

Sum Frequency Generation Imaging of Alkanethiol-covered
Copper and Alloys: Spatial Distribution Analysis of
Monolayer Order

A Dissertation
Presented to
the Faculty of the Department of Chemistry
University of Houston

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

By
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May 2013

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Copper and Alloys: Spatial Distribution Analysis of
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Acknowledgements

I would like to thank the previous members of the group; Imee, Marjorie, Tren, and Cherry for helping me learn my way around the lab in the early clueless years of graduate school. Special thanks to my lab roomies in the Baldelli Lab: Joon Hee, Jack, and Emma. They made my research years in the lab less boring than usual.

To all of the present and past UofH students that I had the pleasure to enjoy my graduate school years with: Nissa, Lette, Uriel, Marlon, Rads, Dru, Gino, and Allan. To the inseparable duo (Jane and Imee), I thank you for all the great advices and friendship. To the Jacob family (Jack, Noemi, and Jaemi), thanks for being the best roomies. I would like to convey a huge thank you to my best friend Arthur, you rock! Kuya Mike and Kuya Willie for being the best off-campus hangout pals.

My special thanks to Dr. Steven Baldelli for the guidance and support throughout this endeavor. Thanks for imparting your valuable knowledge and never-ending passion for Science.

Last, but certainly not the least; I dedicate this work to my family. Tatay and Mama. William and Tinay. The constant encouragement and support from my family made me stronger to achieve my goals and aspirations in life. To my nieces (Fiona and Eida), the new addition to the family, I hope to see you soon. God bless my family and loved ones.

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Abstract

The utilization of the sum frequency generation imaging microscope (SFGIM) to study heterogeneous samples of alkanethiol-covered reactive metals such as Cu and brass was demonstrated in this dissertation. This nonlinear optical microscope provides a spatial distribution overview of the surface as a description of conformation and orientation of these molecules at the interface. In the first study of this dissertation, the length scale dependence of the spatial distribution analysis of the SFGIM technique has been analyzed to provide a comprehensive evaluation of its ability of revealing hidden domains of monolayer defects from averaged SFG signals. By constructing maps from regions-of-interest (ROIs) of different length scales, measuring from 5 to 1000 μm , two-dimensional localized domains of defects are identified to contain populations of less-ordered monolayers. By generating the tilt angle distributions of the scaled ROIs, SFGIM determines the experimental mean orientation, θ , and distribution width, σ_0 , as dictated by the SFGIM resolution limit.

The capability of SFGIM in monitoring surface reactions was demonstrated by defining changes in the monolayer order as an effect of oxide growth on alkanethiol-covered copper. The spontaneous atmospheric oxidation of Cu was observed as a change in the nonresonant phase response of SFG spectral lineshapes obtained from the SFGIM setup (1064 nm). With the growth of the oxidized film, the changes in the methyl tilt orientation are spatially correlated to the shifts in the nonresonant phase. Regions with the most concentration of reduced surface Cu registered as surface domains with lower gauche defect signals and well-oriented molecules.

The remarkable advantage of SFGIM against averaged SFG spectroscopy was demonstrated in its ability to spatially correlate the local structural behavior of interfacial molecules in response to the local physical properties of the surface. The heterogeneous local spatial kinetics was evaluated to have a spatial effect on gauche defect formations. Several experiments were performed to further test the imaging microscope for its capability in characterizing monolayer order on various metals such as gold, silver, copper, and brass in order to exploit its full potential in analyzing surface reactions, particularly atmospheric oxidation.

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Chapter 1: Introduction

For most studies in surface chemistry that utilize vibrational spectroscopy, the surfaces is often assumed to be homogeneous since most of these techniques are spatially averaging; with this methodological limitation, recent improvements on surface analytical techniques were developed with the ability to determine the structure of surface molecules from macroscopic (millimeters) down to atomic level (Ångströms). These innovations in surface techniques have led to new discoveries that the surface is actually more heterogeneously structured than what was initially presumed.

The heterogeneity of a surface has a direct effect on the reactions at the interface. Surface reactions might be observed in the macroscopic scale, but when determined in microscopic length scales, the chemical reactivity is localized in the different regions-of-interest (ROIs) on the surface. Therefore, there is a tendency in most surface studies to analyze the sample with the understanding that the averaged signal of the macroscopic surface is a representative of each individual ROI.

In reality, the averaged spectroscopic signal recovered from the entire surface length scale often does not represent the individual ROIs; analyzing the sample from the different length scales (macroscopic to microscopic) will have different analytical results in terms of the characteristics of the molecules present on the surface. By averaging the spectroscopic signal from the entire surface, the chemical and physical properties are represented only by the most dominant molecules oriented on the surface. Hence, there is a loss of information on the properties of the less-favored molecules. (less favored in terms of the quantity, signal strength, and distribution across the surface).¹ Since these less-favored populations provide local information on possible defect sites, these ROIs are

needed to be accounted into the population distribution of the surface using a spatial distribution analysis.

Analyzing in the microscopic scale will give a two-dimensional overview of the monolayer order of the molecules adsorbed on defect-prone metal substrates (i.e. reactive metals such as Cu). The adsorbed molecules in these ROIs might have interesting contributions on the interpretation of the surface properties. The nature of the metals and the orientation of the molecules on the surface are important factors that influence these surface properties. The surface heterogeneity might be an outcome of an inherent property of the sample or surface defect from the sample preparation.

