fabricated at different angles of ion beam to substrate normal (a) 45° and (b) 60°; (c) (111) pole figure of MgO corresponding to 45° ion beam angle.

(3) Film texture as a function of beam current and beam voltage

Based on the findings, an assist ion beam incident angle of 45° to the substrate normal and small surface roughness of Al₂O₃ less than 1 nm were used for the IBAD MgO growth. In the process, eight samples were deposited onto Al₂O₃ with Y₂O₃ seed layer at assist ion beam current (I_c) of 80 mA and ion exposure time of 80 s. Figure 2.5 shows the RHEED patterns of IBAD MgO on metallic substrates as a function of the assist ion beam voltage (I_v) , increasing from 900 V to 1300 V. The intensity and sharpness of the IBAD MgO diffraction spots increase gradually as I_v increases from 900 to 1150 V, and then remain almost stable with further increase of I_v . The appearance of high quality film texture at high ion beam voltage is consistent with a nucleation growth process. During the early nucleation stage of MgO, increasing I_v will assist the ion beam in more efficiently alignment of the in-plane towards the ion source (220) direction, leading to a film with a greater percentage of aligned grains enabling a more highly-textured film. When the I_v increases to a value at which the assist ion beam energy provided is more than needed to remove most misaligned atoms, there is no further improvement of the texture. Therefore, the assist ion voltage of $I_v = 1150$ V is selected as the optimal ion beam voltage condition.



Figure 2.5 RHEED images of IBAD MgO on metallic substrates with different assist I_{ν} .

Figure 2.6 shows a set of RHEED patterns of IBAD MgO films that were deposited onto Y_2O_3 seed layer using different assist beam current (70 mA – 100 mA) at a constant beam voltage of 1150 V, for 80 s. We observe that below a certain I_c , the RHEED pattern shows only a uniformly diffuse background, indicative of an amorphous film. After the I_c reaches 70 mA, a strong and sharp RHEED pattern is observed. However, the (220) peak shows some polycrystallinity, corresponding to a wide in-plane FWHM. With increasing I_c , it is hard to observe improvement from the RHEED patterns. It is well known that ion bombardment can damage the growing films. At low beam current, a small fraction of adatoms is sputtered away from growing films. More adatoms move off their balance positon and become free atoms on the film surface. Those free atoms are absorbed by the less damaged crystalline grains, corresponding to the <110> channeling direction, to sustain their growth. Therefore the orientation alignment of the IBAD MgO film is optimized at relatively higher I_c . When the I_c reaches 100 mA, the intensity of diffraction spots suddenly decreases, which

means the texture degrades at high assist beam current. It was even hard to measure the FWHM of the omega scan and the phi scan from homo-MgO grown on IBAD MgO films deposited at a I_c of 100 mA. Two reasons may explain this phenomenon. Timothy Weber suggested the out-of-plane texture was destroyed by the high beam current due to some rotation of the grains orienting the caxis toward the ion source, thus accounting for the destruction of out-of-plane film texture (57). E. Wendler suggested the damage on the grains of <110> in-plane orientation started to increase after the damage on the grains of other orientations saturates. The saturation of damage can be explained by the efficient dynamic annealing recovery of defects introduced by ion irradiation (110, 111). Therefore the percentage of grains with <110> in-plane orientation decreases at this high I_c condition, resulting in the decrease of orientation degree of the films.



Figure 2.6 RHEED images of IBAD MgO grown at different ion beam current on metallic substrates.

In order to prove the previous analysis based on IBAD MgO RHEED patterns, a homo-MgO with thickness of 60 nm was deposited on all IBAD MgO templates to study both in-plane and out-of-plane texture. Figure 2.7 (a) shows biaxial film texture as a function of assist beam current at constant $I_v = 1150$ V. The FWHM of the omega scan is in the range of $2.3 - 2.5^\circ$, whereas the FWHM of the phi scan decreases from 11.5° to 7.6° as the beam current increases from 70 to 90 mA. It is noticed that there is a fast degradation of texture at $I_c = 100$ mA, at which it is hard to calculate the FWHM of omega scan ($\Delta \omega$) and FWHM of phi scan ($\Delta \phi$) through XRD. This in-plane texture evolution is consistent with RHEED patterns as we discussed in the previous paragraph. At low assist ion beam current, the film has enough energy to select the preferred (001) out-of-plane texture, but it does not have enough ion bombardment to efficiently select the in-plane orientation for every crystal, resulting in a broad in-plane orientation distribution (*112*). As the beam current increases to the optimal value of 80 mA, both out-of-plane and in-plane texture start to become steady.



Figure 2.7 Biaxial film texture as a function of IBAD (a) beam current, and (b) beam voltage.

Therefore the beam current of 80 mA is selected to check the influence of beam voltage on the film texture, as shown in Figure 2.7 (b). The FWHM of the homo-MgO omega scan is in the range of $2.2^{\circ} - 2.4^{\circ}$ when the IBAD beam voltage falls in the range of 900 - 1250 V, following by a sharp increase up to 2.56° at 1300 V. The in-plane texture deteriorates from 6.2° to 10.2° with the beam voltage increasing from 900 to 1300 V, which is the opposite of the RHEED results in Figure 2.5. This means evaluation of IBAD film texture quality cannot be fully relied just upon the intensity and sharpness of diffraction spots if there is only a slight difference in the diffraction patterns. Many other factors, such as resolution, tape position and vacuum during the measurement of the RHEED patterns will influence their accuracy. In order to resolve this issue, Rhett Ty Brewer provided a quantitative biaxial texture analysis with a RHEED in-plane rocking curve experiment. In that experiment, the substrate was rotated around its vertical axis and the intensities of several diffraction spots were recorded as a function of the rotation angle φ . The rocking curves were characterized by the FWHM from a Gaussian fit (112). By using this method, the IBAD film texture can be evaluated without homo-MgO deposition. However, this deterioration in the film texture with increasing I_{ν} might due to the critical thickness to form the biaxial texture. At low I_{ν} , the ion to atom ratio (r) is higher, therefore the ion beam needs less time (80s) to reach the critical thickness of 10 nm for biaxially-textured growth. However, with further increase of I_{ν} , more atoms will be resputtered off the substrate surface therefore requiring longer time to reach the critical thickness for a highly-oriented thin film.

(4) Film texture as a function of ion exposure time

Following the above discussion, $I_v = 900$ V and $I_c = 80$ mA were used for further study to determine the effect of ion exposure time on the film texture. The RHEED images of IBAD MgO with different ion exposure times (20s - 250s) are shown in Figure 2.8. The images transition from a diffuse-scattering pattern (from the yttria seed layer) to a crystalline pattern of MgO at about 20 s; afterwards the diffraction pattern gradually improves from 20 s to 60 s. After 60 s, the RHEED pattern doesn't improve any longer until 90 s, and then eventually starts to degrade. At 250 s, the pattern shows the polycrystalline feature. These results confirm that well-aligned MgO crystallites are formed at the very beginning of the deposition with (100) out-of-plane direction normal to the substrate and <110> in-plane direction facing the ion source. The rapid development of biaxial texture in the IBAD MgO is due to fact that the (100) direction is the preferred out-of-plane alignment for MgO, as mentioned in Chapter 1. Therefore the assist ion beam only needs to align the in-plane axes, simplifying the texturing process and allowing the biaxial texture to appear at the inception of the deposition (72). In order to confirm the RHEED analysis, the corresponding homo-MgO film texture was evaluated by omega scan and phi scan using XRD.



Figure 2.8 RHEED images of IBAD MgO grown at different ion exposure times on metallic substrates.

In Figure 2.9, the homo-MgO texture as a function of IBAD ion exposure time is quantitatively analyzed based on $\Delta\omega$ and $\Delta\varphi$. It shows the same trend as that revealed by the RHEED patterns. Both $\Delta\omega$ and $\Delta\varphi$ become narrow with ion exposure time increasing from 40 to 80 s. The optimized time is 80 s with $\Delta\omega = 2.2^{\circ}$ and $\Delta\varphi = 6.2^{\circ}$, which corresponds to the critical thickness of IBAD MgO of 10 nm, the thickness at which the substrate is fully covered by textured MgO crystallites. When film thickness is less than 10 nm, the substrate coverage is small and, consequently, there is little material available for texturing. However, when the thickness is beyond the critical value, texture degradation starts as evidenced from the increase of the FWHM of both $\Delta\omega$ and $\Delta\varphi$ at ion expose time beyond 80 s. This phenomenon can be explained by the tilting mechanism (*113*). The planes begin to tilt away from the ion beam in thicker MgO films, which leads the ions not to channel as well along the <110> direction. This induces a greater amount of damage in the surrounding grains with <110> in-plane direction, deteriorating the biaxial alignment between grains (*69*). Therefore, it is critical to select the optimal *I_c*, *I_v* and deposition time to attain high-quality IBAD MgO on metallic substrates.



Figure 2.9 Biaxial film texture as a function of IBAD ion exposure time.

(5) Growth conditions for highly-textured IBAD MgO thin films

Based on the previous discussion, the optimized growth parameters for IBAD MgO films are tabulated in Table 2.1. This optimal condition is applied to grow biaxial-textured MgO on other substrates such as flexible glass and ceramic. Figure 2.10 shows representative RHEED patterns for both optimized IBAD-MgO and homo-MgO. The RHEED pattern for homo-MgO shows sharper and stronger diffraction spots than that for IBAD-MgO, indicating the texture is enhanced after the high temperature homo-epitaxial growth.

Parameter	Value
Substrate roughness	< 1nm
Assist ion beam angle to substrate normal	45°
Assist ion beam voltage	900V
Assist ion beam current	80 mA
Ion exposure time	80s
Film thickness	10 nm
Biaxial-textured homo-MgO	

Table 2-1 Growth conditions for biaxial-texture IBAD MgO films.

Figure 2.10 Schematic of the highly oriented MgO thin film growth on flexible metal substrate via IBAD MgO template. Corresponding RHEED patterns based on the optimized IBAD conditions are shown.

(6) Deposition of IBAD MgO on flexible glass

Another set of IBAD MgO samples was deposited onto flexible glass substrates using the optimized condition as the IBAD MgO on metallic substrates, except for the ion exposure time. Figure 2.11 shows 2D X-ray diffraction patterns for homo-MgO films deposited on IBAD-MgO with different ion exposure times of 40 - 90 s. Only one MgO (200) peak is observed in all samples, confirming their c-axis orientation alignment. However, the integrated $\Delta \omega$ improves from 5.78° to 3.12° when ion exposure time increases from 40 to 60s, following by a peak broadening after 70 s. This follows the same trend as the IBAD MgO grown on metallic substrate: the biaxial alignment increases initially with increasing film thickness, and then decreases when the film thickness surpasses the value of the critical thickness. For IBAD MgO films grown on glass substrate, a deposition time of 60 s is selected as the optimized condition with ion beam voltage of 900 V and beam current of 80 mA. This optimal deposition time for glass substrate (60 s) is different from that for metallic substrate (80 s), probably due to the difference in roughness and microstructure of yttria seed layers on metallic and glass substrates.



Figure 2.11 2D X-ray diffraction patterns for homo-MgO films deposited on IBAD-MgO grown at different ion exposure times of 40- 90s on flexible glass. The 2θ range is 26-74°.



Figure 2.12 XRD (a) θ -2 θ scan and (b) ω scan of the MgO (200) peak for homo-MgO deposited on IBAD-MgO overlaid on flexible glass; (c) RHEED pattern for IBAD MgO grown on flexible glass; (d) in-plane XRD of phi scan integrated from (110) pole figure.

In order to confirm the biaxial-textured growth of IBAD MgO on flexible glass, the typical homo-MgO with IBAD deposition time of 80 s was characterized by XRD, as shown in Figure 2.12. The out-of-plane θ -2 θ scan in Figure 2.12 (a) shows only one MgO (200) peak with $\Delta\omega$ of FWHM 3.12° (Figure 2.12 b). This demonstrates a good out-of-plane texture with *c* axis perpendicular to the substrate. The RHEED pattern shows the biaxial texture in IBAD MgO grown on flexible glass (Figure 2.12 c). In the MgO (220) phi scan in Figure 2.12 (d), four peaks are observed with an interval of 90° and an average FWHM of 8.39°, which confirms the high-quality

in-plane texture of the homo epi-MgO/IBAD-MgO on flexible glass. These results confirm that well-aligned MgO crystallites are formed on flexible glass with strong (100) out-of-plane direction and <110> in-plane direction.



(7) Deposition of IBAD MgO on flexible YSZ

Figure 2.13 AFM surface profile of (a) as-received YSZ substrate and (b) after three layers smoothing process by SOG; (c) and (d) are real time IBAD MgO RHEED patterns deposited on the corresponding YSZ substrates shown in (a) and (b).

Ceraflex (YSZ) is another promising substrate for growing semiconductor due to its high resistivity, high temperature stability and reasonable flexibility (the radius of curvature is approximately 8 mm for the 100 μ m thick ceraflex tape). However, high surface roughness (> 30 nm) restricts its biaxial texture formation during the nucleation stage of IBAD process. As shown from Figure 2.13 (a), IBAD MgO deposited on a raw Ceraflex substrate has a RMS surface roughness of 36.9 nm (Figure 2.13 a) and the RHEED pattern shows polycrystalline characteristics, because the asperities and particles on the rough substrate will prevent the coalescence of the MgO grains. Therefore, multilayers of SOG coatings with intermediate baking were made for

planarization. Each layer has excellent adhesion between SOG layers due to the homogeneity of the layers. After a three layer smoothing process, the surface roughness reduces to 1.12 nm, as shown in Figure 2.13 (b). The IBAD MgO grown on this planarized YSZ shows an almost pure cubic RHEED pattern in Figure 2.13 (d). After homo-MgO growth on IBAD MgO/YSZ, only the MgO (200) peak is observed from a XRD θ -2 θ scan, as seen in Figure 2.14. It confirms a good out-of-plane texture with *c* axis perpendicular to the substrate. However, the in-plane texture is too weak to be measured.



Figure 2.14 XRD θ -2 θ scan of the homo-MgO deposited on IBAD-MgO/flexible YSZ.

2.3.2 Optimization of biaxially-textured CeO₂ growth by IBAD

Due to the large lattice mismatch between MgO (4.21Å) and Ge (5.66Å), multiple transition buffer layers are required between the two materials to achieve epitaxy in Ge. However, multi-layers will induce many other impure elements, which will potentially diffuse into the Ge active layer and deteriorate the device performance. In order to eliminate diffusion from the substrate and multiple buffer layers, a stable substrate (eg. flexible glass) and few buffer layers (eg. only one layer) are preferred to grow epitaxial Ge (or Si) layers with reduced contamination. CaF₂

has been demonstrated to be an excellent buffer layer for the growth of epitaxial Ge due to their good lattice match. However, because of its porous buffer structure, an additional thick CaF_2 capping layer with very slow deposition rate is needed for Ge epitaxy (75). CeO₂, with the same fluorite structure and a similar lattice constant to Ge, is selected to be the IBAD template for Ge growth. However, it takes several hours to reach the biaxially-textured CeO₂ oriented in the <100> direction. During CeO₂ growth, the (111) plane has the lowest surface energy and is expected to grow more rapidly than grains oriented further from (111). Therefore the assist ion beam is needed for longer time processing up to several hours to align both in-plane to <110> direction and out-ofplane to (100) direction (*81-83*).



Figure 2.15 RHEED images of IBAD CeO₂ grown at different process times on glass substrates.

We developed a novel technology to enable epitaxial growth of CeO₂ (111) seed layers with a very fast deposition process on a flexible glass tape. The tape-feeding speed of roll-to-roll process is ~50 cm/min for the deposition of a ~10 nm-thick layer. This technique eliminates the requirement of depositing multiple oxide buffer layers between the flexible substrates and Ge films. The angle of assist-ion beam was set at 54.7° from the surface normal of the substrate. A textured CeO₂ film with a preferred <111> out-of-plane orientation was achieved. The ion-beam angle and out-of-plane texture are consistent with the preferential growth of grains that have the {111} family of planes. The ion-beam sputters away grains with other orientations. A relatively higher assistbeam energy (900 eV) was used to facilitate the atom mobility on the growing surface and to promote the growth on a (111) plane that is thermodynamically stable. At lower bombardment energies, the ions do not have enough energy to remove misarranged surface ad-atoms, resulting in a high mosaic spread. Growth conditions for the textured CeO₂ film by IBAD were optimized using various ion exposure time of 20 to 70s, as seen in the RHEED pattern in Figure 2.15. The RHEED pattern appear at around 20 s, and then it becomes sharper at 30 – 40 s, followed by a fast deterioration beyond 50 s ion exposure time.



Figure 2.16 XRD θ -2 θ scan from (a) homoepitaxial CeO₂ deposited on IBAD-CeO₂ grown at various ion exposure times overlaid on Hastelloy; (b) heteroepitaxial Ge deposited on IBAD-CeO₂ grown with 30s ion beam exposure times overlaid on flexible glass.

The XRD θ -2 θ scans of homo-CeO₂ deposited on IBAD-CeO₂/Hastelloy at different IBAD process times are shown in Figure 2.16 (a). The labelled "X" peaks come from the Hastelloy substrate. A strong and sharp homo-CeO₂ (111) peak appears only on IBAD-CeO₂ grown with 30 s ion exposure time. In contrast, the other CeO₂ samples grown with 20 s and 60 s ion exposure time show polycrystalline characteristics. Enhanced epitaxial Ge (111) growth was observed only on 30 s IBAD CeO₂ as will be discussed in Chapter 3. The Ge grown on both 20s and 40s IBAD CeO₂ all showed polycrystalline texture. Because the projection of the atomic locations in the (111) plane of CeO₂ reasonably matches with the (111) plane of Ge with estimated lattice mismatch of 4%, Ge has been successfully grown heteroepitaxially on IBAD-CeO₂ directly, as shown from Figure 2.16 (b). Both the Ge (111) rocking curve and the three-fold symmetry in the Ge (220) phi scan confirmed Ge biaxial texture. By employing IBAD CeO₂, the buffer layers for epitaxial Ge growth can reduced down to only one thin layer (~10nm).

2.4 Summary

In this work, biaxially-textured MgO and CeO₂ films were fabricated on Hastelloy, flexible glass and YSZ substrates using IBAD. In the IBAD MgO process, the substrate surface roughness, assist ion beam angle, assist ion beam current (I_c) and voltage (I_v), and ion exposure time were systematically investigated to achieve highly textured IBAD MgO. At low I_c , the film has enough energy to select the preferred (001) out-of-plane texture, but it doesn't have enough energy to select the in-plane orientation resulting in broader FWHM in phi scan. When I_c increases to an optimum value, out-of-plane texture stays constant, while ion bombardment is more efficient to select the crystal to (110) in-plane oriented towards the ion beam. At I_c levels beyond the optimum value, ion bombardment causes out-of-plane damage, which broadens the in-plane diffraction peaks as well. The same trend is observed in the effects of the ion exposure time. The biaxial alignment of IBAD MgO increases initially with increasing ion exposure time, and degrades when film thickness increases beyond the optimal value, largely due to the "tilting mechanism". After optimization, the best conditions for IBAD MgO grown on flexible Hastelloy are found to be $I_c = 80$ mA and $I_v = 900$ V for ion exposure time 80 s. XRD reveals that the homo-MgO grown on optimized IBAD MgO/Hastelloy has a strong c-axis orientation alignment with $\Delta \omega = 2.2^{\circ}$ and $\Delta \varphi = 6.2^{\circ}$. The optimized IBAD conditions were applied to grow biaxial textured MgO on flexible glass and Ceraflex.

In IBAD CeO₂ processing, the assist ion beam angle was adjusted to 54.7° from the surface normal of the substrate, consistent with the preferential growth of grains that have {111} family planes. The ion exposure time was studied based on a high ion beam energy of 900 eV. It is found that 30 s is the optimal time to grow biaxial textured CeO₂ with (111) out-of-plane orientation using IBAD. Both homo-CeO₂ and hetero-Ge were directly grown on IBAD CeO₂ templates. The Ge (111) rocking curves and the three-fold symmetry in the Ge (220) phi scans confirmed the Ge biaxial texture. By employing IBAD CeO₂, the buffer layers for epitaxial Ge (or Si) growth can be reduced down to only one thin layer (~10 nm). Both IBAD MgO and CeO₂ templates are used for further epitaxial Si and Ge growth as presented in Chapter 3 and Chapter 4.

Chapter 3 High mobility single-crystalline-like Ge thin film on flexible substrates

3.1 Introduction

Germanium (Ge) has found extensive use in various electronic and optoelectronic device applications such as in integrated circuits, thin film transistors (TFTs), infrared detectors and III-V semiconductor photovoltaics (*114*). Currently, the multijunction approach to high efficiency III-V semiconductor concentrator photovoltaics based on single-crystal Ge wafers has yielded efficiency as high as 40% (*115*, *116*). However, these multijunction photovoltaics are not economical beyond a niche use in power generation partly due to expensive Ge single-crystal wafers which account for more than a third of the total module cost. An affordable multijunction photovoltaic could be achieved by employing polycrystalline Ge wafers with random grain orientations, but it results in a decrease in carrier mobility and efficiency of the device primarily due to the grain boundaries. Moreover, brittleness and rigidity of Ge wafers cause a large possibility of device failure during fabrication. A promising alternative is to use single crystal wafers but also are much less expensive due to reduction of thickness to a micrometer scale.