The evaluation of surface defects will have a great impact on different surface applications of adsorbed organic films such as corrosion inhibition, catalysis reactions, adhesion, and electronics. Therefore, a two-dimensional overview of the surface provides the spatial distribution of the molecules at the surface which will serve as a measure of its overall surface heterogeneity. Microscopic techniques with very high resolution, such as scanning probe techniques (SPM), identify the distribution of the molecules across the surface. These techniques do not provide a direct chemical identification of the molecules at the surface, but may provide the distribution information of the molecules across the surface (i.e. orientation and the domain concentration in an atomic scale). What makes Sum Frequency Generation Imaging Microscopy (SFGIM) unique is that it combines the advantage of the spatial resolution of a nonlinear optical microscope with the abundance of molecular information acquired from vibrational spectroscopy.

Several imaging techniques had been developed that possess the ability to study the monolayers on the surface that, independently, provide chemical, spatial, and temporal resolution. For example, atomic force microscopy (AFM) provides excellent spatial resolution; however, it lacks specific chemical information over the surface. Aside from these known methods, X-ray techniques which include X-ray photoemission electron microscopy and near-edge X-ray absorption fine structure have been used for providing surface contrast with good spatial resolution in evaluating surface with lithographic patterns.^{2, 3} However, these techniques lack the capability of directly probing the adsorbed molecules on the surface. Hence, there is a necessity to incorporate the ability of determining the local chemical environment of the molecules to provide a more fundamental view of interfacial chemistry.

Hence, vibrational spectroscopy provides a crucial contribution as a useful tool in studying the monolayer coverage and intermolecular interactions. Several spectroscopic techniques are used to provide chemical information of the molecules present on the surface such as IR, Raman, or High Resolution Electron Energy Loss Spectroscopy (HREELS). These techniques are beneficial because each technique has a specific role in characterizing the molecules adsorbed on the surface. But, on the other hand, these techniques are not interface specific such as Fourier Transform Infrared (FTIR) microscopy. FTIR spectroscopic/microscopic technique provides chemical information but it is not a surface-specific and monolayer-sensitive which are considered as the limiting factors for the purpose of imaging. The FTIR technique is also less suitable for imaging due to its inherent limitation in spatial resolution. Raman spectroscopic techniques also share this limitation of not being interface specific/sensitive. Lastly, HREELS is also

limited in terms of spectral resolution when probing adsorbed molecules on the surface.⁴ Thus, SFGIM is an excellent combination of spatial imaging and vibrational spectroscopy such that it probes and identifies the molecules at the interface spectrally, temporally, and spatially.

One of the main objectives of this study is to demonstrate the capability of the nonlinear optical microscope in providing a spatial distribution overview of monolayer-metal surfaces. First, a full-length study was performed to understand and obtain more description of the molecules in smaller domains by using different length scales.¹ Studying smaller domains on the surface brings forth a myriad of advantages. For example, these monolayer molecules are deposited on a well-polished or evaporated metal on a substrate with defects from impregnated particles from polishing, scratches, and foreign materials that compete with the solution-based molecules during deposition. The orientation of the absorbed molecules, whether well-ordered or not, has an effect on all the interactions that occur at the surface. The ability to obtain spatial and spectroscopic information of the interfacial molecules will then be applied to areas that will have a great benefit from having a two-dimensional overview of the deposited molecules at the surface such as self-assembled monolayers on metal substrates and adsorption on reactive surfaces.

SFGIM has provided an in situ method to observe the chemical contrast on a two-dimensional form based on the inherent vibrational spectrum of the molecules at the interface whether the molecules on the surface have different functional groups, orientations, stability, and heterogeneity. The microscope has the capability to locate the molecules on the surface and provide chemical identification based on the changes of the

vibrational spectrum. SFGIM is able to address some of these issues since it has a high interface specificity, submonolayer sensitivity, and chemical selectivity, and has spatial resolution of approximately of 2 microns.^{5, 6}

Within the recent years, the imaging microscope has been used to address some experiments that contribute to the fundamental views of surface chemistry. These studies include the initial catalysis/corrosion reactions (carbon monoxide on Pt and cyanide ions reacting on gold forming linearly bound CN⁻ ions and complex compounds); patterned microcontact-printed self-assembled monolayers (SAMs)⁷⁻⁹ on gold with variation in different terminal functional groups and chain lengths that affects the interpretation of chemical two-dimensional contrast; and the adsorbed octadecanethiol on mild steel and zinc surfaces to study the monolayer order which also includes the evaluation of the heterogeneity of the surface.^{5, 10}

With these earlier studies of the SFGIM, the realization of the microscope's ability to chemically identify and locate the adsorbed molecules on real sample surfaces (without the patterns) whether homogeneous or heterogeneous are investigated within the limit of the technique's resolution. These experiments are the pioneers that paved the way to studies on heterogeneously complex surface of reactive metals (copper, zinc, and brass) in addition to the complication of the strong nonresonant signals of these metal surfaces. Comparing the individual spatial distributions of the monolayer order of these metal surfaces is of prime importance in studying surface interactions (i.e. atmospheric corrosion) wherein changes in surface intermolecular environments are needed to be spatially mapped.