As for another application in flexible TFTs, there have been many reports focusing on mobility boost for the active layer such as hydrogenated amorphous Si (a:Si-H) (*117*), organic semiconductors (*118*), and oxide semiconductor In-Ga-Zn-O (IGZO) (*34*); however, the mobility reaches only ~0.1–10 cm². V⁻¹. s⁻¹ that is still too low for a high performance device. Polysilicon TFTs on flexible metal foils with relatively high mobility ~50-300 cm². V⁻¹. s⁻¹ have been achieved (*119*). However, the main issues are the nonuniformity of their field-effect mobility and threshold voltage, caused by the grain size and grain boundaries in Si thin films (*120*). Hence, high-performance flexible electronic devices, based on high mobility and uniform mobility distribution in the thin films are required for next-generation TFTs.
For both applications of multijunction solar cell and TFTs, a single crystalline-like Ge film fabricated by employing biaxially-textured templates made by ion beam assisted deposition (IBAD) is a promising solution. IBAD has been used to achieve biaxial crystallographic texture in thin films on polycrystalline or amorphous substrates, and has been utilized to fabricate single crystalline-like oxide films in lengths of over a kilometer (*121*). We have demonstrated that CeO₂, whose fluorite structure matches the diamond structure of germanium, is a suitable intermediate layer to achieve epitaxial growth of Ge (*96, 122, 123*). In-plane misorientation of grains in the Ge film was reduced to 1° full width at half maximum (FWHM) as measured by phi-scan X-ray diffraction (XRD) (*122*).

This chapter describes results from optimization of growth conditions of single crystallinelike Ge films and fabricate the optoelectronic devices based on those films. It includes three parts: (1) Optimization of the quality of Ge thin film grown on the traditional buffer structures (CeO₂/LaMnO₃/homo-MgO/IBAD MgO) by reducing the surface roughness, film dislocation density and increasing carrier mobility for the device application. Specifically, the influence of deposition temperature as well as film thickness on grain size, texture, surface roughness, carrier mobility and concentration were studied. (2) Elimination of element diffusion from the substrate and buffer layers. Various approaches were studied including increasing the thickness of the Al₂O₃ diffusion barrier to reduce the diffusion from the metal substrate, minimizing buffer layers to $1 \sim 2$ intermediate layers to reduce oxygen diffusion from the oxide buffer layers, using the low temperature process of radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) with less ion bombardment on surface instead of the relative higher temperature process of magnetron sputtering with high ion bombardment impact, and replacing the substrate to flexible glass to avoid metal element contamination. (3) Demonstration of electronic devices with optimized Ge buffer layers, including a Ge p-n bottom junction for future III-V multijunction photovoltaics, and TFT device based on (111) oriented Ge thin film/ flexible glass substrate.

3.2 Theory and experiments

3.2.1 Epitaxial thin film growth

Epitaxial growth has been utilized as an important technique to fabricate electronic and optoelectronic devices in the semiconductor industry. The technique enables a deposition of a crystalline thin film on another crystalline substrate to maintain the same crystal orientation. The crystallinity and orientation of the grown layer is determined by the substrate and deposition condition. Normally epitaxial growth is divided into two categories: homoepitaxy and heteroepitaxy. In homoepitaxy, the film deposited is the same material as the substrate, thus the lattice parameters are perfectly matched and there is no interfacial-bond strain. It is normally used to grow a pure film with different doping levels. Heteroepitaxy is growth of a crystalline film on a crystalline substrate with different material. It is mostly used to grow crystalline films of materials for which single-crystals are difficult to be obtained and is more common in optoelectronic device fabrication. Depending on the extent of lattice mismatch, three distinct epitaxial regimes are observed in heteroepitaxy. If the lattice mismatch is very small, then the heterojunction interfacial structure is essentially similar to that for homoepitaxy. However, differences in chemistry and coefficient of thermal expansion between the grown film and substrate can significantly influence the interfacial properties. When the lattice parameters differ more substantially, two other cases are possible: strained-layer epitaxy and relaxed epitaxy. Strained-layer epitaxy normally happens at an early stage of film growth to accommodate their crystallographic differences, making the interface coherent with atoms on either side lining up. With increasing film thickness, a relaxed structure consisting of an array of misfit dislocations is formed to relieve a portion of the misfit by dislocations. Therefore, there is a critical thickness beyond which dislocations are introduced. These dislocations, twins and stacking faults degrade many device properties by creating states in the energy gap and reducing the minority carrier lifetime and quantum efficiency of photonic devices (124).

Many methods can be applied to fabricate heteroepitaxial thin films, such as liquid phase epitaxy (LPE), metal organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), RF-PECVD, and radio frequency magnetron sputtering (RFMS). In this chapter, RFMS and RF-PECVD are employed to fabricate heteroepitaxial Ge thin films on flexile substrates.

Radio frequency magnetron sputtering:

The epitaxial buffer layers (CeO₂/LaMnO₃/homo-epi MgO) are grown using a reel-to-reel RFMS system. A dual chamber sputtering system, as shown in Figure 3.1, is used to deposit two different materials in sequence in one run. The details of the system are as follows:



Figure 3.1 Schematic of RF sputtering system.

Pumping system: The dual chamber system consists of two independent processing chambers – process chamber 1 (PC1) and process chamber 2 (PC2). Both PC1 and PC2 are connected to turbo molecular pumps. Once the samples are loaded, a roughing pump is used to pump down the chamber to about 100 mTorr. The roughing pump is then isolated from the chamber and two turbo molecular pumps are used to pump down the chamber pressure to less than 10⁻⁵ Torr.

A convection gauge is used to measure chamber pressure from atmospheric to about 100 mTorr, a Baratron® capacitance manometer is used to measure pressure in an operating range of 1 to 100 mTorr, and an ion gauge is used to measure pressure in ultra-high vacuum (UHV) range.

Roll-to-roll system: The samples are spot welded with bare Hastelloy tapes (leader tape) and loaded on two spools. A certain tension between two spools is maintained using two motors to drive the tape and keep the tape flat during deposition. The spool in PC2 is connected to an encoder where the tape speed can be controlled precisely. The thickness of the deposited thin films is controlled by the deposition rate and deposition time, corresponding to the power and tape speed, respectively.

Cooling system: A chilled closed liquid loop is used for cooling the chamber, substrate, RF generator, matching box, heater and turbos. Each of these coolant loops is monitored by a flow sensor and controlled by associated valves via a pneumatic valve manifold.

Heating zone: Each of PC1 and PC2 has its own heater with a susceptor in which five thermocouples are located inside to control the temperature. Twelve USHIO FCL 500 W halogen bulbs are the heat source. The maximum temperature for the heater is 900 °C. The deposition shields are placed above the susceptor, forming a 20 cm \times 5 cm deposition zone.

Target assembly: The target assembly consists of the targets and magnets. The target is made of the materials that are to be deposited, or their metal constituents that will be reacted with the oxygen or nitrogen during the deposition. The magnets confine the plasma discharge to increase deposition rate. The target is mounted on the cathode using a high thermal and electrical conductivity silver (Ag) paste for better cooling of the target. A cylindrical shield is used to cover the target assembly.

Outgassing and sputtering: Ultra-high purity Ar gas (99.999%) is passed into the process chamber at 500 °C for two hours before deposition in order to remove moisture. Then 100 sccm Ar

gas is flowed into the chamber with the turbo valve 80% closed to maintain a relative high pressure $(5 \times 10^{-2} \text{ Torr})$ to create a plasma subjected to a RF potential. The Ar⁺ ions in the plasma are attracted by the negatively charged cathode to bombard the target surface, ejecting atoms from the target. The start-up plasma at a low power of 50 W is generated immediately under the target assembly. The sputter power is then increased slowly to reach the set point value after fully opening the turbo gate valve. Ultra-high purity O₂ gas (99.999%) is passed into the processing chamber for chemical reaction between the target material and O₂ to form oxide thin films, such as MgO, LaMnO₃, and CeO₂. The flow rates of Ar and O₂ are controlled by two mass flow controllers. After pre-sputtering for 30 minutes, the samples are moved to the heater.

Radio frequency plasma enhanced chemical vapor deposition:

A modified Plasmalab100 (Oxford instruments) RF-PECVD system was used for high quality Ge film growth with an inductively-coupled plasma reactor operated at 13.56 MHz radio frequency. The reactor is a stainless-steel cylinder consisting of a reactive gas ring, inductively-coupled coil, RF generator, heating stage and cooling loop, as shown in Figure 3.2. The plasma is generally created by the RF generator using the reactant gases (GeH₄ + H₂). A heating stage capable of reaching a temperature up to 1100 °C is retrofitted to the deposition chamber. The substrate on the heating stage is attached by two screws on 5 cm long customized sample holders and transferred in and out of the reactor using a load-lock assembly. Though epitaxial Ge growth has been reported at lower temperatures on c-Si wafers (*125*), achieving hetero-epitaxy on biaxially textured flexible templates is quite challenging and requires higher growth temperatures. Therefore, a combination of high growth temperature and dense inductively-coupled remote-plasma was employed to achieve high quality crystal growth on flexible templates. The process gases consisted of 30% germane (GeH₄) and 70% H₂. The diluted hydrogen was purified by a palladium cell purifier. Moreover, diborane (B₂H₆) and phosphine (PH₃) gases were introduced for doping in appropriate proportions

with respect to GeH₄ and H₂ using high resolution mass flow controllers to achieve the required electron and hole carrier concentrations, respectively.



Figure 3.2 Schematic of RF-PECVD system.

3.2.2 Fabrication of buffer layers for high-quality Ge growth

Two types of buffer layers on different substrates will be discussed in this chapter: one is the traditional CeO₂ buffer overlying LaMnO₃/Homo-MgO/IBAD MgO on flexible Hastelloy substrate; another is the IBAD CeO₂ on flexible glass with (111) out-of-plane orientation. Both substrates have their own functions: flexible Hastelloy can provide a conductive back contact for the solar cell application, while flexible glass with less buffer layers can reduce the diffusion from the substrates and buffer layers.

CeO₂/LaMnO₃/Homo-MgO/IBAD MgO on flexible metal substrate

A scheme of the typical multilayer architecture of the buffer layer used in this work is shown in Figure 3.3. The substrate consists of a homo-epitaxial MgO film (30 nm thick) on IBAD MgO template, a sublayer of epitaxial LaMnO₃ and a top layer of CeO₂. IBAD MgO template was grown on a flexible electropolished Hastelloy C-276 tape (wide \times thick: 12 mm \times 50 µm) with Al_2O_3 diffusion barrier in between. IBAD was used to achieve biaxially-textured growth on amorphous or nanocrystalline surfaces during the nucleation stage within the first few nanometers, as described in chapter 2. LaMnO₃ and CeO₂ layers were utilized to provide structural compatibility with Ge and accommodate the lattice mismatch between Ge and MgO layer. The (001)-oriented CeO_2 can be achieved by the IBAD process as well, however, it requires several hours to achieve the biaxial-texture (83, 126). All films in the multilayer architecture were grown in reel-to-reel radio frequency magnetron sputtering systems under various conditions. A detailed description and the deposition condition of oxide buffer layers have been provided in our previous work (96, 122, 123). However, since these buffer layers were designed for superconductor rather than semiconductor applications, two issues need to be addressed in this structure for the subsequent deposition of high quality Ge thin films and fabrication of high performance device.



Flexible metal foil, 50µm

Figure 3.3 Scheme of the multilayer architecture developed in this work for the growth of a single-crystalline-like Ge films on metal substrates.

First of all, a small quantity of metal elements diffused into a superconductor film will not harm the superconductor performance to a great extent, but those metallic contaminations and oxygen will severely reduce minority carrier lifetime in semiconductors thus deteriorating device performance. Therefore, the addition of an Al₂O₃ diffusion barrier layer in the flexible Ge thin film architecture is critical for a high efficiency device. It has been shown that a 300-nm-thick Al₂O₃ barrier layer made by atomic layer deposition (ALD) can reduce Fe ion diffusion to the copper indium gallium selenide (CIGS) absorber layer by 95%, leading to increased solar cell efficiency to 13.44% (*127*). Since the high conversion efficiency strongly depends on the effective prevention of the metallic element diffusion, the thickness effect of the Al₂O₃ film is studied by controlling the tape movement speed from 2 cm/min to 10 cm/min. The resulting film thicknesses is measured by ellipsometry. In this process, the Al₂O₃ is deposited in PC1 on electro-polished Hastelloy using two 7.62 cm Al targets and O₂ as the reactant gas. In order to avoid formation of polycrystalline films whose grain boundaries provide fast diffusion paths (*128*), deposition is performed at room temperature. The base pressure is 3.0×10^{-6} Torr before Al₂O₃ thin film growth. An Ar flow rate of 100 sccm and O₂ flow rate varied from 5 ~ 20 sccm are used at a forward power of 1900 W.

Secondly, since the heteroepitaxy Ge thin film growth quality is determined by the orientation and film density of the underlying CeO₂ layer, the CeO₂ film density under different O₂ partial pressures is investigated. In this work, CeO₂ is deposited on LaMnO₃-buffered IBAD MgO template by RF sputtering using a 20 cm \times 8 cm rectangular CeO₂ ceramic target in PC2. The base pressure is 1.6×10^{-6} Torr. Ar flow rate is fixed as 100 sccm, and O₂ flow rate is decreased from 10 sccm to 1 sccm. A susceptor temperature of 850°C is used. The CeO₂ layer is sputtered at 1000 W at a tape speed of 2 cm/min. XRD (111) pole figure measurements on the CeO₂ films confirm hetero-epitaxial growth on LaMnO₃ with an in-plane texture of $3 \sim 4^{\circ}$ FWHM, which is narrower than the previous report in our group 5.35°. The Ge thin film carrier concentration is studied after Ge deposited on both annealed and non-annealed CeO₂ buffer layers.

IBAD CeO₂ on flexible glass

In addition to the route of increasing the thickness of the diffusion barrier to eliminate the element diffusion from the substrate, an alternative way is to replace the metallic substrate with one that is flexibile, light weight, thermally stabel, a good barrier to moisture and oxygen, and compatible with large scale processing of electronic devices. Current flexible plastic substrates are limited for application due to thier low stability temperature < 300 °C. Flexible glass is a good candidate to meet all the requirements.

In this work, ultra-thin, flexible, and thermally stable (up to ~650 °C) OA-10G glass is used as a substrate. A CeO₂ film is deposited by IBAD as a biaxially-textured material in a favorable channeling direction.(*83, 129*). Prior to deposition, the sample was first rinsed in alcohol, and then cleaned *in situ* by Ar⁺ ion beam bombardment with energy of 200 eV for 2 minutes. Then IBAD CeO₂ of ~10 nm thickness was deposited on a flexible glass sample using an assist ion beam of 900 eV Ar⁺ for about 30 seconds. The reason to use the relatively higher assist ion beam energy is to enhance the atom mobility on the growing surface which would favor the (111) growth plane that is the thermodynamically preferred orientation (*80*). A detailed description of the similar oxide buffer deposition conditions using IBAD is described elsewhere (*96*). Different ion beam exposure time (20 ~ 40 s) is investigated for the subsequent RF-PECVD Ge growth. IBAD CeO₂ film growth is monitored using Reflection High Energy Electron Diffraction (RHEED), STAIB Instruments with kSA 400 detector. More details regarding the IBAD processes and technologies were provided in chapter 2.

3.2.3 Fabrication of heteroepitaxial Ge on flexible Hastelloy substrate with radio frequency magnetron sputtering (RFMS)

In order to optimize the Ge thin film quality based on the traditional buffer structures (CeO₂/LaMnO₃/homo-MgO/IBAD MgO), the effect of deposition temperature and tape moving speed are investigated to reduce the surface roughness and film dislocation density, and increase

carrier mobility for device application. The epi-Ge films were first deposited on an optimized CeO₂ film by magnetron sputtering at substrate temperatures of 500 to 850 °C. The deposition chamber was evacuated to a base pressure of 5×10^{-6} Torr before Ge thin film growth. Sputter deposition of Ge was then conducted with p-type boron-doped targets (99.999%) in an Ar-4% H₂ atmosphere. The substrates were heated using a lamp heater up to a maximum of 850 °C. The film thickness was maintained constant at about 1.25 µm. Then, the Ge film thickness was studied by adjusting the tape movement speed from 0.5 cm/min to 6 cm/min with the temperature maintained at 850°C. The resulting thicknesses were between 0.3 µm to 2.8 µm as measured by Focused Ion Beam (FIB)-equipped Scanning Electron Microscope (SEM). The Ge thin films carrier concentration was measured after Ge was deposited on both annealed and non-annealed CeO₂ buffer layers.

3.2.4 Fabrication of low defect density and high mobility crystal Ge with radio frequency plasma enhanced chemical vapor deposition (RF-PECVD)

Since Ge film grown on flexible Hastelloy with RFMS has high defect density (~ 10^{9} /cm³), it is not suitable for device fabrication. RF-PECVD is chosen to deposit Ge on a RFMS Ge buffer layer for the purpose of decreasing dislocation density, because this is more of an equilibrium process with less ion bombardment of substrate compared to sputtering. During the RF-PECVD process, a reactive gas of GeH₄ at a rate of 10 sccm and diluent gas of H₂ at a rate of 80 sccm are introduced into the chamber where the GeH₄ is decomposed by heat and RF-induced plasma resulting in Ge deposition. The formed Ge layer has fewer dislocations due to homoepitaxial growth on the RFMS Ge buffer layer. The byproduct of H₂ is pumped out by the turbo pump.

Materials with different carrier concentrations are needed for various optoelectronics devices. Therefore, a way to control the film doping concentration is critical for the semiconductor thin film process. Since the film doping concentration is determined by the target doping level, it cannot be controlled in the RFMS process. Doping in RF-PECVD can be realized by feeding a dopant gas precursor, such as PH_3 , B_2H_6 or AsH_3 , simultaneously during the deposition process.

The film doping concentration can be controlled by adjusting the dopant gas concentration in the reactive gas.

Epi-Ge grown on flexible Hastelloy

The flexible Ge buffer from RFMS and Ge wafer were cleaned by isopropylalcohol (IPA), mounted on an inconel sample holder and then loaded into the chamber via a loadlock. The Ge wafer is used as an ideal substrate for comparison. The chamber base pressure kept at 2.5×10^{-7} Torr. The Ge samples were first heated to 650 °C for one hour to remove all the oxide layer on the Ge surface (*114*), then deposited at an optimized plasma power of 300 W at a deposition pressure of 75 mTorr. Hydrogen dilution was used (GeH₄-to-H₂ ratio was 1:25) during Ge growth in order to promote crystallinity and passivate the Ge dangling bonds. The deposition temperature was varied from 400°C ~ 600°C to study the influence of temperature variation on film quality. The Ge thin film thickness was 1 µm for a deposition time of 45 minutes.

Ge film grown on flexible glass

Ge film was also directly grown on IBAD CeO₂ (111) / glass substrate by RF-PECVD. Single-crystal-like (111)-oriented Ge was grown at 400 °C ~ 600 °C using 10 sccm of GeH₄ source gas at 75 mTorr on IBAD CeO₂ buffer overlaying on flexible glass. The Ge layers were unintentionally p type doped. It has been mentioned epi-Ge films were normally found to be p-type even without using of p-type dopant in the growth, because point defects, extended crystal defects, or defect complexes unrelated to lattice and thermal mismatch are incorporated into the Ge film which act as the acceptors (*130*). In our case, the Ce impurity from the IBAD buffer layer may also behave as a p-type dopant. The base pressure for RF-PECVD is below 10⁻⁷ Torr. The realization of the (111) textured-Ge is due to the fact that the projection of the atomic locations in the basal plane of fluorite CeO₂ lattice matches perfectly with the basal plane of the diamond structure of Ge.

3.2.5 Characterization of flexible Ge thin film

Scanning electron microscopy (SEM)

The surface morphology was characterized using SEM LEO 1525 operating at 15 kV. SEM and AFM (mentioned in Chapter 2) were used to analyze roughness and also to determine the grain size and surface quality.

Raman spectroscopy

Raman scattering measurements were performed on a triple Horiba Jobin Yvon HR-800 spectrometer equipped with a liquid-nitrogen-cooled CCD detector using a blue 488 nm excitation laser wavelength. The laser intensity was kept low (< 5 mW) to prevent laser-induced modification of the Ge surface. The spectral resolution did not exceed 1.5 cm⁻¹.

Transmission electron microscopy

Microstructural characterization and defect density, especially interfacial studies of the epitaxial films were carried out by high resolution TEM imaging (JEM-2100 LaB6 microscope at 200 keV). Selected area electron diffraction (SAED) patterns of Ge layers confirmed epitaxial growth and the single-crystalline nature of those layers.

Hall Effect measurement

A HMS-5000 Hall Effect Measurement System was used to determine carrier density, electrical resistivity, hall coefficient, and the mobility of carriers in the Ge layer. The van der Pauw technique was utilized to determine resistivity of the thin film samples. A square-shaped sample, containing four very small ohmic contacts placed on the periphery (preferably in the corners) of the sample, was located on a sample holder. The measuring temperature was set as 300 K, and the magnetic field was set as 0.55 Tesla. The test for each sample is repeated for 6 cycles in order to obtain more reliable results.

Other characterizations, such as film texture and roughness were examined by XRD and AFM separately. The crystal quality of the growing film can be monitored in real time by RHEED. The above characterization methods were described in Chapter 2.

3.3 Results and discussion

3.3.1 Study of buffer layers

<u>Thickness study of Al₂O₃ diffusion barrier</u>

Use of flexible Hastelloy as the substrate for optoelectronic devices involves a few challenges. The most crucial issue is the diffusion of substrate components such as Ni, Cr, and Mn into the semiconductor film during the high temperature process and ion implantation effect. In this study, the effect of Al_2O_3 diffusion barrier with different thickness on the cation diffusion from the substrate was investigated.

The influence of different O_2 flow rates (5 ~ 20 sccm) on the formation of the Al₂O₃ films was examined. During Al₂O₃ deposition, twin Al targets were used because metal target generates a higher deposition rate than does on oxide target. By using the metal target, two operating modes are included: metallic mode and oxide mode. If the O₂ has low partial pressure, it normally result in high sputtering rate, therefore, metallic mode for Al deposition. For example, the resistivity of the Al₂O₃ films was about 8 $\mu\Omega$ ·cm at an O₂ flow rate of 5 sccm, and it increased to 32 $\mu\Omega$ ·cm at 8 sccm O₂ flow rate. These values appeared very low compared with those of bulk alumina (1x10¹⁴ Ω ·cm). In XRD measurement, an Al (111) oriented peak was observed for films deposited at an O₂ flow rate 5 ~ 10 sccm, which confirmed that some Al was deposited on the substrate rather than fully oxidized Al₂O₃ thin film. This metallic mode should be avoided because deposited metallic Al will diffuse into the semiconductor active layer and severely reduce minority carrier lifetime thus deteriorate device performance. With O₂ flow rate increase, the Al₂O₃ compound starts to form on both substrate and Al target surface, which causes target poisoning. The fully poisoned target allows for growth of Al₂O₃ films, but the deposition rate is significantly lower than the Al deposition. Therefore, a transition regime between the metallic and the oxide mode is critical for the growth of Al₂O₃ compound films with relatively high deposition rate. During the sputtering process of Al₂O₃, the transition regime was recognized by monitoring the O₂ partial pressure and target voltage. In this process, the target voltage reduced suddenly from 759 V to 528 V as O₂ flow rate increases from 12 sccm to 14 sccm. The resistivity increased to a value beyond the range of the four point probe method at a flow rate of 12 sccm or above. In XRD measurement, no Al peaks were observed at O₂ flow rate 12 ~ 20 sccm, indicating a fully oxidation of Al. These phenomena are attributed to a change of the target mode from metal mode to oxide mode (*131*). Because of the low deposition rate of Al₂O₃ in oxide mode, a transition regime of 12 sccm O₂ with 100 sccm Ar was used for the Al₂O₃ deposition to achieve fast deposition rates and fully oxidized films.

Then different tape speeds were studied to understand its influence on the film thickness. Figure 3.4 (a) shows the Al₂O₃ thickness versus deposition speed from 4 cm/min to 10 cm/min at a forward power of 1900 W. The film thickness increases from 83.2 nm to 190.7 nm when the tape speed decreases from 10 cm/min to 4 cm/min. Considering the deposition zone to be approximately 20 cm, the deposition rate for Al₂O₃ is around 40 nm/min. It has been noted that a 30 nm Al₂O₃ barrier layer starts to prevent Ni from diffusing into the absorber layer (*132*). The element diffusion at different thicknesses of Al₂O₃ substrates was evaluated and the results are shown in Figure 3.4 (b). It is noticed that the following Ge layer carrier concentration decreased from 1.5×10^{19} to 7.6×10^{17} when the Al₂O₃ diffusion barrier thickness is increased from 150 nm to 190 nm. It indirectly proves that a thicker Al₂O₃ layer helps to block diffusion from the Hastelloy. The Al₂O₃ samples were annealed in an Ar atmosphere at 800 °C for 1 hour, and no noticeable change was observed in the film surface through microscopy. This suggests that the alumina films demonstrate good thermal stability at high temperature.



Figure 3.4 (a) Al₂O₃ film thickness as a function of tape moving speed during RFMS process at 1900 W; (b) Ge carrier concentration versus different Al₂O₃ film thickness after Ge film growth on CeO₂/LaMnO₃/MgO/Al₂O₃ buffer layers.

CeO₂ texture optimization for high quality Ge growth

We initially investigated the influence of O_2 flow rate on the crystalline quality of CeO₂ films by reducing the O_2 flow rate from 10 sccm to 1 sccm, while keeping the Ar flow rate constant at 100 sccm and substrate temperature at 850 °C. Detailed XRD analyses were performed to examine the influence of O_2 gas flow rate. The θ -2 θ X-ray pattern in Figure 3.5 (a) verifies that there are no out-of-plane misorientations in the CeO₂ layer. It is clear that the O₂ flow rate plays an important role in the crystallinity of CeO₂ films. The intensity of the CeO₂ (200) peak becomes higher when the O₂ flow rate increases from 1 sccm to 7.5 sccm, indicating a better crystallographic quality of the CeO₂ layer with higher O₂ flow rate.



Figure 3.5 XRD (a) θ -2 θ scan from 20° to 75° and (b) $\Delta \omega$ of the CeO₂(200) peak for CeO₂ film deposited at different O₂ flow rates.

The FWHM of the ω -scan rocking curve for CeO₂ (200) plane in Figure 3.5 (b) shows that the *c*-axis alignment improves from $\Delta \omega = 1.15^{\circ}$ to $\Delta \omega = 0.84^{\circ}$ when O₂ flow rate is increased from 1 sccm to 7.5 sccm. We noticed that no matter how much O₂ flows during the process, the $\Delta \omega$ of CeO₂ (200) is much narrower than that of the standard CeO₂ (1.78°) from Research Buffer (RB) system, which may be caused by the different deposition temperature, discharge power and film thickness in different deposition systems. When the O₂ flow rate increases, the fraction of negative ions consisting of O⁻ and O₂⁻ ions in the plasma increases. Therefore, more low energy negative ions bombard the substrate in the discharge. The transfer of ion energy and momentum to the growing CeO₂ film is enhanced with high O₂ flow rate. This improves the *c*-axis orientation alignment of the growing film by enhancing the energy of the sputtered atoms on the substrate. However, there is no obvious texture improvement with the 10 sccm O_2 flow rate, since if the pressure is too high, the sputtered atoms undergo increased collisional scattering and are not efficiently deposited.



Figure 3.6 (111) Pole figure analysis of: (a) optimized CeO₂ deposited onto LaMnO₃ surface at 850° C with 7.5 sccm O₂ flow rate; (b) a standard CeO₂ provided by RB; and (c) Φ -scans for both standard and optimized CeO₂ films.

Pole figures and Φ -scans are used to study the in-plane orientation alignment of the CeO₂ films. Figure 3.6 shows the pole figures and Φ -scans of optimized CeO₂ deposited onto LaMnO₃ surface at 850°C under O₂ flow rates of 7.5 sccm. A standard CeO₂ provided by RB is included for comparison. The pole figures of the CeO₂ films display fourfold symmetry with the (111) poles at 55° with respect to the *c*-axis, indicating biaxial alignment of the CeO₂ films. The integrated Φ - scans of CeO₂ (111) peaks show four equally spaced peaks, separated by 90°, confirming in-plane alignment in the CeO₂ film. The FWHM values of the Φ -scans are 5.4° and 3.9° for standard and optimized CeO₂ films respectively. Some low intense CeO₂ (111) peaks which lie at 16° with respect to the *c*-axis for the standard CeO₂ were observed. We conjecture that these (111) poles at 16° are due to crystal twinning which occurs at the interface between CeO₂ and LaMnO₃ layers. However, we did not observe the twin defects in the optimized CeO₂.

3.3.2 Optimization of a single-crystalline-like Ge thin film growth on flexible Hastelloy by RFMS

(1) <u>Temperature variation</u>

Thin Ge films with the same thickness of 1.25 µm were sputtered onto CeO₂/LaMnO₃/MgO templates at heater temperatures ranging from 500 °C to 850 °C. The out-of-plane texture was characterized by XRD as shown in Figure 3.7 (a). The θ -2 θ scan of XRD shows only c-axis orientations for all the layers, indicating a good epitaxial relationship between the Ge film and oxide buffer layers underneath. The spread in the out-of-plane texture, i.e. FWHM of the Ge (400) rocking curve, as a function of deposition temperature is shown in Figure 3.7 (b). The FWHM of Ge (400) first increases as the deposition temperature increases to 600°C beyond which the FWHM starts to decrease. The lowest FWHM of Ge (400) rocking curve is around 0.9° at the highest studied temperature of 850 °C. The decrease of Ge (400) FWHM with increasing substrate temperature results from an increasing of the grain size of Ge films and a release of lattice strain. It can be seen from Figure 3.7 (b) that the intensity of Ge (400) peak at 500 °C is very low, indicating that the Ge film does not crystallize well at comparatively low temperature. Upon increasing the substrate temperature to 850 °C, the intensity of the Ge (400) peak increases 11 times over that for 500 °C temperature, suggesting a higher quality of crystallization at higher temperatures. A relatively high temperature can offer enough energy to improve the spread of the sputtered atoms on the substrate, enhancing the probability of directing the atoms to the right

locations for perfect epitaxial growth. It is also noted that Ge (400) exhibits two peaks at 65.932° and 66.108° corresponding to lattice constants 0.5660 nm and 0.5652 nm, respectively. This is attributed to the growth of an initial Ge layer strained at 0.5652 nm for a better lattice match with CeO₂ and a subsequent layer relaxed at 0.5660 nm.



Figure 3.7 (a) XRD θ -2 θ scan on Ge film deposited at various temperatures on flexible metal substrate; (b) the FWHM and intensity of the Ge (400) rocking curve as a function of the deposition temperature as measured by out-plane XRD ω scan.

Another characteristic in the XRD patterns is that the CeO₂ peaks of (200) and (400) shift to smaller angles with the increase of Ge deposition temperature, which is likely due to reduction of cerium oxide (CeO_x) as a result of oxygen loss at the high Ge deposition temperatures. It is well known that the (100) planes of CeO₂ have the highest surface energy among the low-index crystal planes. This high surface energy originates from the instability of the top-layer oxygen, which is located at the bridging positions between two cerium ions (*133*). Once the samples were treated by sputtering and annealing in the ultra-high vacuum system, the oxygen can be removed from the surface layer easily where Ce⁴⁺ ions are reduced to Ce³⁺ ions (*134*). CeO_x with a smaller x value has smaller 20 values for (200) and (400) peaks, corresponding to larger lattice constants. This larger lattice constant reduces the lattice mismatch between Ge and CeO₂ layers from 4.55% (lattice constant of CeO₂ = 5.4110 Å) to 2.69% (lattice constant of CeO_x=5.5083 Å), which is agreement with the decrease of FWHM of Ge (400) peak indicating the relaxation of strain as deposition temperature increases.

Surface roughness and topography of the thin p-Ge films grown at various deposition temperatures are examined by SEM and AFM. As shown in SEM images in Figure 3.8 as well as AFM 3D images in Figure 3.9 (a-e), the grain size of Ge film increases from 200 nm to 1 μ m as the deposition temperature increases from 500 °C to 850 °C which is consistent with XRD results. As summarized in Figure 3.9 (f), the root mean square (RMS) surface roughness of the film is found to be 5 nm at the substrate temperature of 500 °C, and then slowly increases to 8 nm at 700 °C, followed by a sharp increase to 23 nm at 800 °C. However, it decreases to 13 nm at 850 °C. The increase of the surface roughness can reasonably be explained by formation of some undesirable structures like facets, sparse and large initial clusters that appear on the surface. However, as the temperature increases to 850 °C, the larger grains (1 μ m) with fewer grain boundaries compensate for the undesirable structure induced roughness.



Figure 3.8 SEM images of 1.25 μm Ge film deposited at substrate temperature of (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 800 °C and (e) 850 °C on CeO₂/LaMnO₃/MgO templates.

A smoother Ge thin film surface is important since it not only serves as a suitable template to grow GaAs with low dislocation density, but also reduces the surface roughness scattering thus increasing the carrier mobility. Many methods were studied to reduce Ge surface roughness. A twostep Ge growth technique was used to prevent islanding during the ultrahigh vacuum chemical vapor deposition process (*135*). In the initial growth step, a thin epitaxial Ge buffer layer of 30–60 nm was directly grown at 320-360 °C. At such low growth temperatures, the low surface diffusivity of Ge kinetically suppresses the islanding of Ge. Then the temperature was increased to > 600 °C to achieve higher growth rates and better crystal quality. Besides this two-step growth process, a direct post annealing of Ge in H₂ at 825 °C can reduce the surface roughness as well as decreasing the threading dislocation density of epi- Ge thin film (*135, 136*). However, neither approach, two-step Ge growth process nor direct post annealing, is effective in reducing the Ge surface roughness in the RFMS process, probably due to the different substrates.



Figure 3.9 AFM images of substrate temperature (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 800 °C and (e) 850 °C deposited with 1.25 μm thick Ge on CeO₂/LaMnO₃/MgO templates. (f) The RMS surface roughness as a function of Ge temperature.

The larger grain size (1 μ m) formed at 850 °C is accompanied by a decrease in carrier concentration (9.02 × 10¹⁷ /cm³) and an increase in hall mobility (903 cm² V⁻¹ s⁻¹) compared to the

values in lower temperature films, as shown in Figure 3.10. A lower carrier concentration increases diffusion length in the absorption layer. The increase in mobility could be due to the activation of boron dopants in the Ge films as well as to the increase in the grain size at higher deposition temperatures, since fewer grain boundaries lead to less recombination centers for the carrier and hence a longer carrier lifetime (*137*). Moreover, high temperature processing enhances film quality with low density of threading dislocations, which decreases the ionized-defect scattering and subsequently boosts mobility in the film. Therefore, 850 °C is determined as the optimum deposition temperature from the view point of sharpness of texture, hall mobility and film smoothness.



Figure 3.10 Hall mobility and carrier concentration of p-Ge thin films deposited at different substrate temperatures on CeO₂/LaMnO₃/IBAD MgO templates.

(2) Ge film thickness variation

In order to determine the optimum Ge thickness to reach the optimum mobility and smoothest surface, Ge films with different tape moving speeds were fabricated at 850 °C. The effect of the various thicknesses of Ge films on their crystallinity is shown in the XRD θ -2 θ scan in Figure 3.11 (a). All the Ge films grown on flexible Hastelloy substrates are strongly *c*-axis oriented.

However, the XRD scan of the thinnest film $(0.3 \,\mu\text{m})$ shows a very weak Ge (400) peak. The peak intensity increases 16 times when the film thickness increases from 0.3 μ m to 2.8 μ m, as shown in 3.11 (b). Increasing the film thickness from 0.3 μ m to 2.8 μ m also enhances the crystal quality of the film, indicated by the decreasing FWHM from 0.37 degrees to 0.30 degrees. The smaller FWHM means a better crystal quality of the whole film. Such a FWHM decrease reflects a decrease in the concentration of lattice imperfections due to the decrease in the internal micro-strain within the films and an increase in the crystallite size (*138*).



Figure 3.11 (a) XRD θ -2 θ scan on Ge film deposited with various thickness on flexible metal substrate; (b) the FWHM and intensity of the Ge (400) peak as a function of the film thickness as measured by out-plane XRD θ -2 θ scan.



Figure 3.12 AFM images of (a) 300 nm, (b) 650 nm, (c) 800 nm, (d) 1.25 μm and (e) 2.8 μm Ge films deposited at substrate temperature of 850°C on CeO₂/LaMnO₃/MgO templates. (f) The RMS surface roughness as a function of Ge thickness.

AFM images in Figure 3.12 show the surface of Ge films with thickness ranging from 300 nm to 2.8 μ m. The RMS surface roughness was found to decrease with increasing film thickness up to 1.25 μ m. This is attributed to the following reasons: 1) incoming ad-atoms continue to fill the gaps between grains after grain coalescence is completed and 2) the high strain energy generated from the lattice mismatch between the CeO₂ layer and Ge layer is released as the film grew thicker. As the film thickness is increased from 1.25 μ m to 2.8 μ m, the RMS surface roughness increases marginally, indicating the 1.25 μ m is the critical thickness to release the strain energy. Beyond the

critical thickness, texture improvement ends. Further deposition becomes merely a quasi homoepitaxial process on the crystalline Ge film (*139*). An increase in the thickness of the Ge layer was expected to have a reduction in threading dislocations propagating from the Ge-CeO₂ interface, which leads to less defective top layers and, in turn, higher mobility. The Ge film hall mobility showed a maximum of 903 cm² V⁻¹ s⁻¹ at the critical thickness of 1.25 μ m as shown in Figure 3.14.



Figure 3.13 SEM images of Ge film with thicknesses of (a) 300 nm, (b) 650 nm, (c) 800 nm, (d) 1.25 μm and (e) 2.8 μm deposited at 850°C on CeO₂/LaMnO₃/MgO templates.

SEM images in Figure 3.13 show the surface morphology of Ge films with thickness increase from 300 nm to 2.8 μ m. It is noticed that when the film is very thin (300 nm), many gaps are formed between the grains. This can pose serious problems in solar cell fabrication when GaAs is deposited directly on such a thin Ge film. GaAs crystallites can go through these gaps between

the grains and tend to be deposited on the exposed portions of CeO₂. If there is some metal diffusion into the CeO₂ layer, this in turn, may cause short-circuits in the device resulting mainly in reduction in fill factor and low open-circuit voltage (V_{oc}). As the film thickness increases from 300 nm to 650 nm, the grains agglomerated to cover most of the gaps during the longer time deposition though we still can observe some small holes between the grains. When the film thickness further increases to 800 nm, very few gaps and holes are observed. A dense and smooth Ge film is formed when the thickness rises to 1.25 μ m or higher. This can be explained by the different models for Ge film growth at different stages. Initially, Ge follows an island growth since the Ge atoms have stronger bonds to each other than those between Ge and CeO₂ during the early Ge film growth. Many gaps are observed between the islands. As the deposition time increases, some Ge atoms leave small islands to sinter together to form large clusters in order to reduce the surface energy. When the islands merge with each other, the Ge thin film growth changed from hetero-epitaxy growth to homo-epitaxy growth. The Ge film atoms have strong bonds to the Ge substrate, resulting in layerby-layer growth after initial Ge deposition, thus introducing flat and high crystal quality Ge.

The film hall mobility is enhanced from 260 cm²/V.s to 903 cm²/V.s as the film thickness increases from 300 nm to 1.25 μ m, as shown in Figure 3.14. This improvement is mainly due to the improved crystallographic texture and the occurrence of fewer defects in the thicker film. It has been proved from TEM that stacking faults, twins and misfit dislocations concentrate near the Ge/CeO₂ interface and that their density decreases towards the interior and surface of the film, leaving the top region of the Ge film relatively cleaner with fewer defects due to the annihilation of dislocations with the relaxation of the film. This enhances the Ge film mobility by reducing the top layer dislocation scattering (*140, 141*). Moreover, the impurity elements that diffused from the buffer layers and Hastelloy deplete toward the film thickness as the film thickness increases, as supported by the observation that the carrier concentration reduced from 2.3× 10¹⁹ /cm³ to 9×10¹⁷/cm³. Fewer impurities in the film also boost the carrier mobility. However, when the film

thickness increases beyond the critical thickness at which the strain energy and threading dislocations propagating from the Ge-CeO₂ interface has been released, there is little difference in film carrier concentration and mobility between 1.25 μ m and 2.8 μ m thickness film. The roughness exhibits the same trend as shown in Figure 3.12.



Figure 3.14 Hall mobility and carrier concentration of p-Ge thin films deposited with different Ge film thickness on CeO₂/LaMnO₃/IBAD MgO templates.

(3) Diffusion study

The theoretical carrier concentration of a Ge film fabricated by RFMS was calculated according to Ge target bulk doping concentration. N-type Ge from Kurt J. Lesker has a phosphorus concentration around $6.5 \times 10^4 \sim 4 \times 10^5$ ppba (ppba = parts per billion atoms). According to the Ge density, 5.5g/cm³, and molar mass, 72.6 g/mol, the number of Ge atoms deposited per cubic centimeters is:

$$(6.02 \times 10^{23} \text{ atoms/mol} \times 5.5 \text{g/cm}^3) / 72.6 \text{ g/mol} = 4.56 \times 10^{22} \text{ atoms/cm}^3$$
 (equ. 3.1)

Assuming one phosphorus atom substitutes for one Ge atom, then the bulk carrier concentration on the flexible Ge thin film is: $2.96 \times 10^{18} \sim 1.82 \times 10^{19}$ /cm³, based on the target phosphorus concentration. The same method is used to calculate the bulk carrier concentration in

Ge film made with a P-type Ge target from Plasmaterials. The boron concentration in the target is around 350 ppm (ppm = parts per million atoms), which corresponds to a carrier concentration of 1.60×10^{19} /cm³ deposited on the flexible thin film.



Figure 3.15 SIMS depth profile of a sputtered Ge on CeO₂/LaMnO₃/MgO/Al₂O₃ templates on flexible Hastelloy substrate.

According to the theoretical calculation, the bulk carrier concentration should be equal or lower than ~ 10^{19} /cm³ range. However, some experimental data showed higher values (~ 10^{21} /cm³) than the calculated results. Moreover, the n-type dopant was found to change to p-type at relatively higher temperature. One reason lies in the grain boundaries and defects which act as acceptors to increase the p-type carrier concentration in the thin film. Another reason is the p-type element diffusion from the bottom buffer layers to the top Ge layer under the impact of high temperatures and the ion-bombardment surface effect. In order to study element diffusion, we performed a Secondary Ion Mass Spectrometry (SIMS) analysis. Figure 3.15 presents SIMS depth profile of a sputtered Ge on CeO₂/LaMnO₃/MgO/Al₂O₃ templates on the flexible Hastelloy substrate at a sputtered temperature of 800 °C. Ge was detected to diffuse and accumulate near the interface, particularly at the Hastelloy interface. Mg was observed to segregate at the CeO₂ interface. It might

be caused by the incomplete reaction of Mg during the MgO deposition. Al is also present on the top surface which might be caused by the incompletely reacted Al during the Al₂O₃ diffusion barrier deposition. Both Mg and Al can act as p-type dopants in the Ge film. The driving force of Mn and Cr diffusion from the Hastelloy substrate into the Ge layer is the high temperature and ion bombardment of the PVD process.

	Ge/MgO		Ge/LMO		Ge/CeO ₂	
Condition	Non- annealed MgO	Pre- annealed MgO	Non- annealed LMO	Pre- annealed LMO	Non- annealed CeO ₂	Pre- annealed CeO ₂
Mobility ($cm^2/V \cdot s$)	139	138	144	138	360	300
Carrier Concentration (cm^{-3})	1.4E+19	2.6E+18	1.4E+19	2.9E+18	2.3E+20	3.2E+19
Resistivity $(\Omega \cdot cm)$	3.2E-3	1.7E-2	3.0E-3	1.2E-2	7.4E-5	6.4E-4

Table 3-1 Hall mobility, carrier concentration, and resistivity values of Ge films deposited at 800 °C on non-annealed and pre-annealed buffer layers (MgO, LMO and CeO₂).