The SFGIM process of spatial mapping the monolayer properties involves a careful acquisition of nonlinear spectroscopic data. The spatial distribution of real, unpatterned surfaces (i.e. polished copper or brass) is quantitatively obtained by extracting the spectral data from each ROI. Then, the extracted data are plotted and fitted using a Mathematica program. Depending on the data analysis to be performed, the raw intensity values for each vibrational mode/stretch are obtained and analyzed by taking the ratios of the peak intensities recovered from the fitting analysis. For example, if the ratio of the methylene symmetric stretch and methyl symmetric stretch was taken from each ROI, the ratio is interpreted whether the monolayer formed was well-ordered or not. These ratios, as interpretation of gauche defects, are mapped back to their original ROI position to create a two-dimensional view of the distribution of the molecules across the surface. The chemical distribution is determined by presenting these measures of monolayer order in histograms. The interpretation of the statistical data determines the heterogeneity of a surface. Spatial correlations of different measures of monolayer order are carried out to visualize the local molecular interactions (i.e. the increase in local gauche defects translates to less oriented monolayers).

With the demonstration of SFGIM's capability to evaluate the surface heterogeneity of the reactive metal surface, the technique was utilized in studying an important topic in surface chemistry application: atmospheric corrosion. The atmospheric corrosion of metals and methods to inhibit it are two of the most important problems confronted in industry.^{11,}

¹² Exposure of metal surfaces to moisture or corrosive gases causes the metal to react and form oxidation products. The SFGIM techniques was previously employed in investigating the process of surface etching, a form of corrosion; for example, the chemical etching of

gold in the presence of CN^- wherein it attacks the Au atoms and removes it from the surface into the solution.⁵ Most metals, such as gold, silver, copper, zinc, and mild steel,^{10, 13-16} have been studied for occurrences of corrosion using SFG spectroscopy and microscopy, independently. The susceptibility of metal-SAMs surfaces to localized oxide formation is largely dependent on the surface composition and monolayer integrity. These determining factors can be independently evaluated by constructing spatial maps and parameter distributions of nonresonant phase, monolayer orientation and chain packing defects extracted from fitted SFGIM spectral data.

The ability of SFGIM as a spectroscopic imaging technique to characterize the local chemistry of surface oxidation is demonstrated by characterizing a copper surface with alkanethiol SAMs undergoing atmospheric oxidation. The densely packed monolayer of the alkanethiol self-assembled monolayers (SAMs) provides a low-permeability barrier that hinders access of oxidative elements in the air, specifically atmospheric oxygen and water, to the metal surface.¹⁷⁻¹⁹ Previous studies suggest that these molecules are effective against atmospheric and aqueous oxidation of metals, alkanethiols form protective coatings by forming thin (on the order of 2.0-nm thick), high-crystalline molecular barrier films on metals, alloys and semiconductors.^{20, 21} The SFGIM technique was involved in previous analyses making use of alkanethiol SAMs to study fundamental initial corrosion processes.^{5, 22} However, mapping the progression of initial corrosion on Cu-SAMs surface as measured by the SFG nonresonant phase shift and its spatial effect on monolayer order has not been explored with the SFGIM technique.

The nonresonant contribution of the metal surface to the vibrational spectra is unique to the surface electronic properties of the metal. The local spatial correlation of the optical nonresonant response of the metal surface to the conformation and orientation of the adsorbed molecules is impossible to evaluate using averaged vibrational spectroscopy. But with the aid of spectroscopic imaging, the ability to correlate the local changes in monolayer order with the shifts in the local electronic properties of the metal can be demonstrated. A unique visual interpretation of the surface is achieved through SFGIM wherein the local structural behavior of the adsorbed molecules is spatially correlated with the local physical properties of the surface. Spatial correlation is key to the complete understanding of the local chemistry of interfacial molecules in connection to its surface environment.

As an ultimate test of the ability of the spatial distribution analysis on characterizing the monolayer order on complex heterogeneous surface of alloys, metals surfaces with known domain patterns of heterogeneous compositions are initially investigated. The sample of Cu islands deposited on a Zn substrate was utilized as a model surface for brass alloys. By employing this experiment, the ability of SFGIM in defining monolayer orders as a function of composition heterogeneity was performed through a comparison between a surface with controlled (patterned) heterogeneity (binary Cu-Zn surface) and a surface with random (naturally occurring) heterogeneity of the brass alloy sample. The rationale of studying SAMs on reactive metals is to demonstrate the full potential of SFGIM in characterizing realistic chemical processes at the interface. The significance of all these experiments will soon lead to more complicated systems to learn more about the surface chemistry of the molecules adsorbed on the surface

and how the monolayer stability is affected by a change in the surface environment (both aqueous and non-aqueous). The opportunities of studying the adsorbed molecules in a two-dimensional perspective and understanding the nature of the adsorbed molecules (chemical and physical properties) are the primary advantages of the SFGIM technique in probing these reactive surfaces.