In order to confirm the assumption that the Mg and Al elements remain in the film due to incomplete reaction, p-Ge thin film was deposited onto both pre-annealed and non-annealed MgO, LaMnO₃ and CeO₂ buffer layers at the same time. The annealing condition is 1 hour at 800 °C in air. The Ge film carrier concentration and texture were analyzed to check whether annealing can control the Mg and Al diffusion. Table 3.1 summarizes the mobility, carrier concentration, and resistivity of Ge films deposited on both pre-annealed and non-annealed buffer layers. All the carrier concentration values of Ge films deposited onto non-annealed buffers were 10 times higher than those on pre-annealed substrates. Higher carrier concentration is due to the Mg (p type) dopant in the film. Mg is oxidized to MgO during high temperature annealing in the air, which reduces the carrier concentration by suppressing Mg diffusion.

A comparison study of 2D X-ray diffraction patterns from Ge films deposited on both preannealed and non-annealed CeO₂ at 800 °C are shown in Figure 3.16. Faint MgO (111) and CeO₂ (220) polycrystalline rings were observed on Ge grown on a pre-annealed buffer, indicating that the diffused Mg and Ce reacted with O₂ to form polycrystalline MgO and CeO₂ during the annealing process, resulting in Ge (311) ring in Ge film as well. The minor polycrystalline Ge feature reduces Ge mobility from 360 cm²/V·s to 300 cm²/V·s. The comparison experiment confirms that initial MgO and CeO₂ were not fully oxidized during growth of the buffer layers.



Figure 3.16 2D X-ray diffraction patterns for Ge films deposited on CeO₂ at 800 °C on metallic substrates: (a) Ge/non-annealed CeO₂ buffer layer; (b) Ge/pre-annealed CeO₂ buffer layer. The 2θ range covered is 26-74°.

In order to reduce diffusion from the substrate and buffer layers, many methods were applied for film optimization: (1) increase the Al₂O₃ thickness to block diffusion from the Hastelloy more efficiently; (2) replace Hastelloy substrate with flexible glass to eliminate the metal elements from the substrate; (3) create a more stable diffusion barrier to block metal diffusion from the buffer layers; (4) increase the Ge film thickness to terminate the diffusion by using the low temperature process of RF-PECVD with less ion bombardment on the Ge surface. The different thicknesses of Al₂O₃ as a diffusion barrier has been studied in chapter 3.3.1. More efficient approaches based on the simplified buffer layer/flexible glass and increased Ge thickness by RF-PECVD will be discussed in the next section.

3.3.3 Low defect density and high mobility crystal Ge growth on flexible substrate by RF-PECVD

(1) (111) oriented Ge growth on IBAD CeO₂(111) on flexible glass substrate

In order to avoid diffusion from Hastelloy, we have developed a novel technology to enable epitaxial growth of single-crystal-like Ge thin films from a very fast IBAD process of CeO₂ seed layer on flexible glass tapes. It only took 30 seconds deposition to provide 10 nm thickness IBAD CeO₂ templates for epi-Ge growth. This process eliminates the need for depositing multiple oxide layers between the flexible glass and Ge. Ge thin films were deposited using a RF-PECVD system. This near single crystal Ge with (111) orientation has superior mobility and reasonable carrier concentraions that is sufficient to modulate the channels to be applied to fabricate high-performance flexible TFTs.

Figure 3.17 (a) is a schematic illustration of a simplified buffer layer structure for (111) oriented Ge depositon. Thin, flexible, and thermally stable (up to ~ 650 °C) glass is used as a substrate. A CeO₂ film is deposited by IBAD for a biaxially-textured template. A relatively higher assist ion-beam energy (900 eV) was used to enhance the atom mobility on the growing surface and to promote growth on a (111) plane that appears to be thermodynamically preferred (*83, 129*). RHEED is used to characterize the surfaces of various layers. Figure 3.17 (b) shows a featureless RHEED pattern from the amorphous glass substrate, as expected. After ~10 nm of CeO₂ deposition, spots in the RHEED pattern appear indicating cubic (111) texture is formed, as shown in Figure 3.17 (c). Further improvement of the RHEED patterns for the Ge film, as shown in Figure 3.17 (d), suggests hetero-epitaxial growth of the Ge layer. However, we also observed that the RHEED pattern of the Ge layer contained weak secondary reflections, suggesting mosaic spreads and twin defects possibly originating from the lattice mismatch between CeO₂ and Ge interface. The Ge thin film surface morphology is studied by SEM in Figure 3.17 (e). It shows Ge with uniform coverage on the glass substrate with CeO₂ buffer layer. However, there are some gaps between the grains as

they agglomerate during deposition. Some elongated Ge grains can reach $5 \sim 10 \ \mu m$ length while maintaining the estimated width of 500 nm.



Figure 3.17 (a) Schematic of the Ge thin film grow on flexible glass. In situ RHEED analysis showing the evolution of the surface texture: (b) bare flexible glass, (c) after IBAD CeO₂ growth, and (d) after Ge epitaxy. (e) SEM image of Ge thin film.

Thin Ge films were deposited onto IBAD CeO₂ templates at temperatures ranging from 400 °C to 600 °C. The out-of-plane texture was characterized by XRD as shown in Figure 3.18 (a). The θ -2 θ scan of XRD shows (111) dominated orientation when deposition temperature is higher than 550 °C, signifying that the Ge film has improved crystallinity at high temperatures. A dominant peak with high intensity corresponding to Ge (111) indicates a well-aligned uniaxial texture along [111] for out-of-plane orientation. The (004) peak is almost negligible, suggesting suppressed texturing along this direction. Very small Ge (220) and (311) peaks suggest minor polycrystalline features in the film. This may be related to the temperature of the growing surface for the RF-PECVD process. A high substrate temperature enhances adatom surface mobility, and this increases the nucleation rate of the Ge epitaxial grains rather than that of grains of random orientation. At the same time, the Ge (111) plane has the lowest surface energy and is expected to grow more rapidly than grains oriented away from (111) (74). It has also been proven that Ge film grown on glass was polycrystalline with a slight preference for the <111> texture (142). When the

temperature is lower than 550 °C, the Ge film is either amorphous or polycrystalline, indicating that the Ge film does not have enough energy to crystallize well at a comparatively low temperature. Although GeH₄ can decompose efficiently at 300 °C ~ 900 °C, normally, a different activation energy is required for heterogeneous and homogeneous reactions (*114*). A higher temperature is needed to form heteroepitaxial Ge thin film on IBAD CeO₂. Figure 3.18 (b) shows a rocking curve (ω scan) around the (111) diffraction peak of Ge grown at a deposition temperature of 600 °C. The out-of-plane mosaicity is evaluated from the linewidth of the peak in terms of FWHM. The value of FWHM of the peak is 4.56°, indicating small mosaic spreading in the film. A pole figure was also measured to characterize in-plane rotation.



Figure 3.18 (a) XRD θ -2 θ scan on Ge film deposited at various temperatures on IBAD CeO₂ on flexible glass substrate; (b) the FWHM of the (111) rocking curve of Ge grown at a temperature 600 °C, as measured by out-plane XRD ω scan.

The Ge texture was investigated in CeO₂ samples deposited at different ion beam exposure times. The Ge was grown at the same conditions of 600 °C for 45 minutes in RF-PECVD on different CeO₂ buffers. Enhanced epitaxial Ge (111) growth was observed only on 30 s IBAD CeO₂ (Figure 3.19a). In Figure 3.19 (b), a φ scan is shown for Ge(220) measured at fixed $\omega = 22.5^{\circ}$ and $2\theta = 45^{\circ}$. The three-fold symmetry of the Ge film indicates that the Ge film is biaxially oriented with both out-of-plane and in-plane preferred orientations. The Ge does not exhibit any poles corresponding to growth twins. Ge deposited on both 20 s and 40 s IBAD CeO₂ showed polycrystalline textures. At the very beginning of the IBAD CeO₂ process (less than 20 s), the ion beam does not have enough time to align the crystals to grow along the (111) direction even though the (111) direction is preferred for out-of-plane growth of CeO₂; further, the assist ion beam needs to align the crystals in the in-plane orientation as well. With the time increased to 30 s, the biaxial texture of CeO₂ is improved, but it starts to degrade at 40 s. The degradation of the texture of IBAD CeO₂ film grows beyond a critical thickness, the planes begin to tilt away from the ion beam, which leads the ions not to channel as well along the channeling direction. This induces a greater amount of damage in the surrounding grains with <111> in-plane direction, which thereby deteriorates the biaxial alignment between grains (71).



Figure 3.19 (a) XRD θ -2 θ scan from Ge films deposited on IBAD CeO₂ grown with various ion beam exposure time. (b) (220) pole figure analysis of the Ge layer deposited on 30 s IBAD CeO₂.



Figure 3.20 Raman spectra from Ge wafer and Ge film deposited on 30 s IBAD CeO_2 template on flexible glass substrate.

The Ge film deposited onto 30s IBAD CeO₂ was further characterized by Raman spectroscopy in Figure 3.20, a very effective tool for the evaluation of crystallinity of Ge deposits. A sharp Raman peak, centered at 301.8 cm⁻¹ with a narrow bandwidth of 6.7 cm⁻¹, corresponding to Ge optical mode, is observed in the Ge thin film. However, a small shoulder seen at the left side of the epitaxial Ge thin film peak suggests the Ge film is partly nanocrystalline and/or disordered. In order to evaluate the crystallinity volume fraction in the flexible sample, the Raman spectrum was decoupled into two Lorentzian peaks at 288.5 and 301.8 cm⁻¹. The volume fraction of crystallites of the Ge thin film is estimated by the definition of Fc = $I_{301.8}/(I_{301.8} + I_{288.5})$, where $I_{301.8}$ and $I_{288.5}$ represent integrated intensities of Lorentzian peaks located at 301.8 cm⁻¹ and 288.5 cm⁻¹ respectively. Thus, more than 92% crystalline phase exists in the Ge films. Compared to the single crystal Ge wafer position at 300 cm⁻¹ and bandwidth of 4.0 cm⁻¹, the Raman peak of Ge thin film
shifts to a higher wavenumber (301.8cm⁻¹) presumably due to the compressive stress in the films. The stress in the films can be attributed to the thermal and lattice-mismatch between the Ge film and underlying layers and may also arise from the stress in the Ge-Ge bonds at the grain boundaries.

(2) Well-(400)-oriented Ge with high carrier mobility grown on flexible Hastelloy

Epitaxial Ge has been achieved by RFMS with intermediate layers of CeO₂/LaMnO₃/MgO on flexible Hastelloy. The Ge film showed high mobility (903 cm²/V.s) as well at a high deposition temperature of 850 °C. However, the high mobility may potentially be caused by the metal diffusion from the underlying Hastelloy (Zr, Ni, etc.) or non-fully reacted buffer layers (Al, Mg, Ce), during high temperature processing and due to ion bombardment effect. Therefore, a lower temperature process is preferred to reduce diffusion while maintaining good Ge epitaxy. The problem is the high defect density that is unavoidable in a lower temperature RFMS process. Moreover, the film carrier concentration cannot be controlled since the Ge target doping concentration is stable. An alternate low temperature and dopant-controllable process is required to achieve high mobility with lower dopant in the active layers.

In RF-PECVD process, we employed remote inductively-coupled plasma to generate highdensity plasma, thereby promoting epitaxial growth at lower temperatures while causing significantly less ion-bombardment damage to the film surface (*143*). For good and reproducible Ge homoepitaxy and heteroepitaxy, substrate surface preparation, pre-epitaxy and nucleation conditions are extremely important. We first annealed the samples in the PECVD reactor at 500 °C for 10 mins to remove the oxide from the surface because GeO₂ formed in air can be thermally decomposed at 500 °C by H₂ treatment (*114*). The working gas of GeH₄ diluted with H₂ at a volume ratio of 1: 25, was introduced into the chamber, where GeH₄ is decomposed by heat and RF-induced plasma to form a homo-epitaxy Ge layer on RFMS Ge. It is noticed that the reforming new oxide is thermally removed in the reactor. A heater temperature ranging from 400 °C to 600 °C was employed, since at a higher temperature, there is a strong tendency for cracking of GeH₄ in the gas phase and Ge deposition onto the reactor walls which often subsequently falls on the substrate. Therefore, a high temperature process (> $600 \, ^{\circ}$ C) has a detrimental effect on the growth process and increases the reactor downtime for cleaning, and needs to be avoided.



Figure 3.21 (a) XRD θ -2 θ scan on Ge film deposited by RF-PECVD on RFMS Ge buffer at various temperatures. (b) Ge (400) rocking curve, and (c) FWHM of Ge (400) rocking curve as measured by out-plane XRD ω scan.

The precise control of the Ge electronic properties (i.e. mobility) over large areas is necessary to enable flexible Ge-based optoelectronics applications. The first step to realize it is to understand process parameters dependence of Ge orientation, crystallinity, roughness and film strain, which in turn enriches knowledge of the process-property-performance relationship. The detailed influences of the deposition temperature on the FWHM of Ge (400) omega scan and Raman wavenumber, film roughness and the final film electronic performance are studied below.

The out-of-plane texture of Ge samples grown between 400 °C and 600 °C were characterized by XRD as shown in Figure 3.21 (a). The θ -2 θ scan of XRD shows a good epitaxial growth of Ge film on a RFMS Ge buffer layer. The spread in the out-of-plane texture of the Ge (400) rocking curve, as a function of deposition temperature is shown in Figure 3.21 (b). Compared to the RFMS Ge buffer layer, a better crystallinity was observed at the lower process temperature of RF-PECVD Ge as indicated from the reduction of FWHM of Ge (400) (Figure 3.21 (c)), which boosts the film electrical performance (see Figure 3.23). The optimal temperature is determined to be 450 °C considering the film mobility, roughness and crystallinity.



Figure 3.22 Raman spectra and FWHM of Ge TO mode peak from Ge wafer, RFMS Ge buffer and PECVD Ge films.

The Ge films deposited onto RFMS Ge buffers were further characterized by Raman spectroscopy as shown in Figure 3.22, which also includes results obtained at the same conditions for the RFMS Ge buffer and Ge wafer. All the Ge films show a sharp Raman peak around 300 cm⁻ ¹ corresponding to Ge transverse optical (TO) mode, with slightly different peak position and FWHM of wavenumber. Compared to the single crystal Ge wafer position of 301 cm⁻¹, the Raman peak of the Ge buffer shifts to a higher wavenumber (303.5cm⁻¹) presumably due to compressive stress in the films resulting from lattice mismatch between Ge (4% larger) and CeO₂. The thermal expansion coefficients of the two materials are also significantly different ($\alpha_{CeO2} = 9.0 \times 10^{-6} \text{ °C}$ compared to $\alpha_{Ge} = 5.9 \text{ x } 10^{-6} \text{ °C}$) which could produce a compressive strain during the temperature cool down. The stress in the Ge-Ge bonds at grain boundaries may also cause the Ge peak shift. However, the TO vibration peak of RF-PECVD Ge thin films approaches that of the Ge wafer, indicating relaxation of the stress in these films. There is no nanocrystal or amorphous feature observed on RF-PECVD Ge thin films, which confirms the well-aligned and good crystalline quality of Ge on CeO₂. Compared to the RFMS Ge buffer layer, a better crystallinity formed at the lower process temperature of RF-PECVD Ge as observed from the FWHM reduction, which boosts the film electrical performance. With the temperature increase beyond the 500 °C, the FWHM of the wavenumber increased dramatically from 3.5 cm⁻¹ to 4.5 cm⁻¹, corresponding to a hall mobility decrease from 1000 cm²/V.s to 500 cm²/V.s (see Figure 3.23). However, the XRD rocking curve scan shows an improved texture as $\Delta \omega$ is reduced from 1.04° to 0.89° with deposition temperature increase from 400 °C to 450 °C. The different trend between the Raman spectroscopy and the XRD results may be caused by the different penetration depths of the optical and X-ray beams in the two measurements. It is likely that the uppermost 100 nm Ge is formed with good morphology and crystallinity at a relative low deposition temperature (400 °C ~ 450 °C), but the full stack of Ge with 1 µm thickness has a less mosaic spread and better crystallization at higher deposition temperatures (450 °C ~ 600 °C). Essentially, no meaningful variation of $\Delta\omega$ was observed when

deposition temperature is higher than 450 °C, which means 450 °C is an optimum temperature to reduce the film mosaic spread to enhance the film texture and quality.



Figure 3.23 (a) RMS surface roughness and (b) hall mobility as a function of Ge deposited at different temperatures on RFMS Ge buffer layers.

AFM images in Figure 3.23(a) show the surface morphology of Ge films with process temperature increasing from 400 °C to 600 °C. The lower roughness with 13 nm and 15.7 nm of RF-PECVD Ge thin films are observed at the deposition temperatures of 400 °C and 450 °C, indicating that a smoother surface is formed at a lower deposition temperature. The smoother surface may enhance the carrier mobility due to lower surface roughness scattering, as shown in Figure 3.23 (b). During mobility measurement, four samples for each deposition temperature were measured by hall measurement to confirm the film uniformity. It is noticed that the RF-PECVD Ge mobility is increased 10 ~ 20 times higher than that of the RFMS Ge buffer. The lowest deposition temperature ($400 \sim 450$ °C) resulted in highly enhanced mobility up to $1000 \sim 1100$ cm²/V.s, corresponding to a narrow FWHM of Raman wavenumber 3.45 cm⁻¹, which is very close to the bulk Ge wafer 3.40 cm⁻¹. Therefore, 450 °C is an optimum temperature to reach a high carrier mobility with improvement of the film crystallinity, texture and roughness.



Figure 3.24 Cross sectional TEM image of RF-PECVD Ge grown on sputtered Ge buffer layer. The insert image is a selected area electron diffraction pattern from RF-PECVD Ge.

Microstructural characterization of the Ge film was carried out by high resolution TEM imaging. Figure 3.24 shows the dark-field cross-sectional TEM micrograph of a representative PECVD Ge thin film grown at 600 °C on the RFMS Ge buffer layer on flexible metal tape. Corresponding selected area electron diffraction (SAED) pattern of RF-PECVD Ge is shown at the top left. SAED showed a diffraction pattern characteristic of diamond lattice structure, confirming epitaxial growth and the single-crystalline nature of Ge. A high density of defects is observed in the RFMS Ge film as well as near the RF-PECVD Ge/ RFMS Ge interface. The defect density decreases towards the RF-PECVD Ge surface making the top surface relatively free of defects. This is attributed to the relaxation of the films and release of initial strain from lattice-misfit and also to gliding and annihilation of dislocations as the film grows thicker. Moreover, compared with magnetron sputtering, RF-PECVD process induces less ion-bombardment damage to the Ge film surface since the high-density plasma is generated by remote inductively-coupling, thereby promoting epitaxial Ge growth with high orientation and low defect density.

3.4 Device application

3.4.1 III-V multi-junction solar cell

A p-n junction was constructed by magnetron sputtering a thick boron-doped p-Ge film (2.8 μ m) on an optimized thin p-Ge film followed by deposition of a thin arsenic-doped n-Ge film (200 nm) as shown in Figure 3.25 (a). A thick p-Ge layer is required to serve as a suitable absorber layer for the solar cell. A low hole concentration (1.7×10^{18} cm⁻³) is required to increase the diffusion length. Al contacts of 20 nm thickness were deposited on the surfaces of thin p- and n-Ge films by e-beam evaporation (Thermionics eBeam evaporator) in order to reduce the doping element diffusion. Al pellets (99.99%, 0.3175 cm in diameter) were used for evaporation. The active area of the fabricated p-n bottom junction was 0.04 cm².





Figure 3.25 (a) Designed n-Ge/p-Ge structure on the epitaxial buffer layer; (b) an I-V characteristic curve obtained from the structure.

A smoother p-Ge contact layer facilitates growth of a thick absorption p-Ge layer with lower dislocation density while higher hall mobility in the contact layer enhances the junction performance. Figure 3.25 (b) shows the I-V characteristics of p-n bottom junction both in dark and under illumination. The Ge solar cell exhibits a short-circuit current density (J_{sc}) of 1.36 mA/cm², an open-circuit voltage (V_{oc}) of 154.0 mV and a fill factor (FF) of 25.1%. The fabricated Ge p-n junction, however, only exhibits an energy conversion efficiency of 0.05% compared to the reported highest one of 7.8% for stand-alone Ge solar cells using diffused Ge substrates under AM 1.5 (*144*). The lower efficiency is partly attributed to the easy diffusion of dopants from one polarity to another polarity at high deposition temperature, which destroys the Ge p-n interface. A higher defect density in films made by sputtering could have also contributed to the lower cell conversion efficiency, because it results in a higher carrier recombination rate, thus reducing diffusion length (50). A few modifications are required to improve the performance of p-n junction. The thickness of the n-Ge emitter layer needs to be optimized: it should be minimized to reduce optical losses while being thick enough to support the electric field necessary to induce band bending. Additionally, the surface of the n-Ge emitter layer needs to be passivated to reduce the surface recombination velocity. The thin p-Ge film at bottom as back contact needs heavier doping for efficient collection of carriers that are likely lost in the transport process in the contact layer before they arrive at the small area of Al metal contact.



Figure 3.26 Simulation of modified triple junction III-V solar cell architecture conducted using recent results on carrier life time of 1 ns measured in GaAs on metal substrate.

In a further step, our group has already successfully grown both n and p type singlecrystalline GaAs thin films on flexible Ge templates via roll-to-roll metal organic chemical vapor deposition (MOCVD). Fabrication of multi-junction solar cells based on these high quality biaxially-textured GaAs and Ge thin films is underway. Figure 3.26 shows a simulation of I-V characteristics of a modified triple junction III-V solar cell architecture using a carrier life time of 1 ns as an input parameter, based on the value previously measured in GaAs on a metal substrate. The simulation shows that it is possible to attain an energy conversion efficiency of 30% under 1 sun and AM 1.5 G, with the fill factor reaching 82%.

3.4.2 Flexible thin film transistor

In a collaboration with Prof. Jae-Hyun Ryou's group, a top-gate TFTs were fabricated using a single-crystal-like *p*-type [111]-oriented Ge thin film with a carrier concentration of $\sim 3 \times 10^{16}$ cm⁻³ grown on flexible glass. The processing steps include gate dielectric deposition, ion implantation, source/drain (S/D) ohmic-contact electrode formation, and gate metal formation. S/D contacts, gate metal, and gate insulator were defined by standard photolithography and lift-off techniques. A SiO₂ layer was deposited as the gate insulator on Ge layer. S/D engineering such as ion implantation (as a common approach to dope the S/D regions in traditional semiconductor devices) was required for better current spreading to form a well-defined channel and to lower contacts due to the low specific contact resistivity (ρ_c) by formation of nickel germanide(*145*) at the metal-semiconductor interface after anealing. The transmission line method (TLM) is used to evaluate ρ_c for S/D. Aluminum (Al) is selected for gate metal. The channel length and gate width were 20 µm and 80 µm, respectively, corresponding to a width-to-length ratio of 4:1.

Figure 3.27 (a) shows a schematic device and layer structure of the TFTs. Figure 3.27 (b) shows an optical image of the top view of TFT device on flexible glass. Figures 3.27 (c) and (d) show typical TFT characteristics where source-to-drain current (I_{ds}) increases dramatically as source-to-drain voltage ($-V_{ds}$) increases at a negative gate bias V_{gs} , confirming that holes are the majority charge carriers and the semiconducting channel is *p*-type. The TFT device exhibited the highest on-current of ~3.5 mA for the top-gate modulation when the top-gate bias is -20 V. The extracted field effect mobility of the flexible Ge-TFTs is ~300 cm². V⁻¹. s⁻¹, as calculated from the I_{ds} - V_{gs} and $log_{10}I_{ds}$ - V_{gs} curves that was measured at a drain bias of -3 V. The field effect mobility at the magnitude of ~300 cm². V⁻¹. s⁻¹ is significantly higher than that of previously reported values

with flexible TFTs and comparable to that of TFTs made with single crystal wafers. The channel can also be completely switched off with a positive gate voltage to achieve the highest on-off ratio reaching $\sim 10^6$, sufficient for high-performance device operations. The single-crystal-like Ge TFTs developed in this study have exceptional performance characteristics as compared to the other flexible TFTs using amorphous, organic, polymers, and polycrystalline semiconductor channels.



Figure 3.27 (a) A schematic device and layer structures of the TFTs; (b) a microscopy of Ge TFT on flexible glass; (c) output characteristics obtained from the TFT with a W/L = 80/20 for V_{GS} varying from -20 to 5 V and (d) transfer characteristics of the TFT.

3.5 Summary

Epitaxial Ge growth by both RFMS and standard RF-PECVD was demonstrated at various conditions on both flexible Hastelloy and glass substrates. Investigation of the material quality by means of SEM, TEM, AFM, XRD and Raman spectroscopy has proven the high crystalline quality of the Ge films.

For the RFMS Ge layer, the effects of deposition temperature and film thickness on the film texture, surface roughness and hall mobility were studied. The hall mobility of p-type Ge increases from 6.0 cm² V⁻¹ s⁻¹ to 903 cm² V⁻¹ s⁻¹ with an increase in deposition temperature from 500 °C to 850 °C while surface roughness saturates at 850 °C. The monotonic increase of hall mobility with increasing deposition temperature is attributed to the increase in grain size and release in strain energy. The hall mobility increases while surface roughness decreases until the film thickness reaches a critical thickness 1.25 μ m due to the decrease in defect density of the Ge films. However, high temperature processing enhanced the metal element diffusion from the bottom layers, and so, the lower temperature process with less ion bombardment surface is preferred for the high quality Ge growth.

In order to reduce the diffusion extent from the Hastelloy, RF-PECVD was utilized for the epi-Ge growth. We first replaced the Hastelloy substrate with flexible glass with only one intermediate layer of IBAD CeO₂ for the Ge (111) growth. Even though the texture of Ge (111) cannot be compared with that of Ge (400) in previous RFMS Ge, the crystalline quality (biaxially-textured nearly single-crystalline features) and its associated hall mobility (300 cm²/V.s) are superior to that of materials used in flexible TFTs. Then we deposited high quality RF-PECVD Ge on RFMS Ge buffer layers at a relatively lower process temperature (400 °C ~ 600 °C), for the purpose of reducing diffusion while maintaining good Ge epitaxy. The hall mobility of the RF-PECVD Ge thin film increases 20 times (up to 1100 cm²/V.s) than that of RFMS Ge buffer layer, due to better texture, crystallinity and less defect density verified by the XRD, Raman and TEM results.

Finally, a flexible p-n Ge bottom junction based on the optimal thin p-Ge contact layer was fabricated, which shows a conversion efficiency of only 0.05%. The low efficiency could have resulted mainly from the inter-diffusion of dopants at high deposition temperature. Either a modification to the p-n junction layers or to the deposition method, such as chemical vapor

deposition at lower temperatures, may address this issue. The Ge p-n bottom junction made on the flexible substrate provides a promising future for GaAs multi-junction solar cell device fabrication. A simulation result shows that energy conversion efficiency can reach 30% under 1 sun at AM 1.5G with a modified triple junction III-V solar cell architecture made using a carrier life time of 1 ns that was previously measured in GaAs on metal substrate. In another application, top-gate TFT was fabricated using a single-crystal-like *p*-type [111]-oriented Ge thin film with a carrier concentration of $\sim 3 \times 10^{16}$ cm⁻³ grown on flexible glass. This device achieved on-current of ~ 3.5 mA for the top-gate modulation when the top-gate bias is -20 V. The channel can also be completely switched off with a positive gate voltage to achieve the highest on-off ratio of $\sim 10^6$, sufficient for high-performance device operations.

Chapter 4 Single-crystalline-like Si thin films on affordable and flexible metal substrates

4.1 Introduction

Silicon (Si) is by far the most widely-used semiconductor material for electronics and optoelectronics, such as transistors, integrated circuits, photodetectors and photovoltaics (PV) since it is abundant in nature and environmentally benign. Nowadays, flexible electronic devices raise a huge market in wearable computers, printed sensors, paper displays, electronic skin, and flexible solar cells (106). So far, flexible devices are mainly based on hydrogenated amorphous Si (a:Si-H) (117), organic semiconductors (118), and the oxide semiconductor In-Ga-Zn-O (IGZO) (34). However, the performance of these devices has been insufficient for use as high-performance thin film transistors (TFTs) due to their low mobility ($< 10 \text{ cm}^2/\text{V.s}$). To overcome this limitation, polysilicon (poly-Si) with relatively high mobility ~50-300 cm². V⁻¹. s⁻¹ has been employed (7). However, this material suffers from non-uniformity of the field-effect mobility and threshold voltage, caused by the small grain size and numerous grain boundaries in Si thin films (120). Furthermore, for solar cell application, grain boundaries in polycrystalline Si films function as electron traps that act as recombination centers to reduce minority carrier lifetime, thus reducing the solar cell performance (47). Single crystal Si (c-Si) wafer is still the best candidate to fabricate electronics with high mobility and least negative impact of grain boundaries. However, c-Si wafer is rigid, brittle, and expensive, which is not suitable for flexible and large-area processing electronics. A more promising alternative is employing near single-crystalline Si thin films with tunable thickness on a nanometer scale on inexpensive flexible substrates, which not only reduces cost and weight of electronic devices by replacing the Si wafers, but also opens up opportunities for novel applications of flexible electronic devices.

Efforts to achieve near single c-Si thin films on flexible platforms have largely focused on epitaxial lift-off and transfer printing techniques, where epitaxially grown Si thin films are separated from wafer substrates and transferred onto desired flexible substrates for device fabrication (*146*). Others have employed post-deposition techniques such as excimer laser annealing and metal-induced crystallization of disordered Si thin films grown on flexible substrates to obtain c-Si-like properties, mainly, higher carrier mobilities (*147*). However, technical effectiveness and commercial viability of these indirect processes are yet to be proven. Instead, direct growth of single crystal-like Si thin films on low-cost flexible substrates by standard deposition techniques is highly desirable for economical and scalable mass production of flexible electronics. The most popular direct approach to grow epitaxial single crystal-like Si thin films on non-crystalline flexible substrates is the "seed and epitaxy" technique using ion-beam assisted deposition (IBAD) technology. In this process, starting with a flexible polycrystalline or amorphous substrate, a biaxially-textured template is developed by IBAD, and subsequently, biaxially-textured buffer layers are grown using standard epitaxial deposition methods.

In order to grow near single c-Si films on flexible substrates, a robust buffer stack is employed to perform three critical functions: 1) prevent metal diffusion from the substrate during Si growth at elevated temperatures (~700-900 °C); 2) provide a surface crystal structure and chemistry that enables heteroepitaxial growth of Si; and 3) offer adequate adhesion to prevent delamination of layers from the underlying flexible substrates during cool down after Si growth, considering the large difference in the coefficient of thermal expansion between Si (~ 2.5 ppm K⁻¹) and the substrate (for example, Ni alloy foil ~ 13 ppm K⁻¹). It has already been demonstrated that well-oriented Si can be grown on a γ -Al₂O₃ template layer using hot-wire chemical vapor deposition (HWCVD) system. However, the density of misfit dislocations and stacking faults was extremely high within the Si film due to the large lattice mismatch between Si (a = 0.543 nm) and γ -Al₂O₃ (a = 0.791 nm) (94). In order to reduce the significant strain resulting from lattice mismatch, a transition layer having lattice matching with Si is required. Although cubic fluorite CeO₂ (a = 0.541 nm) has an excellent structural compatibility and close lattice match ($\varepsilon_m \sim 0.3\%$) with Si, the CeO₂/Si interface is apparently not chemically stable at the elevated temperatures (~ 700-900 °C) required for Si film growth. Additionally, the formation of a thin amorphous SiO₂ layer at the interface hinders epitaxial Si growth (88). Ge (a = 0.565 nm) can also be used as a transition layer material. Although Ge has a lattice mismatch of 3.9% with Si (relatively larger than that between CeO₂/Si), it forms a Si-Ge graded interface which is beneficial in reducing the strain in the deposited Si film. Growth of a Ge film with (111) out of plane orientation on textured CaF₂ (a = 0.546 nm) seed layers using the ion-beam-assisted deposition (IBAD) technique has been achieved (74). The reported CaF₂ seed layer, however, is not well textured, and this quality propagates to the subsequent Ge film resulting in a low degree of crystallinity (full-width at half-maximum, FWHM = 2.7°) and a low quality of biaxial-texturing. Our group has successfully demonstrated growth of superior biaxially-textured Ge film (FWHM < 1°) with (001) out of plane orientation on CeO₂ buffer surface with high mobility (833 cm²/Vs) (95-97), which can be used as the buffer layer for the epi-Si growth.

In this chapter, biaxially-textured Ge template, which has been previously developed in Chapter 3, was employed to grow heteroepitaxial Si thin films on flexible, polycrystalline metal alloy tapes for the application of crystalline Si PV cells and TFTs. The schematic of the Si multilayer architecture and photograph of epitaxial Si thin film are shown in Figure 4.1. In the present study, two approaches, radio frequency magnetron co-sputtering (RF-MCS) and radiofrequency plasma enhanced chemical vapor deposition (RF-PECVD), were employed to grow Si films. The quality of biaxially-textured Si films in terms of the deposition factors was comprehensively studied. Moreover, controllable doping of Si films with gas phase precursors was explored for future practical device application. Finally, a flexible Si TFT device based on this structure was demonstrated.



Figure 4.1 (a) Photograph of epitaxial Si thin film on flexible metal foil. (b) Schematic of the multilayer architecture developed in this work to grow epitaxial Si thin films on metal foils.

4.2 Theory and experiments

4.2.1 Technologies of Si thin film fabrication

So far, several growth techniques such as chemical vapor deposition, e-beam evaporation, molecular beam epitaxy (MBE), and sputter epitaxy have been applied to Si epitaxy (98). HWCVD was a primary choice for biaxially-textured Si growth on flexible substrates (11, 99-102), but RF-MCS and RF-PECVD have not been widely explored. RF-MCS takes the advantage of low kinetic energy particle bombardment of a growing Si film surface, which enables epitaxy at low temperature and high growth rate (98). Moreover, the Si_xGe_{1-x} graded layer can be formed between the Si and Ge buffer layers to reduce the lattice and thermal mismatch, by controlling the ratio of power applied Si and Ge targets during reactive co-sputtering. The drawback is the fixed dopant

concentration in the target which restricts the film carrier concentration. RF-PECVD is known as one of the most popular techniques to grow device-quality crystalline thin films at lower temperatures and often with improved electrical properties compared to HWCVD (*103, 104*). It can be used to achieve the required electron or hole carrier concentrations by controlling diborane (B_2H_6) or phosphine (PH₃) gas flowing rate, in order to meet the device requirements.



Radio frequency magnetron co-sputtering (RF-MCS)

Figure 4.2 Schematic of co-sputtering system.

The custom-designed RF-MCS system contains four targets (five centimeters diameter each) in one chamber, as shown in Figure 4.2. The targets are made of the materials that are to be deposited, or their metal constituents that will be oxidized during the deposition. The magnets confine the plasma discharge to increase deposition rate. The target is mounted on the cathode using a high thermal and electrical conductive silver (Ag) paste for better cooling of the target. A cylindrical shield is used to cover the target assembly. The angle and distance of the target to the substrate can be adjusted through the target holder screw, which can then control film uniformity and deposition rate. Ultra-high purity forming gas $(4\% H_2 + 96\% Ar, 99.999\%)$ is passed into the process chamber, subjected to a RF potential generated by a RF power supply to create plasma. The Ar⁺ ions in the plasma are attracted by the negative charged cathode to bombard the target surface, ejecting atoms from the target, which deposit onto the substrate directly. The residual gases are pumped out by a turbomolecular pump. The plasma parameters of target 1&3 and 2&4, including power, current, and DC bias voltage, can be controlled by two independent matching network controllers respectively. This gives the opportunity to grow a film with graded composition by adjusting the power to each sputtering target in the magnetrons. All the targets are soaked by plasma for 30 minutes prior to the process in order to stabilize the sputtering process parameters and clean the target surface. The substrate is fastened by two screws on a 5 cm customized samples holders. The sample stage rotates at 10 rpm during the process for uniform deposition. The thickness of the deposited thin film is monitored by a deposition rate controller. During the process, the samples were transferred in and out of the reactor using a load-lock assembly, which helped to keep the chamber clean and in high vacuum during the sample transfer process, enabling high purity and reproducible film quality.

Radio frequency plasma enhanced chemical vapor deposition (RF-PECVD)

A modified Plasmalab100 RF-PECVD system was used for high quality Si film growth with an inductively-coupled plasma reactor operated at 13.56 MHz radio frequency. The details of the system configuration have been discussed in Chapter 3. The process gases consist of high purity silane SiH₄ (6N) and hydrogen purified by a palladium cell purifier to an ultrahigh level of purity. The diborane (B_2H_6) and phosphine (PH₃) gases were introduced in appropriate proportions with SiH₄ and H₂ using high-resolution mass flow controllers to achieve the required electron and hole carrier concentrations respectively.

4.2.2 Fabrication of heteroepitaxial Si thin films on flexible metal substrates

(1) Fabrication of epitaxial Si thin films on Ge template by RF-MCS

Metal foils with a buffer of single-crystalline-like Ge thin film were cut into short pieces (1.2 cm wide, 4 cm long) and loaded on an inconel sample holder, especially designed to hold flexible samples. The chamber base pressure was kept at 5.0×10^{-7} Torr or lower. Before Si deposition, the Ge templates were first annealed for 10 min in Ar-4% H₂ atmosphere at 750 °C at a pressure of 5 mTorr to remove the native oxide on the Ge surface (114). Then, Si films were deposited onto a Ge film with a Si_xGe_{1-x} graded layer by control of the ramping power of both boron-doped Si and Ge targets at multiple substrate temperatures 650 °C ~ 720 °C. The Si film is amorphous when the deposition temperature is lower than 650 °C, but polycrystalline if deposition temperature is higher than 720 °C. A forming gas flow rate of 35 sccm is used through the Ar gas line. The power to the Si target was increased from 0 W to 200 W while power to the Ge target was decreased from 200 W to 0 W with the same ramping rate of 0.1 W/s, in order to get a smooth graded layer of Si_xGe_{1-x} . After the 2000 s Si_xGe_{1-x} deposition, the power of the Ge target was reduced to 0 W, and that Si target was maintained at 200 W for another 45 minutes deposition. In order to confirm the function of Si_xGe_{1-x} graded layer to reduce the lattice strain between Ge and Si, a Si film was directly deposited on a Ge template (with no composition grading) at 720 °C for comparison study. The thickness of both deposited Si films was 400 nm.

(2) Fabrication of single-crystalline-like Si thin films by RF-PECVD

Sample preparation and clean: The RF-PECVD system has the same sample stage, heater assembly, and sample holder as RF-MCS. The flexible Ge templates (1.2 cm wide, 4 cm long) were cleaned by IPA, then loaded into the chamber by loadlock. The chamber base pressure was kept at 2.5×10^{-7} Torr. Before Si deposition, the Ge templates were first annealed for 10 min in vacuum at 750 °C to remove the native oxide on the Ge surface. Then, the plasma was started at a pressure of 75 mTorr with 40sccm purified H₂ to passivate the Ge dangling bonds.

Un-doped sample process: After 5 mins of H_2 plasma cleaning, the Si films were deposited at an optimized plasma power of 300 W and deposition pressure of 75 mTorr, at heater temperatures ranging from 700 to 900 °C. It is confirmed by Raman spectra that the Si film is amorphous or nano-crystalline if the heater temperature is lower than 650 °C. Hydrogen dilution was used (SiH₄-to-H₂ ratio was 1:4) with 100% pure SiH₄ at a flow rate 10sccm during Si growth in order to promote crystallinity and passivate the Si dangling bonds (*104*). The Si thin film thickness is 1 μ m, corresponding to deposition time of 45 minutes.

Control of film doping concentration: Optimized plasma power of 300 W and temperature of 750 °C were used as the standard to study the impact of the PH₃ (consisting of 10 ppm PH₃ with remainder H₂) and SiH₄ flow rate on the film quality and carrier doping concentration. After the sample cleaning process, un-doped Si was deposited in an atmosphere of 20 sccm SiH₄ and 80 sccm H₂ for 20 mins. Then, different proportions of PH₃ (0.4 sccm ~10 sccm) were introduced into the chamber as the n-type dopant for another 25 minutes. After the process, the n-Si films quality were studied based on the film texture, morphology and doping concentration. In order to meet the TFT structure design requirements, a low carrier doping concentration was required; therefore, a fixed PH₃ flow rate of 0.4 sccm was used with different SiH₄ flow rates from 10 sccm to 40 sccm. In order to reduce the cross contamination issue, the chamber was cleaned by perfluorinated gas such as CF₄ for 30 minutes before the dopant change from PH₃ to B₂H₆. Mechanically robust and specularly shiny Si thin films with good adhesion were obtained on flexible Ge templates. No cracks or visible defects were observed on the surface.

4.2.3 Characterization of the Si thin film

The film texture, crystallinity and morphology of the epi-Si were examined by XRD, SEM, AFM, TEM, and Raman spectroscopy. The electrical property of Si was characterized by Hall measurement. The above characterization methods have been described in Chapter 3. Additional characterization techniques are explained as follows:

Electron back scattered diffraction (EBSD)

EBSD mapping was used to determine the texture and misorientation in the Si grains and to confirm the local structure and phase of the Si crystals. EBSD was carried out in a 55VP Zeiss SEM at 20 kV in a variable pressure mode using a current of 10–15 nA.

Focused ion beam (FIB)

Samples for cross sectional microstructure analysis were prepared by FEI 235 focused ion beam milling system at an acceleration voltage of 30 kV and an ion emission current of 2 mA.

4.3 **Results and discussion**

4.3.1 Heteroepitaxial Si thin films with Si_xGe_{1-x} graded layer by RF-MCS

The crystallographic orientation and epitaxial relationship of Si film grown on the Ge template were analyzed by XRD. The XRD θ -2 θ scans of Si films deposited at different temperatures with Si_xGe_{1-x} graded layer are shown in Figure 4.3 (a). In the samples deposited at temperatures from 650 °C to 720 °C, a strong (004) peak of Si along with {001} peaks of all oxide buffers and Ge layer can be observed, indicating a sharp out-of-plane c-axis orientation. No peaks related to other orientations of Si are visible. However, the intensity of the Si (004) peak is significantly weaker at 650 °C indicating that the Si film does not crystallize well at comparatively low temperature. Upon increasing the substrate temperature to 690 °C, the intensity of the Si (400) peak increases, signifying that the Si layer becomes more crystalline at higher temperature. The reason for this phenomenon is proposed as follows. At a high substrate temperature, the Si nucleation rate of the (001) epitaxial orientation is increased relative to that of random orientations because of enhanced adatom surface mobility. Only preferred substrate surface sites can serve as nucleation sites at low supersaturation while at great supersaturation, random nucleation is possible (*148*). The values of FWHM of the peak were measured from a ω scan of rocking curve, as shown in Figure 4.3 (b). The values of FWHM of the Si films decrease from 2.67°, 1.59° to 1.36° when

the substrate temperature is increased from 650 °C, 690 °C to 720 °C. The smaller FWHM indicates that the Si film texture is improved as temperature increases. This result reveals that the temperature is a dominant factor that determines the crystallinity of the Si film. A relatively high temperature can offer enough energy to improve the spread of the sputtered atoms on the substrate, enhancing the probability of directing the atoms to the right spots for strong epitaxial growth.



Figure 4.3 XRD patterns from (a) θ -2 θ scans and (b) out-of-plane rocking curves of the (004) peak of Si films deposited at different temperature with Si_xGe_{1-x} graded layer ranging from 650 to 720 °C.