References

1. Santos, G.; Baldelli, S. *J. Phys. Chem. C* **2012**, *116*, 25874-25887.
2. Zharnikov, M.; Shaporenko, A.; Paul, A.; Golzhauser, A.; Scholl, A. *J. Phys. Chem. B* **2005**, *109*, 5168-5174.
3. Hu, W. S.; Tao, Y. T.; Hsu, Y. J.; Wei, D. H.; Wu, Y. S. *Langmuir* **2005**, *21*, 2260-2266.
4. Vickerman, J. C.; Gilmore, I. S., *Surface analysis: the principal techniques*. Wiley Online Library: 2009; Vol. 2.
5. Cimatu, K.; Baldelli, S. *J. Am. Chem. Soc.* **2008**, *130*, 8030-8037.
6. Cimatu, K. L. A., *Sum frequency generation imaging microscopy*. University of Houston: 2008.
7. Cimatu, K.; Baldelli, S. *J. Phys. Chem. B* **2006**, *110*, 1807-1813.
8. Cimatu, K.; Moore, H. J.; Barriet, D.; Chinwangso, P.; Lee, T. R.; Baldelli, S. *J. Phys. Chem. C* **2008**, *112*, 14529-14537.
9. Cimatu, K.; Moore, H. J.; Lee, T. R.; Baldelli, S. *J. Phys. Chem. C* **2007**, *111*, 11751-11755.

10. Hedberg, J.; Leygraf, C.; Cimatú, K.; Baldelli, S. *J. Phys. Chem. C* **2007**, *111*, 17587-17596.
11. Jones, D. A., *Principles and prevention of corrosion*. 2nd ed.; Prentice Hall: Upper Saddle River, NJ, 1996; p xvi, 572 p.
12. Leygraf, C., Graedel, T. , *Atmospheric Corrosion*, 1st ed. Wiley & Sons: New York: 2000.
13. Cimatú, K.; Baldelli, S. *J. Phys. Chem. C* **2007**, *111*, 7137-7143.
14. Hosseinpour, S.; Hedberg, J.; Baldelli, S.; Leygraf, C.; Johnson, M. *J. Phys. Chem. C* **2011**, *115*, 23871-23879.
15. Hedberg, J.; Henriquez, J.; Baldelli, S.; Johnson, C. M.; Leygraf, C. *J. Phys. Chem. C* **2009**, *113*, 2088-2095.
16. Hedberg, J.; Baldelli, S.; Leygraf, C. *J. Phys. Chem. C* **2009**, *113*, 6169-6173.
17. Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 9022-9028.
18. Jennings, G. K.; Yong, T.-H.; Munro, J. C.; Laibinis, P. E. *J. Am. Chem. Soc.* **2003**, *125*, 2950-2957.
19. Jennings, G. K.; Munro, J. C.; Yong, T.-H.; Laibinis, P. E. *Langmuir* **1998**, *14*, 6130-6139.
20. Sheen, C. W.; Shi, J. X.; Maartensson, J.; Parikh, A. N.; Allara, D. L. *J. Am. Chem. Soc.* **1992**, *114*, 1514-1515.
21. Schoer, J. K.; Ross, C. B.; Crooks, R. M.; Corbitt, T. S.; Hampden-Smith, M. J. *Langmuir* **2002**, *10*, 615-618.
22. Cimatú, K.; Baldelli, S. *J. Phys. Chem. C* **2007**, *111*, 7137-7143.

Chapter 2: Theory and Instrumentation

2.1. Nonlinear Optical Spectroscopy

To understand how SFG gives rise to a vibrational spectrum of molecules from the surface, its origins from nonlinear optical must be established. Almost all optical phenomena are governed by linear optics. In linear optics, an electric field of an ordinary (non-laser) light source is weak in an isotropic medium. Hence, when a weak electric field of light interacts with the molecule, the induced dipole, μ , is linearly proportional to the strength of the electric field, E , given by,

$$\mu = \mu_0 + \alpha E \quad 2-1$$

where μ_0 is the static dipole of the material and α is the polarizability of the electrons in the molecule. In a condensed phase, the dipole moment per volume, P , is conveniently used parameter. Thus, the induced polarization by the electric field is given as

$$P = P^{(0)} + \epsilon_0 \chi^{(1)} E \quad 2-2$$

where $\chi^{(1)}$ is the nonlinear susceptibility, considered as the macroscopic average of the polarizability, and ϵ_0 is the vacuum permittivity.^{1, 2} Since few materials have static polarization, $P^{(0)}$, the term is usually dropped and is no longer considered.

In contrast to this linear optical process, when a high intensity light, such as lasers, is source of electric field that interacts with the molecule, the magnitude of nonlinearity is increased and higher order terms must now be taken into account in the description of the induced polarization. The equation above becomes,

$$\mu = \mu^0 + \alpha E + \beta : EE + \gamma : EEE + \dots, \quad 2-3$$

where β and γ are the first- and second-order hyperpolarizabilities, respectively. The expression for polarization of the material now becomes,

$$P = P^{(1)} + P^{(2)} + P^{(3)} + \dots \quad 2-4$$

$$P = \epsilon_0 (\chi^{(1)} E + \chi^{(2)} : EE + \chi^{(3)} : EEE + \dots) \quad 2-5$$

where $\chi^{(2)}$ and $\chi^{(3)}$ are the second- and third-order nonlinear susceptibilities, respectively. In the presence of intense light from lasers, the electric fields match the electronic field of the molecules. The response of the electrons to the electric field is no longer harmonic and the higher order terms of the polarization are needed to be accounted into the equation.³⁻⁵