The Si films were further characterized by Raman spectroscopy, a very effective tool for the evaluation of crystallinity of films. Figure 4.4 compares the Raman spectra of biaxially-textured Si films grown from 650 ~ 720 °C. A sharp Raman peak, centered at 523.52 cm⁻¹ with a narrow bandwidth of 6.45 cm⁻¹, corresponding to Si transverse optical (TO) mode, was observed at a deposition temperature of 720 °C. The characteristic peak of amorphous Si around 480 cm⁻¹ was not observed, suggesting 100% crystallized phase in the Si films. Compared to single crystal Si wafer position at 520 cm⁻¹ and bandwidth of 4.37 cm⁻¹, the Raman peak of Si thin film shifts to a higher wavenumber (523.5cm⁻¹) presumably due to the stress in the films. The stress in the films can be attributed to the thermal and lattice-mismatch between the Si film and underlying layers and may also arise from the stress in the Si-Si bonds at the grain boundaries (*149*). The TO mode but with a broader bandwidth of 9.26 cm⁻¹ was observed in the Si film at a deposition temperature of 650 °C. In addition, another peak centered at 500 cm⁻¹ appears. These results suggest the Si film is

partly nanocrystalline and/or disordered, which is consistent with the XRD results shown in Figure 4.3. The volume fraction of crystallites of the Si thin film deposited at 650 °C is around 86%, as roughly estimated from the peak decomposition (*150*). It is confirmed that the higher deposition temperature facilitates the formation of crystallinity in the Si film.



Figure 4.4 Raman spectra of flexible Si films deposited onto Ge template with Si_xGe_{1-x} graded layer at temperature of 650 and 720 °C.

The roughness and surface morphology of the flexible Si films were analyzed by AFM as shown in Figure 4.5. The root mean squared (RMS) surface roughness (R_q) was found to increase from 25.1 nm to 39.2 nm with the deposition temperature increasing from 650 °C to 720 °C. The increase in surface roughness is attributed to two reasons. First, the initial Ge with island shape provides a rough template (R_q =11 nm), which will propagate to the Si_xGe_{1-x} layer to make the top layer surface rougher. During the Si_xGe_{1-x} growth, the atoms grown on top of the Ge islands have higher growth velocity, while the atoms grown in the valleys between two grains have lowest growth velocity. With the temperature increasing to 720 °C, the Si_xGe_{1-x} grown on the top of the island has higher growth velocity than that grown at 650 °C, but that grown in the valley has the opposite order of growth velocities. Thus the difference between the island top and valley become larger, which cause a rougher surface. Second, the higher temperature provides more energy to enhance the surface atom mobility and diffusion length to attach existing initial clusters rather than to form a new nucleus (*151*). Therefore, relatively more sparse and large initial Si_xGe_{1-x} clusters are formed at relatively higher process temperatures. At the beginning, the nucleation sites act as seed crystallites for the diffusing adatoms and form the initial Si_xGe_{1-x} grains in a crystallized film. Then more Si adatoms are attached to the Si_xGe_{1-x} initial grains at higher temperature, roughening the film surface.



Figure 4.5 AFM images of flexible Si films deposited onto Ge templates with Si_xGe_{1-x} graded layer, at different temperatures ranging from 650 °C to 720 °C.

Obtaining smooth surfaces is particularly important for practical applications because rough surfaces induce surface and interface defects causing carrier lifetime reduction; also, increased surface roughness scattering results in decreasing carrier mobility (152). Many methods were studied to reduce the Si surface roughness. It was mentioned that a higher processing pressure helped to provide a smoother Si surface due to the formation of initial clusters with smaller size and dense population as a result of the rise in the nucleation density (151). Mechanical polishing is another way to obtain a smoother surface resulting in an improvement of the TFT drain current; for example, a 20% enhancement was achieved after reducing the roughness by 50% (153). In this work, RF-PECVD was utilized to obtain a smooth Si surface by layer-by-layer growth (152). It will be described in the next section.

Owing to a large lattice mismatch between Ge and Si of about 4.2%, deposition of Si on Ge is unavoidably accompanied by the formation of misfit dislocations at the interface, as will be shown later in Figure 4.11. Therefore, we introduced Si_xGe_{1-x} graded buffer layers in previous experiments to reduce the number of threading dislocations that are responsible for the degradation of electrical properties of Si. In order to confirm the importance of Si_xGe_{1-x} layer for epi- Si growth, XRD θ -2 θ scans of Si films deposited with and without Si_xGe_{1-x} graded layer at a deposition temperature 720 °C are compared in Figure 4.6. We observed all the Si and Si_xGe_{1-x} films showed epitaxial growth with sharp out-of-plane c-axis orientation especially as seen on a linear scale. However, if we zoom in to the Si (400) peak in log scale, it is found that this peak is located at 69.14° close to the bulk Si located at 69.13° when the Si_xGe_{1-x} graded layer is used. Without the Si_xGe_{1-x} graded layer, the Si (400) peak is seen to be shifted to 68.85°. The stretching of the Si cell might result in a shift of the X-ray reflection towards lower 2θ angles. It also might be attributed to the grading layer decreasing the density of threading dislocations crossing the Si layer and therefore to improvement in the quality of the layers deposited on the top. Moreover, the Si (400) peak intensity is much stronger with a Si_xGe_{1-x} graded layer due to the larger size of the scattering domains, as will be shown from SEM results later in Figure 4.10.



Figure 4.6 XRD scans of Si films deposited on Ge at 720°C: a comparison of Si (400) texture with and without Si_xGe_{1-x} graded layer.

2D X-ray diffraction was performed to examine the texture of Si layers. Figure 4.7 shows the 2D X-ray diffraction pattern from Si films deposited with and without Si_xGe_{1-x} graded layer at a substrate temperature of 720°C for 45 minutes. It is confirmed that only *c*-axis orientations are found in the Si film with a Si_xGe_{1-x} graded layer, indicating that all the layers have excellent *c*-axis alignment. However, we observe a weak Si (311) peak if the Si layer is deposited without a graded layer, which may be generated from the Ge (311) buffer layer as shown in Figure 4.7 (a). We notice that two symmetric peaks, located at $\chi = 74^{\circ}$, are present at the Si (111) position in Figure 4.7 (d). This is consistent with the Si (111) poles at 16° with respect to the *c*-axis direction observed in the pole figure shown in Figure 4.8.



Figure 4.7 2D X-ray diffraction patterns for Si films deposited on Ge at 720°C: (a) Epitaxial Ge buffer layer; (b) Si directly grown on Ge film; (c) Si_xGe_{1-x} graded layer co-sputtered on Ge film; (d) Si grown on Ge with Si_xGe_{1-x} graded layer. The 2θ range covered is 26-74°.

The Si (111) and Si (220) pole figures in Figure 4.8 reveal the in-plane texture of the Si film. In Si (111) poles, a clear four-fold symmetry was observed at 55° with respect to the *c*-axis, indicating strong biaxial texture. The Φ -scan of Si (111) peaks shows four equally spaced peaks with the FWHM of 4.5°, separated by 90°, confirming the in-plane alignment of the Si film. It is noticed that some Si (111) peaks with low intensity lie at 16° with respect to the *c*-axis, which is attributed to the primary crystal twinning occurring at the interface between Si and Ge layers. It is

also observed that some very weak Si (111) peaks appear, oriented at 32° and 43° with respect to the *c*-axis, due to the secondary twins in the Si film. The additional diffraction spots originating from the primary and secondary twins located at the Si/Ge interfaces, are confirmed by TEM as shown later in Figure 4.11. A similar finding can be observed in the Si (220) pole figure analysis. In the Si (220) pole figure, there is fourfold symmetry of the Si (220) peak which is located at 45° with respect to the normal to the sample surface, indicating biaxial alignment of the Si films. Crystal twinning at the interface between the Si and Ge layers was also observed at 15° in the Si (220) pole figure. In summary, the 2D X-ray diffraction pattern for both in-plane and out-of-plane analysis confirm the biaxially-textured alignment of the Si film grown on Ge template with a Si_xGe_{1-x} graded layer.



Figure 4.8 The Si (111) and (220) pole figure analysis with Si_xGe_{1-x} graded layer.

Figure 4.9 compares the Raman spectra of epi-Si films deposited on Ge buffer with and without a Si_xGe_{1-x} graded layer at 720 °C. The Si wafer, Ge buffer and the Si_xGe_{1-x} graded layer are also characterized as the references. Only a small peak, located at 293 cm⁻¹ corresponding to the Γ_{25} phonon in crystalline Ge, is observed from the Ge buffer layer. After deposition of a Si_xGe_{1-x} layer, Ge-Ge (~292 cm⁻¹), Si-Ge (~410 cm⁻¹) and Si-Si (~495 cm⁻¹) peaks appear representing

the Ge-Ge, Si-Ge and Si-Si bonds, respectively. The Ge-Ge and Si-Ge peaks are not seen after epi-Si is deposited. The peak located around 525 cm^{-1} representing Si TO mode emerges on both Si/Ge and Si/Si_xGe_{1-x} /Ge samples. However, a left shoulder in the Si peak is observed for the Si/Ge sample, suggesting the Si film is partly nanocrystalline, whereas there is no such shoulder peak is seen from the Si/Si_xGe_{1-x} /Ge sample, suggesting fully crystallized phase of the Si films. The high density dislocations at the Si/Ge interface (see Figure 4.11) may suppress the high quality epi-Si growth which results in partial disorder. Compared to the Si wafer TO mode position at 520 cm⁻¹, the Raman peak of the Si thin film shifts to a higher wavenumber (~525 cm⁻¹), which is observed from Figure 4.4 as well. This shift is caused by the stress in the film, due to the thermal and latticemismatch between the Si film and the underlying Ge layer or arising from the stress in the Si-Si bonds at the grain boundaries (*149*). We noticed that the Si film with a Si_xGe_{1-x} graded layer shifts 1 cm⁻¹ less than that without the graded layer, possibly because the graded Si_xGe_{1-x} reduces the stress between the Si and Ge layers.



Figure 4.9 Raman spectra from Si wafer and Si films deposited on Ge buffers with and without Si_xGe_{1-x} graded layer.



Figure 4.10 SEM images of (a) Ge buffer layer, (b) Si/Ge, (c) Si_xGe_{1-x} graded layer, (d) Si/ Si_xGe_{1-x} graded layer, (d) Si_xGe_{1-x} graded layer, (d) Si_xGe_{1-x} graded layer, (d) Si_xGe_{1-x} graded layer, (d) Si_x graded layer, (d) Si_xGe_{1-x} gra

The SEM images in Figure 4.10 compare the surface morphology of epi-Si grown on a Ge buffer with and without a Si_xGe_{1-x} graded layer. The Ge buffer and the Si_xGe_{1-x} graded layer are also imaged as the reference. Initially, a small grain size with diameter of ~ 100 nm is observed in the Ge buffer layer as seen in Figure 4.10 (a). After the Si growth, the grain size increases to around $1 \,\mu\text{m} \times 0.5 \,\mu\text{m}$ (long × width) as shown in Figure 4.10 (b). The increased grain size is owing to the higher processing temperature for Si (720 °C) than for the Ge buffer (550 °C). As mentioned previously, the higher temperature provides more energy for deposited adatoms to attach to the nucleation sites, thus generating large grain sizes. The Si_xGe_{1-x} graded layer grown on the Ge buffer is shown in Figure 4.10 (c). The Si and Ge agglomerate and coalesce with each other to form a rougher surface due to increased strain in the Si_xGe_{1-x} film. After Si deposition in Figure 4.10 (d), the Si grain size increased to around $1 \,\mu\text{m}$ with deep gaps between all grains. Those gaps and large initial Si clusters come from the Si_xGe_{1-x} morphology, since the Si adatoms attach more likely to an existing initial Si_xGe_{1-x} clusters than to form a new Si nucleus, resulting in a very rough Si

surface. For surface-based sensing and detection, and other flexible electronics applications where surface modification is essential, a low value of surface roughness is desirable.



Figure 4.11 Cross sectional TEM images of RF-MCS Si grown on Ge buffer layer without Si_xGe_{1-x} graded layer. Right two images are the zoomed-in areas of the top Si layer and the intermediate layer between the Si and Ge.

Dark-field cross-sectional TEM images in Figure 4.11 show RF-MCS Si grown on Ge buffer layer without a Si_xGe_{1-x} graded layer. SAED pattern acquired from the top region of the Si film showed a diffraction pattern characteristic of diamond lattice structure, conforming successful epitaxial growth of Si on Ge. A high density of defects such as misfit dislocations and (111) twin defects are observed near the Si/Ge interface, as shown in the high magnification image of the Si

and Ge interface in the lower right image. The strain induced by the 4.2% lattice-mismatch and 50% thermal coefficient difference between Si and Ge may be the likely cause of the interfacial defects. Also, gliding of threading dislocations in the Ge layer creates additional misfit dislocations in the Si and Ge interface. It has been reported that the core of threading dislocations has deep traps that enhance recombination to increase leakage current in p-n junction diode (*154*). Thus it is critical to reduce the threading dislocations and misfit dislocations in Si films for device fabrication. A relaxed Si_xGe_{1-x} graded buffer has been believed to reduce lattice constant on a Ge substrate while providing low dislocation densities for the Si film, as revealed in the following TEM images.



Figure 4.12 Cross sectional TEM of Si grown with Si_xGe_{1-x} graded layer: a) a low-magnification view of the multilayer architecture, (b-c) high-magnification view of Si, Si_xGe_{1-x} and Ge layers and (d) SAED patterns and correlating EDX analysis of Si, Ge, and Si_xGe_{1-x} films.

Structural and chemical analyses of the Si on the Ge stack with an intermediate Si_xGe_{1-x} graded layer are studied by dark-field cross-sectional TEM. Figure 4.12 (a) shows a well-defined interface between Si and Si_xGe_{1-x} graded layer. A clean interface is observed between the Si_xGe_{1-x} and Ge layer in the high-magnification view in Figure 4.12 (b). The defects present in the Si and Ge interface are much less than that without the Si_xGe_{1-x} graded layer (in Figure 4.11), because the Si_xGe_{1-x} buffer helps reduce the lattice strain between the Si and Ge layer caused by the lattice mismatch as well as reduce the threading dislocations gliding into the Si film. Although there are many other concepts for attaining a relaxed Si_xGe_{1-x} buffer, not much has been reported on gradient composition technique (155). The graded Si_xGe_{1-x} layer discussed in this chapter, fabricated by RF-MCS process, is different from the traditional compositional grading. It used co-sputtering of both Si and Ge with very slow ramp rate of 0.1 W/s to ensure Si incorporation into the Ge gradually and uniformly, thus propagating a low dislocation interface. In order to confirm there is no interdiffusion between the Si functional layer and Ge buffer layer, Energy-dispersive X-ray spectroscopy (EDX) analysis was performed on Si, Ge, and Si_xGe_{1-x} films at different spots as shown in Figure 4.12 (c). It can be observed from Figure 4.12 (d) that only Ge is present in the Ge buffer layer and only Si present in the Si active layer. A small concentration of Si and a large concentration of Ge appears in the middle part of Si_xGe_{1-x} graded layer, because of a higher deposition rate for Ge than Si. An absence of any diffusion in the Si layer is noted above the EDX resolution of 5 at.%. Corresponding SAED patterns of Si, Si_xGe_{1-x} and Ge layer are shown along with EDX in Figure 4.12 (d). All the film patterns show diamond lattice structure, confirming epitaxial growth and single-crystalline-like nature of Si.

In summary, it has been proven that near single crystalline-like Si thin film has been heteroepitaxially grown on flexible Ge template with the assistance of a Si_xGe_{1-x} graded layer by the RF-MCS method at 720 °C. Compared with Si growth without Si_xGe_{1-x} layer, it shows better texture and crystallinity as well as less defects. However, the surface of the Si film fabricated by

magnetron sputtering is still too rough to make a high quality flexible electronic devices. Moreover, the Si film carrier mobility cannot be measured due to the low concentrations of dopant (B or P) in the film resulting from the low target doping level. For the low dopant Si film, a good ohmic contact is needed to allow charge to flow easily to measure the mobility, thus the contact materials (Al, Ag, Al-Si, etc.) are required on the Si sample by either soldering or annealing. However, the local high temperature process easily creates electrical short in the Si film because of diffusion of contact materials along grain boundaries and defects to the bottom Hastelloy substrate. Therefore, a fabrication process for the Si film with less defects, smoother surface, and controllable dopant level is needed for the various device purposes.

4.3.2 Well-oriented and high carrier mobility single-crystalline-like Si thin films by RF-PECVD

The RF-PECVD process, as we mentioned in chapter 3, employs remote inductivelycoupled plasma to generate high-density plasma, thereby promoting epitaxial growth with less defect density because of less ion-bombardment damage to the film surface (*143*). But moderate ion bombardment helps to disrupt the surface dimers leading to a restoration of surface reactivity and enhancement of the doping process. In this way, RF-PECVD provides significant advantages for phosphorus doping including increased dopant incorporation and doping flexibility, while maintaining good c-Si film texture and superior surface morphology. In this section, we used the Ge template, optimized in chapter 3, as the buffer layer to grow the epi-Si thin film for TFT application. The first step is to understand temperature dependence of undoped Si orientation, crystallinity, roughness and growth rate, which in turn enriches the knowledge of the processproperty-performance relationship. Then, a detailed analysis (i.e. local texture, defects, etc.) of the optimized Si film was performed by RHEED, EBSD and TEM. After that, the precise control of the electronic properties (i.e. carrier concentration and mobility) in doped Si is achieved by tuning different proportions of PH₃ and SiH₄ flow rate.



Figure 4.13 (a) XRD patterns of θ -2 θ scans and (b) average FWHMs of Si (111) pole figure of Si films deposited onto Ge template at different temperatures by RF-PECVD.

The crystallographic orientation and epitaxial relationship of Si films grown on the Ge template were analyzed by XRD. The XRD θ -2 θ scans obtained from films grown at various process temperatures (700 °C ~ 900 °C) are shown in Figure 4.13 (a). The θ -2 θ scan of XRD shows
that only c-axis orientations exists for all the layers, indicating a good epitaxial relationship between the Si film and Ge template underneath. The intensity of the Si (004) peak significantly increases with increase of processing temperature suggesting a higher quality of Si formed at higher temperature, because a relatively high temperature can offer enough energy to enhance the probability of directing the Si atoms to the right locations for better epitaxial growth. The spread in the in-plane texture, i.e., average FWHM of Phi scan of Si (111) for Si films, as a function of deposition temperature is shown in Figure 4.13 (b). It decreases as the deposition temperature increases from 700 °C to 900 °C. The lowest FWHM is around 1.7° at the highest studied temperature of 900 °C. The decreasing of FWHM of in-plane texture results from an increasing of the grain size of Si films at relatively higher temperature. Figure 4.13 (b) also shows a representative Si (111) pole figure for the Si film deposited at 750 °C, suggesting a single crystallographic in-plane orientation and strong four-fold symmetry. The additional diffraction spots which lie at 16° with respect to the *c*-axis originate from the primary twins at the Si/Ge interface as shown in the TEM image. Although the higher temperature helps increase the out-ofplane peak intensity and sharpen in-plane film texture, the Si film adhesion decreases. It is easy for Si to be exfoliated from the underlying Ge and CeO₂ layers at high temperature due to different thermal expansion coefficients, thus deposition of epi-Si on a Ge template is limited to below 850 °C. However, all the FWHMs of the Si (111) pole figures $(1^{\circ} \sim 3^{\circ})$ in this experiment were significantly smaller than that in biaxially textured Si films on NiW metal substrates grown by the hot wire chemical vapor deposition (HWCVD), where FWHMs are around $5^{\circ} \sim 7^{\circ}(156, 157)$. They are also smaller than the Si film (4.5°) fabricated by the RF-MCS approach mentioned in the last section. It clearly presents higher quality Si films based on flexible Ge templates deposited by the RF-PECVD.



Figure 4.14 (a) Raman spectra of flexible Si films deposited onto Ge templates at different temperature ranging from 700 to 900 °C; (b) FWHM and wavenumber for Si TO mode peak as a function of the deposition temperature.

The crystalline quality of the Si films was further characterized by Raman spectroscopy. Fig. 4.14 (a) shows Raman spectra of c-Si wafers and biaxially-textured Si films grown on Ge templates at 700 °C ~ 900 °C. Sharp and strong Raman peaks, corresponding to the Si TO mode, were observed in both flexible Si thin films and c-Si wafers (*158*). Compared to Raman spectra of RF-MCS Si films, the peak associated with amorphous feature (around 480 cm⁻¹) was not observed in RF-PECVD Si films, suggesting a purely 100% crystalline phase of the Si films. Figure 4.14 (b) compares FWHMs and positions at different process temperatures, which is determined by fitting the peaks using Lorentzian functions. There is a peak shift by $4 \sim 5 \text{ cm}^{-1}$ wavenumbers in flexible Si films with respect to a c-Si wafer, indicating a stress in the films, as also observed in RF-MCS Si (*149*). The Si peak shifts to a higher wavenumber when process temperature increases, indicating a higher stress formed in the Si film. The FWHM of the Si thin films is around $5.1 \sim 6.4 \text{ cm}^{-1}$, which is comparable to the reference Si wafer with a peak width of ~ 4.6 cm⁻¹, suggesting a high crystalline quality nearly equivalent to that of a c-Si wafer. Though higher growth temperatures result in sharper Raman line-width, growth of a temperature beyond 800 ^oC often caused surface roughening, poor adhesion and delamination of film, possibly due to thermal mismatch of the underlying buffer layers. Therefore, to maintain a specular film surface, good adhesion and reasonable film quality, a growth temperature at 700 °C ~ 800 ^oC is favored.

A smoother Si thin film surface is critical in reducing the surface roughness scattering and increasing the carrier mobility. Therefore, surface roughness and topography of the undoped Si films grown at various deposition temperatures were evaluated by AFM in Figure 4.15. Each one of these images was obtained over an area of $5 \,\mu\text{m} \times 5 \,\mu\text{m}$. The Si RMS roughness slowly increases from 18.6 nm to 20 nm when the process temperature increases from 700 °C to 850 °C. However, the roughness increases dramatically to 24 nm when the process temperature increases to 900 °C. In general, the deposition temperature strongly influences the final film surface structure such as the grain size and surface roughness (*151*). Therefore, as the epi-Si process temperature increases, more sparse and large initial Si clusters are observed, because the Si adatoms are more likely to attach existing initial clusters than to form a new Si nucleus with the increased temperature. More sparse and large initial Si clusters contribute to the increase in the surface roughness. Consequently, a lower roughness Si sample deposited at lower temperature is preferred for device fabrication.



Figure 4.15 The RMS surface roughness as a function of Si process temperature. Corresponding AFM images at different temperature ranging from 700 °C to 900 °C.

Since the Si films deposited at temperatures ranging from 700 °C ~ 800 °C have good texture, smooth surface morphology, and good adhesion to the buffer layer, the growth rate was studied in this optimum temperature regime. The growth rate is calculated by dividing thickness by deposition time. The thickness was measured from cross-sections made using the FIB. Figure 4.16 shows a profile of the growth rate of undoped Si vs. deposition temperature. There exists a significant dependence of growth rate on temperature, with the growth rate peaking at around 750 °C. A significantly lower growth rate is observed at 650 °C, indicating kinetic growth-controlled surface-reaction limited regime. On the other hand, decrease in growth rate beyond 850 °C may indicate increased rate of desorption of film matrix elements from the growth surface at high temperatures. Therefore, the optimal temperature is 750 °C taking into account the film crystallinity,

texture, roughness, growth rate and good adhesion to the buffer layer. The phosphorus-doped Si films investigated in this chapter were optimized based on this growth temperature.



Figure 4.16 Dependence of growth rate on deposition temperature of RF-PECVD Si films.

Undoped Si film deposited at 750 °C was further characterized by RHEED, EBSD and TEM to confirm its local texture. Figure 4.17 (a) shows a schematic of the multilayer buffer architecture that was developed for the heteroepitaxial growth of Si films on a flexible, polycrystalline Ni-alloy tape. The growth of each layer was characterized by RHEED as shown in Figure 4.17 (b). As expected, RHEED results show disorder in the amorphous α -Al₂O₃ layer. After 10 nm of IBAD MgO deposition, spots in the RHEED pattern indicate cubic (001) out-of-plane oriented texture. The pattern sharpens considerably after further homo-epitaxial MgO growth without further ion-beam assistance. The continuing improvement of the RHEED pattern as the films grow confirms the hetero-epitaxial growth of additional LMO, CeO₂ and Ge layers. It is pointed out that all the layers show clear patterns without secondary reflections. Sharpening of the RHEED pattern is finally observed in the RF-PECVD Si layer, implying further improvement of texture. It is also important to note that it was unable to grow epitaxial Si directly on CeO₂ buffer

layer, although fluorite CeO₂ has an excellent structural and lattice/thermal match with Si. Epitaxy is likely disrupted due to the formation of a thin layer of amorphous SiO₂ at the Si/CeO₂ interface during growth, as reported previously (88). Therefore, an intermediate Ge layer, where Ge-O is easy to remove at high temperature to maintain epi-Ge (*114*), was developed to enable Si epitaxy.



Figure 4.17 (a) Schematic of the multilayer architecture, from Hastelloy substrate to Si film. b) RHEED patterns for the Si film and buffer layers.



Figure 4.18 (a) EBSD map of Si surface showing preferred (001) growth. (b) Misorientation distribution profile. (c) (111) pole figure with four fold symmetry indicating biaxial texture.

EBSD was performed to determine the local texture and misorientation of the Si grains and to confirm the local structure and phase of the Si crystals. Figure 4.18 (a) acquired from Si film shows an inverse pole figure map along the out-of-plane direction overlaid on the pattern quality image. Regions of similar crystallographic orientation on the surface were assigned by the same colors. A predominant red color stands for the majority of the grains aligned along the (001) direction. The pattern quality was poor at the defective grain boundaries and crystal imperfections, indicated by darker regions on the map. The misorientation distribution profile in Figure 4.18 (b), revealing the relative frequencies of the local angular deviation from cube orientation, shows the

misorientation angle was less than 2 degrees in more than 98% of the grains. The highly oriented grains in a preferred direction with very low misorientation, particularly in the grain interiors, suggest good structural quality of the Si film. Low-angle grain misorientation may be relatively less detrimental to the electrical properties of semiconductors (*88*). The EBSD (111) pole figure in Figure 4.18 (c) reveals a strong four-fold symmetry, suggesting biaxial cube texture and a high degree of alignment of the Si crystals. Therefore, biaxially-textured Si films with low grain misorientation, demonstrated in this chapter, can potentially exhibit improved electrical properties and be suitable for electronic devices application.



Figure 4.19 Bright field TEM micrographs of the cross-section multilayer structure with Si deposited by RF-PECVD: (a) a low-magnification view of the multilayer architecture, (b) a high-magnification view of Si film, and (c) SAED pattern of Si film.

The selected undoped Si film grown by RF-PECVD was further characterized by TEM. Figure 4.19 (a) shows the bright-field cross-sectional TEM micrographs of the composite structure. The formation of a Ge-Si graded layer during the RF-PECVD process is considered to contribute to a reduced lattice mismatch between the Ge layer and the Si layer, thus reducing the dislocation density. After that, some dislocations appeared in the Si layer after Ge-Si formation, but the dislocation density is much lower than that reported in Si films grown on a γ -Al₂O₃ transition layer with a IBAD MgO buffer layer (94) and on a Ge transition layer with IBAD-fabricated CaF₂ seed layers (74). Moreover, it is observed that, as the films grew thicker, as shown in high magnification in Figure 4.19 (b), the defect density decreased towards the surface making the region near the top surface of Si films relatively clean and free of defects. This may be attributed to the relaxation of the films and release of initial strain resulting from lattice-misfit and gliding and annihilation of dislocations as the films grow thicker, as previously reported in Si films grown on sapphire and Ge films on metal substrates (94, 105, 159). The SEAD pattern in Figure 4.19 (c) confirmed epitaxial growth and single-crystalline nature of Si, consistent with the RHEED, XRD and Raman analysis described earlier.

In summary, Si film deposited at 750 °C by RF-PECVD has single crystallographic orientation, smooth surface morphology, and good adhesion to the buffer layer. The temperature of 750 °C yielded the highest deposition rate, which is suitable for inexpensive substrates such as display glass or metallic foils (*160*). Moreover, the lower temperature process also reduces the energy input and simplifies the requirements for substrate heating (*11*). Therefore, 750 °C is an optimum temperature for the optimization of the phosphorus-doped Si film based on different SiH₄ and PH₃ flow rate for TFTs devices.

4.3.3 Control of Si film carrier concentration and defect density for the device fabrication

Based on simulation results, in order to fabricate good TFTs based on near c-Si film on flexible Ge buffer, three critical functions have to be satisfied for an active n-channel layer: (1)

channels with lower carrier concentration ($< 10^{16}$ /cm³) to ensure higher on/off ratio; (2) smooth and uniform Si surface without (or with minimal) pinholes in the film to ensure TFT consistency; (3) high field effect mobilities (> 200 cm²/V.s) of the channel materials to ensure superior device performance. Therefore, the control of c-Si film quality and carrier concentration are the key steps for successful fabrication of TFTs.

(1) Controllable n-type doping by varying PH₃ flow rate

Epitaxial Si films were grown in a RF-PECVD reactor from the decomposition of SiH₄ gas (20 sccm) at a plasma power of 300 W, pressure of 75 mTorr and process temperature of 750 °C. The phosphine (PH₃) source with 10 ppm concentration balanced by H₂ was introduced into the chamber with a flow rate ranging from 0.4 sccm ~10 sccm. The morphology, texture, crystallinity, carrier concentration and mobility for P-doped Si films are studied in this section to understand how the P incorporated into the flexible Si film, and provide guidance to choose the right process conditions for the best TFT device performance.

Figure 4.20 shows SEM images of the Si films with various P concentrations incorporated into the film. A change in growth mechanism induced by the addition of PH₃ could be observed through differences in surface morphology. The undoped c-Si film grown on flexible Hastelloy possesses uniform small grains with size 100 nm ~ 200 nm. When 10 ppm PH₃ at 0.4 sccm was introduced into the chamber, the c-Si surface starts showing small, square (around 0.5 μ m × 0.5 μ m) features distributed randomly on the Si surface; but the rest of the locations are flat without small grains. With the PH₃ flow rate increasing from 0.4 sccm to 5 sccm, the density of small squares increases as well. Finally, these complete square features disappear when PH₃ flow rate reaches 10 sccm. It was also observed that the roughness of the Si films increases with the increase of PH₃ flow rate.



Figure 4.20 SEM images of Si films deposited at various PH_3 flow rates (0 sccm ~ 10 sccm) with 20 sccm SiH₄ at 750 °C.

The texture and crystallinity of n-Si films were examined by XRD and Raman spectroscopy and the results are exhibited in Figure 4.21. In order to incorporate P doping without inhibition of the crystal growth, a hydrogen sputter clean was used to remove native oxide prior to epitaxial deposition, then pure SiH₄ was introduced for 20 minutes prior to dopant introduction in order to minimize complications induced by the presence of dopants on the surface (*161*). The n-Si films maintained a good texture with P incorporated into the film, as confirmed by XRD θ -2 θ scan in Figure 4.21 (a). However, it was noticed that the FWHM of the ω -scan rocking curve for Si (400) plane increases from $\Delta \omega = 1.30^{\circ}$ to $\Delta \omega = 1.48^{\circ}$ when PH₃ flow rate increase from 0 sccm to 2 sccm as shown in Figure 4.21 (b), but declines to $\Delta \omega = 1.20^{\circ}$ when the PH₃ flow rate increases up to 10 sccm. A previous study has shown that diborane enhances c-Si growth quality in the normal CVD process while phosphine suppresses its deposition (*162*). However, plasma enhancement provides a significant advantage for phosphorus doping even in low temperature epitaxial growth with improved film growth rate control, increased electrically active dopant incorporation, and improved surface morphology (*161*). Therefore, the XRD intensity in the θ -2 θ scan and FWHM of the omega scan of the phosphorus incorporated Si films does not exhibit much difference with different flow rates of the PH₃. The narrowest $\Delta \omega$ (1.20°) at 10 sccm PH₃ flow rate may be caused by the surface morphology change on the Si surface, as shown in Figure 4.20.



Figure 4.21 (a) XRD θ -2 θ scan on Si films; (b) FWHM of the Si (400) rocking curve as measured by out-plane XRD ω scan; (c) Raman spectra of flexible Si films; and (d) FWHM of Si TO mode peak as a function of the PH₃ flow rate.

Furthermore, the c-Si thin film samples were characterized by Raman spectroscopy to better understand the impact of the PH_3 gas flow rate on the crystal quality. Figure 4.21 (c) and (d) show the Raman spectra and FWHM of the Si TO mode peak at different PH_3 gas flow rates, respectively. For comparison, a Raman spectrum was also taken for a single crystal Si wafer. The Raman spectrum obtained on the c-Si wafer displays a sharp Lorentzian peak at 520 cm⁻¹ with a measured FWHM of 3.5 cm^{-1} . The FWHM values of the flexible Si films are in the range of 4.5 -4.7 cm⁻¹ at PH₃ flow rate below 2 sccm, but it increases to 5.1 cm⁻¹ when PH₃ flow rate increases to 10 sccm. Although the peak is broadening as PH_3 flow rate increases, it is still nearly equivalent to c-Si wafer, representing a high crystalline quality with less defects in the flexible n-Si films. But the higher FWHM value caused by higher PH₃ flow suggests relatively more disorder in the crystal quality when a higher phosphorus concentration is incorporated into the Si film. This is because the higher fraction of PH_3 , the more the silicon surface is covered with phosphorus. This increased fractional coverage has a dramatic effect on the rate of Si deposition. Some phosphorus blocks selected active sites or some Si adsorbates strongly bond to phosphorus that hinders further decomposition (163). The reason for the FWHM of the XRD rocking curve and the Raman Si peak show different trends might be because of different penetration depths for these measurements. Raman spectroscopy is more focused on the top ~ 100 nm thickness but XRD samples several micrometers. That means that the top surface has a better crystallinity than the whole Si stack at the lower PH₃ flow rate. It was also noticed that all the wavenumbers of Si TO mode shift 5 cm⁻¹ with respect to the c-Si wafer, suggesting a stress in the films, as mentioned previously. But the Si TO peak position is maintained as PH_3 flow rate increases, indicating that the incorporated phosphorus hardly influences the stress in the Si-Si bonds at the grain boundaries. The detailed growth kinetics and surface interactions between the SiH₄ and PH₃ are explained below.

The calculated and measured P concentrations in the Si films as a function of phosphine flow rate is shown in Figure 4.22. The method for calculation have been presented in details in Chapter 3.3.2. Three reasons impact the real carrier concentration in the Si films: (1) the percentage of phosphorus incorporated into the film due to the growth kinetics and surface interactions between the SiH₄ and PH₃; (2) the possible diffusion of elements from the substrates (Ni, Cr, Mn, etc.) and buffer layers (O, Mg, Al, etc.) may enhance or compensate the n-type doping; (3) the defects (point defects, extended crystal defects, defect complexes, etc.) and grain boundaries in the Si film that may act as acceptors (130). Therefore, the carrier concentration theoretically increases along with the increase of PH₃ flow rate but experimentally it does not show the same trend. At the beginning, the P concentration was found to increase almost linearly at a smaller phosphine flow rate (0 sccm ~ 2 sccm). After that, it becomes almost saturated at a higher phosphine flow rate, which results in a lower carrier concentration $(5.4 \times 10^{17} \text{ cm}^{-3})$ than the calculated value $(1 \times 10^{18} \text{ cm}^{-3})$ ³). This result could be explained by Uhrberg's work in which angle-resolved photo emission data and *ab initio* pseudopotential calculations were used to study the electronic and atomic structure of arsenic-terminated Si (100) surfaces (164). In our case, when the Si surface is only partially covered with small amount of P, there will be little chance for interaction among adsorbed P atoms. Therefore, the majority of dopants on the Si surface may exist as atomic P, which will be readily incorporated into the n-Si crystal growth process. As the density of P atoms on the surface increases, a higher probability for interacting to form the stable dimers or perhaps aggregates. A symmetric P-P dimer model is a stable structure at high coverages based on energy minimization calculations. In the proposed model, the P atoms form symmetric dimers on top of the Si (100) surface in which each P atom bonds to two Si atoms and to the other P atom of the dimer. This arrangement leaves the P atoms fully coordinated with a doubly-occupied lone-pair state. Because of the full coordination, the P atoms act as a passivating layer and adsorption of additional P is highly reduced. As the phosphorus portion keeps increasing, it starts saturated at a monolayer and thus serves as an effective passivating layer. Thus a balance will exist on the surface between dissociative adsorption of P, dimer formation, monomer incorporation, and dimer desorption (161). This also explains well that the saturation of P concentration at higher PH₃ flow, which is accompanied the depression in

the Si growth rate, due to the blocking effect of phosphorus. Additional support for the existence of n-type dimers on a Si surface was the observation that P-P is the primary species observed during desorption from a saturated surface (*162*).

The corresponding hall mobilities of n-Si thin films deposited with different PH₃ flow rates are shown in the Figure 4.22. It shows the reverse trend with the film carrier concentration. Hall mobility starts in the range of 190 ~ 200 cm²/V.s at the lower PH₃ flow rate (0.4 sccm – 2 sccm), followed by a sharp decrease to 131 cm²/V.s at higher PH₃ flow rate (> 5sccm). The decreased mobility is partly because of the deterioration of the Si crystal quality at higher PH₃ flow rate, as confirmed by the Raman spectrum in Figure 4.21 (c). Also, since the phosphorus concentration increases in the film, the free carriers collide with impurities more frequently resulting in decrease of the drift velocity, and thus the lower mobility.



Figure 4.22 Hall mobility and carrier concentration (both calculated and experimental results) of n-Si thin films as a function of the PH₃ flow rate.

(2) Controllable n-type doping by various SiH₄ flow rate

It was shown in the previous section that the experimental carrier concentration has almost a linear relationship with the PH₃ flow rate. For lateral TFTs based on flexible c-Si substrate, a lowdoped channel layer (< 1×10^{16} /cm³) with well-controlled doping and thickness is needed. Therefore, the effects of SiH₄ on the epitaxial Si growth process with the lowest PH₃ flow rate were studied by measuring the growth rate, surface morphology, crystal quality, and dopant incorporation. 10 ppm of PH₃ at a flow rates of 0.4 sccm (the smallest range of mass flow controller) and 100% pure SiH₄ at various flow rate (10 sccm ~ 40 sccm) were used to grow n-Si at a plasma power of 300 W, pressure of 75 mTorr and process temperature of 750 °C. Purified hydrogen was introduced into the chamber with SiH₄-to-H₂ ratio of 1:4 to dilute the SiH₄ during Si growth in order to promote crystallinity and passivate the Si dangling bonds. It is well known that appropriate hydrogen adsorption prevents island growth whereas too high a hydrogen coverage may etch away weak bonds leading to crystalline-amorphous transition. The utilized ratio of SiH₄-to-H₂ of 1:4 is the optimized one for the epi-Si growth.

Figure 4.23 presents the surface morphology of the Si films deposited at various SiH₄ (10 sccm ~ 40 sccm) flow rates at the same level of PH₃ (0.4 sccm) incorporation. At the lowest SiH₄ flow rate of 10 sccm, a high density of small squares (around 0.5 μ m × 0.5 μ m) feature was seen distributed randomly on the Si surface. With the SiH₄ flow rate increase to 20 sccm, the density of small squares decreases with most of rest of the area flat. It is assumed that the high density of the small squares is probably caused by the high P concentration incorporated into the film. When the SiH₄ flow rate reaches 30sccm, the Si surface morphology changes. More flat small squares appear with small holes between the grains, which might be caused by the increasing arrival of the precursors. This promotes the formation of surface valleys that finally evolve into nanosized voids in the Si film. When the SiH₄ flow rate is set at 40 sccm, the islands features distribute uniformly on the Si surface with smooth morphology. Normally, increasing the deposition rate at a given

temperature, accomplished by raising the SiH₄ partial pressure in the reactor during growth, leads to a smoother surface morphology and the formation of a continuous Si layer. In this case, high SiH₄ flow with small portion of PH₃ is in favor for undoped Si growth. Epitaxial Si on Ge follows the Stranski-Krastanov (SK) growth mechanism under a variety of experimental deposition conditions, in which Si films remain continuous up to a few monolayers and then breaking into high density Si islands, as shown in the last image in Figure 4.23.



Figure 4.23 SEM images of Si films deposited at various SiH₄ flow rates (10 sccm ~ 40 sccm) with 0.4 sccm PH₃ at 750 °C.

The influence of SiH₄ flow rate on the texture and crystalline quality of Si films was investigated by XRD and Raman spectra. The θ -2 θ X-ray pattern in Figure 4.24 (a) verifies that there are no out-of-plane misorientations in the Si layer. The intensity of Si (400) peak becomes higher when the SiH₄ flow rate increases, indicating a higher deposition rate of the Si layer with 40 sccm SiH₄ flow rate. The FWHM of the ω -scan rocking curve for Si (400) plane in Figure 4.24 (b) shows that the *c*-axis alignment improves from $\Delta \omega = 1.58^{\circ}$ to $\Delta \omega = 1.17^{\circ}$ when SiH₄ flow rate increases from 10 sccm to 40 sccm, since more SiH₄ is decomposed to the Si at higher flow rate. And more H_2 under glow-discharge plasma enhances the energy of the decomposed Si atoms on the substrate improving the c-axis orientation alignment of the growing Si film. Similar results are shown in Figure 4.24 (c) and (d) by Raman spectroscopy. Only Si TO mode peaks are observed in all the films which represent fully crystalline quality of the flexible n-Si films. FWHM of the Si peak decreases from 5.8 cm⁻¹ to 4.2 cm⁻¹ as the SiH₄ flow rate increases from 10 sccm to 40 sccm. Two reasons can explain this: (1) more c-Si formation at higher SiH₄ flow rate, which enhances the Si film crystallinity; (2) relatively higher fraction of the PH₃ in less SiH₄ content may block selected active sites or some Si adsorbates strongly bonds to P and further decomposition is hindered (*163*), which results in a broader FWHM of Si peak. However, all the FWHMs of Si peaks are close to that of single crystal Si wafer (3.6 cm⁻¹) with a slightly peak position shift caused by the stress in the films.



Figure 4.24 (a) XRD θ -2 θ scan from Si films; (b) FWHM of the Si (400) rocking curve as measured by out-plane XRD ω scan; (c) Raman spectra of flexible Si films; and (d) FWHM of Si TO mode peak as a function of the SiH₄ flow rate.



Figure 4.25 Hall mobility and carrier concentration (both calculated and experimental results) of n-Si thin films as a function of the SiH₄ flow rate.

Well-controlled doping profiles are important for device fabrication. In the last section, it was shown that the doping profile could be controlled to the level of 5.4×10^{16} /cm³, but a lower doped channel layer (< 1×10^{16} /cm³) is needed for specially-designed TFTs. Therefore, Si films were made with a higher SiH₄ flow rate while maintaining a stable PH₃ flow rate at 0.4 sccm. Figure 4.25 shows the calculated and measured P concentration and carrier mobility in n-Si film as a function of SiH₄ flow rate. Both calculated and measured results show decrease in carrier concentration with the increase of SiH₄ flow rate, since relative less P is incorporated into the reactive gas. The huge carrier concentration difference at the beginning (especially at 10 sccm SiH₄) may be due to diffusion of elements from the substrates and buffer layers which enhances the n-type doping. The n-Si film is thinner at lower SiH₄ flow rate (as shown from FIB in Figure 4.26), thus the elements from bottom layers are easier to diffuse through grain boundaries onto the top

active layer. Also, more defects at the thin Si layer will act as the dopants to increase the carrier concentration. As shown from TEM results later in Figure 4.27, lots of the threading dislocations are present at the first ~500 nm range. Those dislocations are annihilated when the film becomes thicker. With the SiH₄ flow rate increasing to 40 sccm, the carrier concentration decreases to 5.0×10^{15} /cm³ and hall mobility increases to 230 cm^2 /V.s, which meet the requirement of electrical properties to fabricate flexible TFTs based on this unique structure.



Figure 4.26 (a) Dependence of Si film thickness on various SiH₄ flow rate at 750 °C for 45 mins RF-PECVD process; (b) Corresponding Si growth rate based on Si film thickness.