By using the definition of an electric field, $E = E_1 \cos \omega t$, is considered, the second-order polarization takes the form,

$$P^{(2)} = \epsilon_0 \chi^{(2)} : (E_1 \cos \omega t)^2 \quad 2-6$$

$$P^{(2)} = \frac{1}{2} \epsilon_0 \chi^{(2)} : E_1^2 (1 + \cos 2\omega t)^2 \quad 2-7$$

where ω is the frequency of the light. In this optical process, the dipole oscillates at twice the frequency of the incident light, 2ω , which is known as the second harmonic generation (SHG). The same argument applies to the origin of sum frequency generation, which employs two laser beams that have different frequencies, ω_1 and ω_2 ,

$$E = E_1 \cos \omega_1 t + E_2 \cos \omega_2 t \quad 2-8$$

Such that incorporating these two frequencies the expression for $P^{(2)}$ would have following form,

$$P^{(2)} = \frac{1}{2} \epsilon_0 \chi^{(2)} : (E_1 \cos \omega_1 t + E_2 \cos \omega_2 t)^2 \quad 2-9$$

Applying the corresponding trigonometric identities,

$$P^{(2)} = \frac{1}{2} \epsilon_0 \chi^{(2)} : E_1 E_2 [\cos(\omega_1 + \omega_2)t + (\omega_1 - \omega_2)t]^2 \quad 2-10$$

The electric dipole, induced from these two incident fields, oscillates at the sum, $\omega_1 + \omega_2$, and difference, $\omega_1 - \omega_2$, frequencies. These optical processes are known as sum frequency generation (SFG) and the difference frequency generation (DFG), respectively.^{3, 4, 6} In contrast to the linear processes such as Raleigh and Raman scattering, the nonlinear emission is coherent and directional.

2. 2. SFG Background

A pulsed laser which provides high energy output is required to observe the second-order nonlinear process of sum frequency generation spectroscopy. This process involves the sum of two beams to generate a third beam at a specific wavelength and polarization angle.⁵ The spatial and temporal overlap of the 1064 nm beam and tunable infrared beam generates the sum frequency generation (SFG) signal.

A laser which generates a fundamental 1064 nm beam pumps an optical parametric generation/amplification (OPG/OPA) system. This system converts the fundamental beam to 532 nm and tunable IR beams. For the microscope set up, the fundamental beam was used instead of the 532 nm beam. The reason for utilizing 1064

nm beam are due to the inherent sensitivity of the imaging detection to near-IR frequencies.⁷ The beams pass through a series of different optics where the two beams, finally, overlap at the surface. After overlapping, the coherent SFG signal is directed towards the detection system which is composed of a telescope, diffraction grating, microscope, and a charge-coupled device (CCD) camera.

As a surface technique used since the 1980s, SFG spectroscopy has evolved and has become a very effective method in obtaining the vibrational spectrum of different molecules at the interface.⁵ Since SFG is a nonlinear surface-sensitive process, the signal is generated most efficiently if no inversion symmetry property exists on the system under study. Most of the time, the inversion symmetry exists at the bulk because the system is isotropic and since the interface is present in between two regions which are identified (i.e. air-liquid, solid-liquid interfaces, etc.), these regions are considered non-isotropic.

In Figure 2-1, the SFG process involves the overlap of two pulsed laser beams at the same time and space to emit and generate the SFG signal. As the IR is tuned, the SFG intensity is enhanced since the IR laser is now in resonance with a specific vibrational mode of the sample at the interface. Thus, plotting the SFG intensity as a function of IR.⁸ SFG light is generated by the sum of two frequencies, fixed 1064 nm pump beam and a tunable infrared beam, which spatially and temporally overlap at the interface.

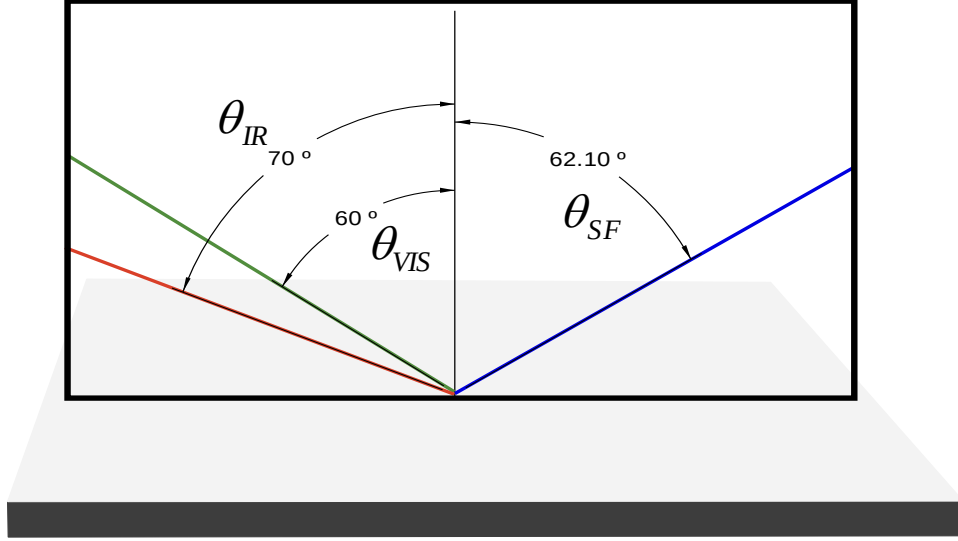


Figure 2-1. The schematic diagram of overlapping beam geometry of SFGIM on the surface: the fixed 1064 nm beam (green) and tunable infrared beam (red), and the sum frequency generation beam (blue).