The thickness of the Si channel layer is critical for a successful device. If the active channel layer is too thick, the transport characteristics cannot be modulated and the film flexibility will be restricted; if the channel layer is too thin, the Ge may diffuse into the Si layer and a high concentration of dislocations and stacking faults will appear in the first ~ 100 nm, arising from the 4.2% mismatch between Si and Ge lattice. Therefore, $1 \sim 2 \,\mu m$ is a proper range for the channel layer thickness depending on the film quality and simulation results. In Figure 4.26 (a), the c-Si films thickness was measured from cross-sectional images using FIB. The thickness increased from 960 nm at SiH₄ flow rate of 10 sccm to 2 μ m at a SiH₄ flow rate 40 sccm. The corresponding growth rate based on the different SiH₄ flow rates is calculated from 22 nm/min to 43 nm/min by dividing thickness by deposition time of 45 minutes and the results are shown in Figure 4.26 (b). As observed in the figure, the Si film thickness does not show a linear relationship with the SiH₄ flow rate. At low SiH₄ and H₂ flows, the growth rate is proportional to flow pressure because the gas is highly depleted of SiH₄ by decomposition at the plasma and by gas phase reactions. However, at high SiH₄ flow, the SiH₄ is not fully decomposed with high pressure of H_2 thus the growth rate is independent of SiH₄ flow pressure. Normally, epitaxial growth with high perfection is suppressed by the high pressure of the H_2 ambient, because H_2 suppresses both the decomposition of SiH₄ and the migration of atoms on the surface. However, if we consider the film thickness, crystallinity, texture, roughness, mobility and especially the carrier concentration, the 40 sccm SiH₄ with 0.4 sccm PH₃ is the optimized gas flow rate for the TFT fabrication.

The microstructure of n-Si deposited at 750 °C by RF-PECVD with 40 sccm SiH₄ and 0.4 sccm PH₃ is characterized by the cross section of high resolution TEM. Figure 4.27 shows the dark-field cross-sectional TEM micrographs of the Si thin film on flexible metal tape. Corresponding SAED patterns of Si and Ge are shown at the top left. Both SAED patterns show diffraction pattern with characteristic of diamond lattice structure, confirming epitaxial growth and single-crystalline nature of Si on Ge template, consistent with the RHEED, XRD and Raman analysis described

earlier. A high density of misfit dislocations and twins at an angle of 54.7° to the interface, were observed at Si and Ge interface. The source of these defects may be from 1) replication of existing defects in the Ge buffer layer; 2) strain caused by the large lattice mismatch (4.2%) at the Si/Ge interface, and 3) strain induced upon cooling from the growth temperature caused by different thermal expansion coefficient between Si (~ 2.5 ppm K⁻¹) and Ge (~ 5.9 ppm K⁻¹) (*157*). We also noticed the defect density as the Si thickness increases. Only few threading dislocations are observed at the top surface of the Si film. This is attributed to the relaxation of the films and release of initial strain from lattice-misfit and also to gliding and annihilation of dislocations as the film grows thicker (*159*). We believe that the decreasing defect density of the Si top layer contribute to a high Si hall mobility of 230 cm²/V.s.



Figure 4.27 Cross sectional TEM image of RF-PECVD Si grown on Ge buffer layer at 750 °C with SiH₄ flow rate of 40 sccm and PH₃ flow rate of 0.4 sccm for 45 mins. The spotty patterns are SAED patterns of Si and Ge films.

In summary, the texture, crystallinity, and doping concentration of epitaxial n-type Si thin films were studied by adjusting the SiH₄ and PH₃ flow rate to reach the optimized deposition condition. Based on an optimized SiH₄ flow rate (40 sccm) and PH₃ flow rate (0.4 sccm), the n-Si film was highly oriented along (004) direction with narrow spread in out-of-plane (1.2°) texture. Raman spectroscopy also revealed fully crystallized of n-Si films with sharp Si TO mode peak (4.2 cm⁻¹), nearly comparable to that of Si wafer (3.6 cm⁻¹). The highest electron mobility of 230 cm²/V-s was achieved corresponding to the narrow FWHMs of Raman and XRD. A film thickness of 2 μ m and very few defects at the top surface of the n-Si film were confirmed. Controllable P doping was achieved in the range 10¹⁵ to 10¹⁸/cm³, which is suitable for the flexible TFT fabrication.

4.4 Application in TFTs

Top-gate TFTs were fabricated using a single-crystal-like *n*-type [100]-oriented Si thin film with a carrier concentration of ~5×10¹⁵ cm⁻³ grown on flexible metal substrate. The processing steps were smiliar to the c-Ge TFT fabricated on flexible glass, as discribed in chapter 3. The difference was in choosing nickel mono-silicide (NiSi, 30 nm) metallization scheme as source/drain (S/D) contacts due to the low specific contact resistivity (ρ_c). Aluminum (Al) was still selected as gate metal. The channel length and gate width were 14 µm and 30 µm, respectively, corresponding to a width-to-length ratio of ~2:1.

The inset in Figure 4.28 (a) shows an optical image of the top view of c-Si TFT device on flexbile hastelloy, and the inset in Figure 4.28 (b) shows the Si TFT in a bent test during testing. The bending radius is 3 cm. The graphs in Figure 4.28 (a) and (b) show typical TFT output characteristics where source-to-drain current (I_{ds}) increases dramatically as source-to-drain voltage (V_{ds}) increases at a positive gate bias V_{gs} , confirming that electrons are the majority charge carriers and the semiconducting channel is *n*-type.



Figure 4.28 (a) Si TFT output characteristics obtained with a W/L = 30/20 for V_{GS} varying from - 3 to 15 V. The left inset image is a photo of Si TFT on flexible Hastelloy. (b) Transfer characteristics of the Si TFT at V_{DS} = -3 V.

The TFT device achieved the highest on-current of ~1.6 mA (before bending) and ~ 1.4 mA (after bending) for the top-gate modulation when the top-gate bias is 15 V. The extracted field

effect mobility of the flexible c-Si-TFTs is ~200 cm². V⁻¹. s⁻¹, as calculated from the I_{ds} - V_{gs} at a drain bias of 0.5 V. The field effect mobility at the magnitude of ~200 cm². V⁻¹. s⁻¹ is a remarkable improvent, significantly higher than that of previously reported flexible TFTs and comparable to that of single crystal wafer. The channel can also be completely switched off with a negative gate voltage to achieve the highest on-off ratio reaching ~10⁶ when it is measured before bending. The ratio became to ~5×10⁵ when it is measured after bending, which is also sufficient for high-performance operations. Unlike all other existing flexible TFTs which have orders of magnitude lower saturation current and field effect mobility, our transistors show superior performance before and after bending owing to their single crystal like channel, which open up a new era toward the realization of TFTs for next-generation flexible electronics.

4.5 Summary

Single-crystalline-like Si thin films grown by both RF-MCS and RF-PECVD were fabricated at various conditions on Ge templates on flexible hastelloy. Investigation of the materials quality by means of RHEED, SEM, TEM, AFM, XRD, EDX, FIB and Raman spectroscopy has proven the high crystalline quality of the Si films. Precise control of the n-type Si film electronic properties (i.e. carrier concentration and mobility) over large areas is achieved by controlling PH₃ and SiH₄ flow rate at optimized deposition condition by RF-PECVD, which is suitable for the TFT fabrication.

For the RF-MCS c-Si thin film, the effect of deposition temperature and Si_xGe_{1-x} graded layer on the film texture, crystallinity and surface morphology was studied. It has been shown that the n-Si film is highly oriented along (00l) direction with narrow spread in out-of-plane (1.16°) and in-plane (4.5°) texture with assistance of Si_xGe_{1-x} graded layer at 720 °C. Raman spectroscopy also revealed n-Si films with sharp Si TO mode peak (6.5 cm⁻¹), close to Si wafer (4.4 cm⁻¹). Compared with Si growth without Si_xGe_{1-x} layer, it showed better texture, crystallinity and less defects. However, the surface of Si film fabricated by magnetron sputtering is still too rough to make high quality flexible electronic devices. Also, the Si film carrier mobility cannot be measured and controlled due to low dopant (B or P) associated into the film resulted from low target doping level. Therefore, the Si film with less defects, smoother surface, and dopant controllable process is needed for the TFT device purposes.

In order to control the film doping concentration while maintaining or promoting highlyoriented Si epitaxial growth with less defect density, RF-PECVD used applied to fabricate high quality un-doped c-Si thin film. Different process temperature was applied to understand temperature impacts on Si film orientation, crystallinity, roughness and growth rate, which in turn enriches the knowledge of the process-property-performance relationship. It has been found 750 °C is the optimized temperature for the Si film with single crystallographic orientation, smooth surface morphology, good adhesion to the buffer layer, and the highest deposition rate. Then the detailed analysis, such as local texture and defects of the Si film grown at 750 °C was performed by the RHEED, EBSD and TEM. Afterwards, 750 °C is the selected temperature for the optimization of the P-doped Si film based on different SiH₄ flow rate and PH₃ flow rate for the TFTs device purpose.

After un-doped Si optimization, the film texture, crystallinity, and doping concentration of epitaxial n-type Si thin films grown by RF-PECVD were studied by adjusting the SiH₄ and PH₃ flow rate at optimized process temperature 750 °C. It has been found that the SiH₄ flow rate (40 sccm) and PH₃ flow rate (0.4 sccm) are the optimized reactive gas flow rates. The resulting n-type Si film is highly oriented along (004) direction with narrow spread in out-of-plane (1.2°) and inplane (2.5°) texture. Raman spectroscopy also revealed fully crystallized of n-Si films with sharp Si TO mode peak (4.2 cm⁻¹), nearly comparable to Si wafer (3.6 cm⁻¹). The highest electron mobility can reach 230 cm²/V-s. The FIB and TEM confirmed the film thickness of 2 μ m and very few defects at the top surface of the n-type Si film. Controllable P doping was achieved in the range 10¹⁵ to 10¹⁸/cm³, which is suitable for the flexible TFT fabrication.

Finally, a top-gate TFT was fabricated using a single-crystal-like *n*-type [100]-oriented Si thin film with a carrier concentration of $\sim 5 \times 10^{15}$ cm⁻³ grown on flexible metal substrate. The resulting devices exhibited exceptional performance with on/off current of $\sim 10^6$, a threshold voltage of 0.6 V and a field-effect mobility of ~ 200 cm²/V-s. These devices with superior saturation current of ~ 1.6 mA opens up a new era toward the realization of TFTs for next-generation flexible electronics.

Chapter 5 Summary and future work

5.1 Summary

The widespread use of high efficiency III–V multi-junction solar cells is limited by the high cost and brittleness of Ge wafers that are used as bottom templates for epitaxial GaAs growth. This work aimed to achieve epitaxial growth of Ge and Si films on inexpensive and flexible substrates by roll-to-roll continuous deposition in order to provide an affordable and scalable bottom template. These single-crystalline-like Si and Ge thin films on metal substrates can also be utilized in high mobility TFTs well beyond the realm of current TFTs based on amorphous silicon and organic materials.

The strategy of "seed and epitaxy" was employed for epitaxial growth of Ge and Si films. It consists of an initial growth of biaxially-textured seed layer on a flexible non-crystalline substrate by ion beam assisted deposition (IBAD) and a subsequent deposition of lattice and thermallymatched epitaxial layers.

The biaxially-textured MgO seed layer on metallic substrate was first developed by using IBAD. The process factors including the substrate surface roughness, assist ion beam angle, assist ion beam current (I_c) and voltage (I_v), and ion exposure time were systematically investigated to optimize IBAD MgO texture. The optimized growth condition for IBAD MgO is $I_c = 80$ mA and $I_v = 900$ V for ion exposure time of 80 s at assist beam angle of 45°. A homo-MgO was then deposited on IBAD-MgO to check the film texture by XRD. Both an out-of-plane texture of 2.2° and an in-plane texture spread of 6.2° confirm the biaxial texture growth of homo-MgO on flexible Hastelloy. To eliminate the metallic element diffusion from the metal substrate to the semiconductor active layer, the biaxially-textured MgO was also designed and grown on flexible glass and YSZ at the IBAD condition optimized on metal substrate. The resulting homo-MgO film is highly oriented along (001) direction with narrow spread of out-of-plane (3.1°) and in-plane (8.3°) textures on flexible glass substrate.

Due to large lattice mismatch between the MgO (4.21 Å) and Ge (5.66 Å), multiple oxide transition buffer layers (LaMnO₃ and CeO₂) are required to achieve the Ge epitaxy. These layers could potentially result in impure elements that diffuse into Ge active layer and deteriorate the device performance. In order to eliminate the element diffusion from both substrate and multiple buffer layers, a thin biaxially-textured CeO₂ (111) was developed at a very fast IBAD deposition rate on a flexible glass tape for epitaxial Ge thin film growth. The tape-feeding speed of roll-to-roll process is ~50 cm/min for the deposition of ~10 nm-thick layer. A single-crystal-like *p*-type [111]-oriented Ge thin film was then successfully realized on flexible glass with a carrier concentration of ~3×10¹⁶ cm⁻³. A top-gate TFT based on this Ge thin film exhibits exceptional performance with on/off current of ~10⁶, a threshold voltage of ~1 V and a field-effect mobility of ~105 cm²/V·s.

The issue for [111]-oriented Ge / IBAD CeO₂ is the large in-plane misorientations of Ge film, resulting in a relative low mobility of 105 cm²/V·s compared with Ge wafer. In order to get a better texture in both out-of-plane and in-plane orientations, a highly-oriented buffer stack of "CeO₂/LaMnO₃/homo-MgO" was employed. Then biaxially-textured Ge films were deposited by medium frequency magnetron sputtering. The effect of deposition temperature and film thickness on the film texture, surface roughness and hall mobility was studied. The hall mobility of p-type Ge increases from 6.0 cm² V⁻¹ s⁻¹ to 903 cm² V⁻¹ s⁻¹ with an increase in deposition temperature from 500 °C to 850 °C. The monotonic increase of hall mobility with increasing deposition temperature is attributed to the increase in grain size and release in strain energy. The root mean square (RMS) surface roughness is found to be increase from 5 nm to 23 nm when substrate temperature is increased from 500 °C to 800 °C, then decrease to 13 nm at 850 °C, because the larger grains (1 µm) with fewer grain boundaries compensate for the undesirable structure-induced roughness. The hall mobility increases while surface roughness decreases until the film thickness reaches a critical thickness 1.25 µm due to the decrease in defect density of the Ge films. However, the high temperature process (850 °C) enhanced the diffusion of elements from the bottom layers, and so,

the lower temperature process with less ion bombarded surface is preferred for the high quality Ge growth.

Radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) was utilized to grow the highly-oriented epitaxial Ge thin film on sputtered Ge surface at a low process temperature (400 ~ 600 °C) for the purpose of reducing the diffusion issue while maintaining good Ge epitaxy. XRD results confirmed the single-crystalline-like Ge film growth with a sharp out-ofplane texture of 0.9° and an in-plane texture spread 3.3° . Full width at the half maximum values of the relevant peaks in the first-order Raman spectrum also indicate the highly crystallinity of Ge (3.5 cm^{-1}) thin films, comparable with that of Ge (3.4 cm^{-1}) wafer. TEM result shows that the defect density decreases towards the RF-PECVD Ge surface making the top surface relatively free of defects. This contributes to a higher carrier mobility (~1100 cm²/V.s) for the Ge film, about 1000 times higher than that of amorphous Ge. These epi-Ge templates were utilized to successfully grow n- or p-type single-crystalline GaAs thin films by metal organic chemical vapor deposition which have been used to fabricate solar cells.

Epi-Si thin film was grown on "Ge/CeO₂/LaMnO₃/MgO" buffer stacks by both magnetron co-sputtering (RF-MCS) and RF-PECVD. For the RF-MCS c-Si thin film, the effect of deposition temperature and Si_xGe_{1-x} graded layer on the film texture, crystallinity and surface morphology was studied. The n-Si film is highly oriented along (001) direction with a narrow spread in out-of-plane (1.16°) and in-plane (4.5°) texture with assistance of Si_xGe_{1-x} graded layer at 720 °C. Raman spectroscopy also revealed n-Si films with sharp Si TO mode peak (6.5 cm⁻¹), close to that of Si wafer (4.4 cm⁻¹). These films exhibit better texture, crystallinity and less defects compared to Si film grown without Si_xGe_{1-x} layer, However, the surface of Si film fabricated by magnetron sputtering is still too rough to make high quality flexible electronic devices. Also, the Si film carrier mobility can't be controlled due to low dopant (B or P) concentration resulting from low doping

level in the target. Therefore, the Si film with less defects, smoother surface, and controllable dopant concentration is needed for the device application.

In order to control the film doping concentration while maintaining or promoting highlyoriented Si epitaxial growth with less defect density, RF-PECVD was applied to fabricate high quality un-doped c-Si thin film. Different process temperatures were examined to understand temperature impacts on Si film orientation, crystallinity, roughness and growth rate. It was found 750 °C is the optimized temperature for the Si film with a single crystallographic orientation, smooth surface morphology, good adhesion to the buffer layer as well as the highest deposition rate. Then a detailed analysis, such as local texture and defects of the Si film grown at 750 °C was performed by the RHEED, EBSD and TEM. It was then found that a SiH₄ flow rate (40 sccm) and a PH₃ flow rate (0.4 sccm) with plasma power of 300 W are the optimal conditions for n-Si growth in PECVD process. The resulting n-type Si film is highly oriented along (004) direction with a narrow spread in out-of-plane (1.2°) and in-plane (2.5°) texture. Raman spectroscopy also revealed fully crystallized of n-Si films with sharp Si TO mode peak (4.2 cm⁻¹), comparable to Si wafer (3.6 cm^{-1}). The highest electron mobility of the n-Si films reached 230 cm^2/V -s. TEM analysis showed a film thickness of $2 \mu m$ and revealed only few defects at the top surface of the n-type Si film. High performance TFTs fabricated on single-crystalline-like n-Si channel exhibit an on/off ratio of $\sim 10^6$, a field-effect mobility of ~200 cm²/V-s, and a threshold voltage of -0.7V. These devices with superior performance open up a new era toward the next-generation flexible electronics and optoelectronics.

5.2 Future work

This work achieved single-crystalline-like Ge and Si films growth on inexpensive and flexible substrates by roll-to-roll continuous manufacturing based on IBAD, magnetron sputtering and RF-PECVD techniques. These single-crystalline-like n-Si and p-Ge thin films exhibiting high mobilities were successfully utilized to fabricate high performance TFTs, confirming the superior

electronic quality of the grown films. In order to develop more electronic and optoelectronic devices based on single-crystalline-like Si and Ge, and transfer the product from research lab to the market, some more work has to be emphasized in the future.

- (1) **Defect density reduction of Ge thin film by post laser annealing.** Although the Ge thin films fabricated by RF-PECVD exhibit less defects on the top surface, threading dislocations still exist due to the strain released at the lattice and thermal mismatched interface. Laser annealing is a promising solution to reduce the dislocation density (*165*), but it can cause the diffusion problems because our unique buffer structure. Dr. Yasuhiko Ishikawa used a near-infrared (NIR) laser to anneal the Ge film, which has two advantages: one is selective heating of Ge under the NIR irradiation $(1.0 1.5 \,\mu\text{m})$ due to the optical absorption limited in Ge, while the other one is the short annealing time (< 1 s), minimizing the thermal diffusion of atoms (*166*). However, the defect density reduced from $5 \times 10^8 \,\text{cm}^{-2}$ only to $2 \times 10^8 \,\text{cm}^{-2}$ after the NIR laser annealing. Dr. Ziheng Liu used a continuous wave (CW) laser to scan a Ge sample for melt and recrystallization, form a less defective Ge film (*167*). The threading dislocation density (TDD) of Ge films could be reduced in this work by three orders of magnitude to $10^6 \,\text{cm}^{-2}$. Both of approaches are worth to try to reduce the Ge TDD for fabrication of high efficiency III-V solar cells.
- (2) Strain study on Si and Ge thin films for flexible electronics. For flexible electronics, the effects of mechanical strain, including intrinsic strain, thermal expansion mismatch strain and bending strain, on materials property are crucial. Many researches have focused on the flexible device strain based on the polycrystalline and amorphous semiconductor materials (*168*), but none of them disclose the failure mechanics of single-crystalline-like thin film materials. It would be useful to determine the changes in texture and morphology of the thin films during the bending and in turn, on the effect on the device performance.

- (3) **Printed TFTs on Si and Ge thin films by roll-to-roll processing.** Fully printed integrated circuits were fabricated on single-crystalline-like Si and Ge thin films on metal substrates by a customized TFT printer in Dr. Chuan Wang's group (*169*). However, the device failed because of large leak current possibly due to the diffusion from the bottom layers and large pad size (W/L = 2000/100 μ m). The gravure printing in Dr. V. Subramanian's group (*170*) is a promising technique to increase the probability of successful device fabrication since the pad size can be controlled as small as ~5 μ m. Moreover, a gravure roll with sub-5 μ m feature size can lead to a highly-scaled and high-speed gravure printed transistors with low variability and low voltage operation.
- (4) Well (001)-oriented Ge growth on flexible glass substrate. For the purpose to eliminate the diffusion from the metal substrates, (111)-oriented Ge was fabricated on flexible glass with IBAD CeO₂ buffer layer. However, it shows relative low mobility due to large in-plane misorientations. A highly oriented Ge with both good out-of-plane and in-plane was achieved through the buffer stack of "CeO₂/LaMnO₃/homo-MgO" on flexible Hastelloy, but it will introduce metal impurities in the Ge film. Therefore, a combination of these two approaches might resolve metal diffusion issue and low mobility of Ge. It is critical to fabricate highly-oriented Ge on flexible glass based on existing highly-oriented "CeO₂/LaMnO₃/homo-MgO" buffer stack.
- (5) Study of alternative conductive buffer layers for epi-Ge. The existing buffers are oxides to texture the Si and Ge, which isolate the semiconductor and potential back contact layer (metal substrate). Therefore, a front contact by a few etching steps is needed. TiN is a good electrical conductor and its textured film has been achieved by IBAD (65-68), which enables the realization of a conductive buffer to provide a good back contact. It can thus simplify the design of multi-junction solar cell structure.

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