Hence, the second-order induced polarization for the SFG is proportional to the second-order nonlinear susceptibility and the electric fields of the incident beams, shown as

$$P^{(2)} = \epsilon_0 \chi^{(2)} E_{1064\text{nm}} E_{\text{IR}} \quad 2-11$$

Based on the conservation of momentum, it has to be noted that the two laser beams are co-propagating along the plane of incidence and the emitted SFG signal at a specific angle is directional and coherent. This coherence pertains to the phase-matching conditions and shown as

$$n_{\text{SF}} k_{\text{SF}} \sin \theta_{\text{SF}} = n_{\text{VIS}} k_{\text{VIS}} \sin \theta_{\text{VIS}} + n_{\text{IR}} k_{\text{IR}} \sin \theta_{\text{IR}} \quad 2-12$$

where n is the refractive index, k is the wave vector for each beam, and θ are corresponding angles against the surface normal.

The SFG intensity is directly proportional to the square of the induced polarization such that

$$I_{\text{SFG}} \propto |P_{\text{SFG}}^{(2)}|^2 \propto |\chi_{\text{eff}}^{(2)}|^2 I_{1064\text{nm}} I_{\text{IR}} \quad 2-13$$

where the effective susceptibility is composed of a resonant susceptibility, due to the molecules at the interface, and the nonresonant susceptibility, due to the metal substrate, as shown in Figure 2-2. If the dielectric materials are used instead of the metal substrates, the nonresonant susceptibility is almost negligible compared to the resonant susceptibility intensity values. Thus, for dielectric materials, the SFG intensity is entirely dominated by resonant susceptibility.

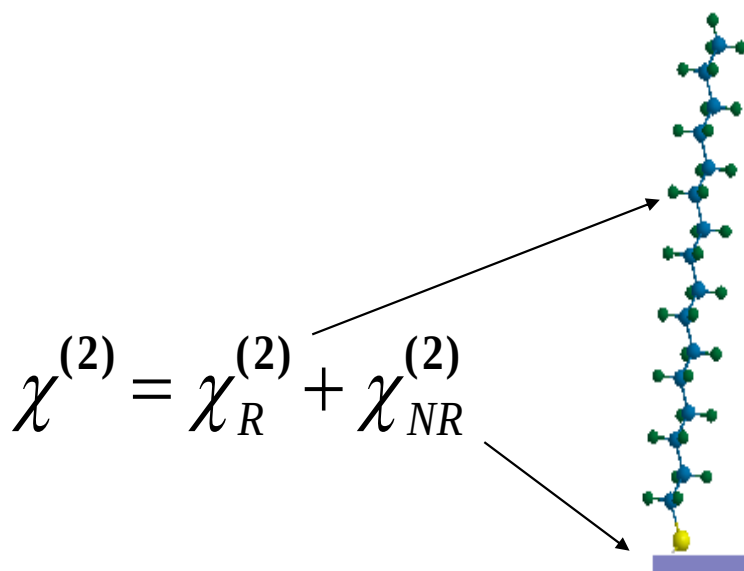


Figure 2-2. An illustration of an alkanethiol molecule on a metal surface.

The vibrational molecular information of the interface is contained in the second-order nonlinear resonant susceptibility as written

$$\chi_R^{(2)} = \sum_q \frac{N \langle \beta^{(2)} \rangle}{\omega_q - \omega_{\text{IR}} - i\Gamma} \quad 2-14$$

As the IR laser frequency approaches any of the q^{th} vibrational modes of the molecules at the interface, the SFG intensity will be resonantly enhanced. Thus, plotting the SFG intensity as a function of the IR wavenumber yields a vibrational spectrum which will either have a peak or a dip that presents the present resonant modes.^{3, 9, 10}

The combination of both resonant and nonresonant signals is known to be a complex quantity. The total SFG signal greatly depends on the relative phases of the two complex susceptibilities. In contrast to incoherent spectroscopic techniques, a coherent process such as SFG carries information in terms of magnitude and phase such that the summation is shown as

$$I_{\text{SFG}} \propto |\chi_{\text{eff}}^{(2)}|^2 = \left| \chi_{\text{R,ijk}}^{(2)} e^{i\delta(\omega_{\text{IR}})} + \chi_{\text{NR,ijk}}^{(2)} e^{i\varepsilon} \right|^2 \quad 2-15$$

where the $\delta(\omega_{\text{IR}})$ is the resonant phase dependent on the IR frequency and ε is referred to as the fixed nonresonant phase which is taken as invariant with IR frequency and dependent on the intrinsic properties of the metal, frequency/wavelength of the pump beam and the surface plasmon resonance.^{5, 11, 12} For dielectrics, this term is negligibly small such that it is not accounted into the SFG intensity equation. However, the magnitude of the nonresonant contribution is much higher for metal surfaces. The complication of the SFG spectral lineshape is essential quality of spectral data for ODT on metals and, hence, is needed to be expounded.

Thus, the total SFG light intensity from a metal surface may then be

$$I_{\text{SFG}} \propto |\chi_{\text{eff}}^{(2)}|^2 = \left| \chi_{\text{R,ijk}}^{(2)} e^{i\delta(\omega_{\text{IR}})} + \chi_{\text{NR,ijk}}^{(2)} e^{i\varepsilon} \right|^2 \quad 2-16$$

$$|\chi_{\text{eff}}^{(2)}|^2 = |\chi_{\text{R,ijk}}^{(2)}|^2 + |\chi_{\text{NR,ijk}}^{(2)}|^2 + 2|\chi_{\text{R,ijk}}^{(2)}||\chi_{\text{NR,ijk}}^{(2)}|\cos(\varepsilon - \delta(\omega_{\text{IR}})) \quad 2-17$$

The first two terms of susceptibilities remains positive in magnitude while the cross-term may have positive or negative value. Since the resonant factor and the nonresonant background are complex susceptibilities, the convolution of the two factors dictate the lineshape of the SFG spectrum. A positive cross-term creates a constructive interference; thus, giving rise to a peak. On the other hand, a negative cross-term generates a destructive interference which gives rise to a dip. Therefore, the relative phase difference in the cross-term between the two susceptibilities may give rise to peaks, dips or semi-interference peaks or dips between the two complex quantities. The resonant derivative line shapes are also known to depend on the properties of the metal substrate and the polar orientation of the molecules at the interface.^{4, 13} From the expression for $\chi^{(2)}$, it is expected for it to have Lorentzian peak shape (equation 2-14) as a function of IR frequency. In reality, the spectra are complicated by the nonlinear optical response of the metal surface as seen from the convolution of the crossterm in equation 2-17.

To simulate the effect of the nonresonant signal, the following equation used for the spectral fitting was applied to a theoretical vibrational mode in resonance at 2900 cm⁻¹:

$$I_{SFG} \propto \left| \sum_q \frac{A_R}{\omega_q - \omega_{IR} - i\Gamma} + A_{NR} e^{ip} \right|^2 \quad 2-18$$

Where A_R and A_{NR} are the amplitudes of the resonant and nonresonant components of the effective susceptibility $\chi_{eff}^{(2)}$ and p represents the relative nonresonant phase. As seen from Figure 2-3, the effects of the phase on the spectral lineshape is demonstrated wherein a resonance can be resolved as a peak, dip or derivative line.

SFG Intensity

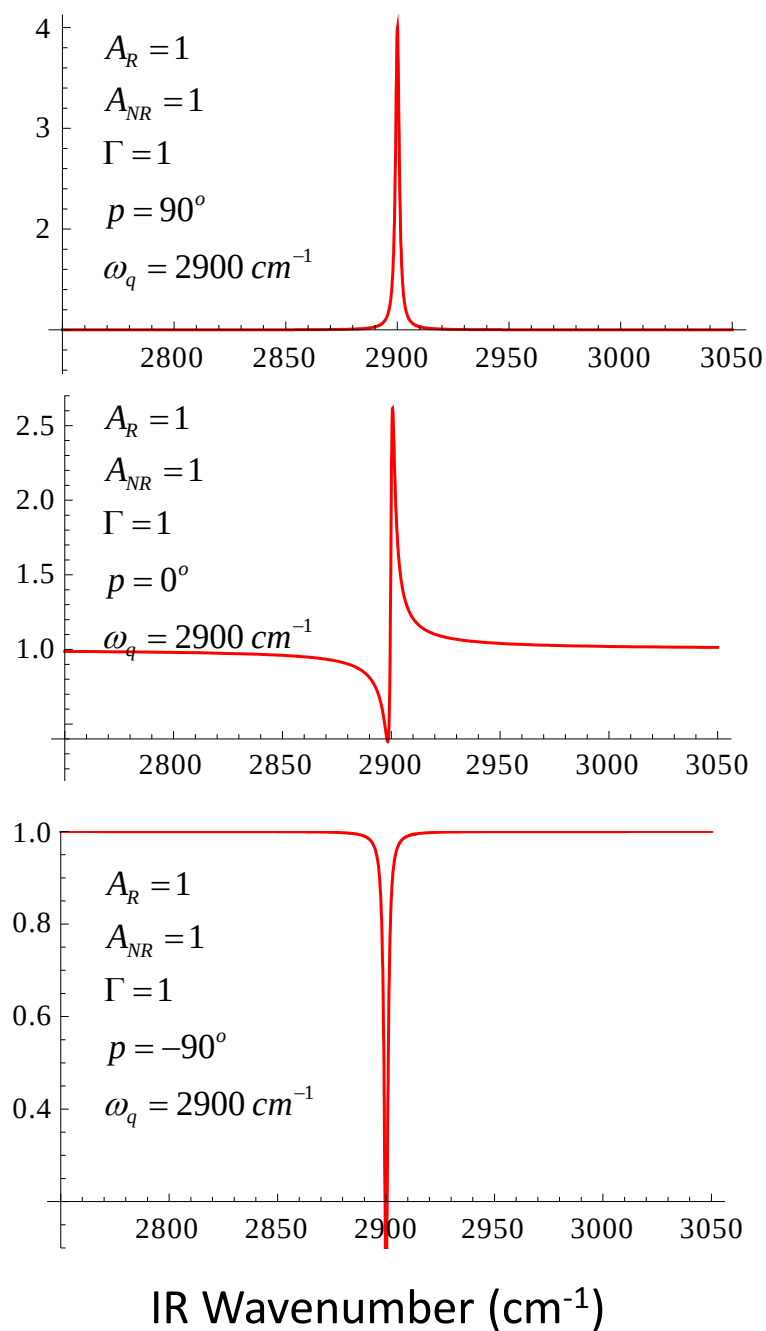


Figure 2-3. Simulation of SFG spectra using different relative nonresonant phase values.

Hence, in order to capture the effects of the interference of the nonresonant signal to each vibrational modes present in a molecule at a certain IR frequency range, the spectral data

obtained from metal surfaces must be fitted to an equation of the SFG intensity that accounts for both magnitude and relative phase of the nonresonant signal that resulted from the oscillations of the surface electrons of the metal.

To illustrate the spectral appearance of SFG, Figure 2-4 shows a spectrum of a monolayer of ODT adsorbed on different metals: Au, Cu and brass.

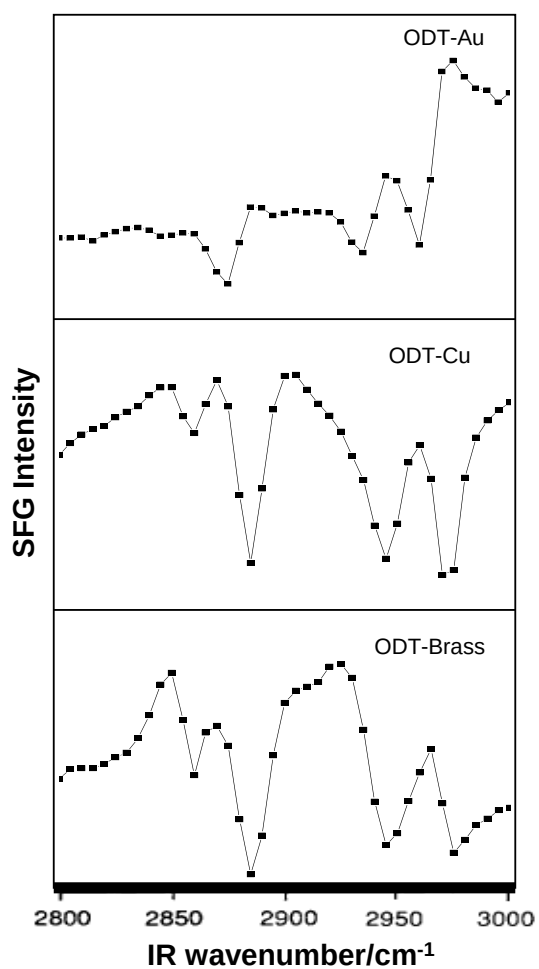


Figure 2-4. Illustrative SFG spectra of ODT on metal. The different appearances of these spectra are a consequence of the nonresonant background of the metal surface.

Each SFG spectrum has been fitted to Lorentzian lineshapes as shown in equation 2-18 using a spectral fitting program written in Mathematica code. This fitting process involves estimation of the initial values of all spectral parameters (for amplitude, peak widths, vibrational frequency, and relative phase) through spectral simulation similar to the procedure done in the results shown in Figure 2-3. It also requires setting the range of constraints for each spectral parameter. The optimization of the number of iterations needed to reach a good fit is also considered in the spectral fitting process. The procedural overview of the fitting process on SFGIM images is further explained in the instrumentation section while the vibrational assignments are discussed in Chapter 3.

2.3. Optical Instrumentation

The optical setup of the SFGIM technique consists of four main components: the fundamental laser, optical parametric generator/optical parametric amplifier (OPG/OPA), SFGIM instrumentation, and detection system. Each of these components will be explained in detail in the following sections.

2.3.1. Nd:YAG Laser

The acronym LASER stands for light amplification by stimulated emission of radiation. Typically common light sources release incoherent photons over a wide range of wavelengths. In contrast, a laser is an optical source which emits a coherent beam of photons. Laser light is typically near-monochromatic, consisting of a single wavelength, and emitted in a narrow beam.¹⁴⁻¹⁶

The laser used to create the fundamental beam is the most critical component to a sum frequency generation spectroscopic technique. The fundamental beam from the laser is used to generate both the fixed 1064nm pump beam and the tunable infrared beams. Unstable energy outputs of the fundamental beam or a misshapen beam profile are typical problems that adversely affect the rest of the laser experiments. High energy pulsed lasers use components on the cutting edge of optics and electronics, most of which are fragile and expensive. A strong knowledge of how to maintain and troubleshoot problems with the laser is a necessity in order to perform SFG experiments. This section will include a detailed description of the laser used for all SFG experiments. The imaging experiments require specific laser conditions such as: (1) Laser stability for both 1064nm and IR beams and (2) good beam size and shape.

In all of the SFG experiments, the laser system employed was an active/passive mode-locked Q-switched Nd:YAG laser (Ekspla, PL2250/20) with a fundamental output of 1064 nm, generating pulses of 20-30 picoseconds. The repetition rate of the laser is 20 Hz and the maximum output energy per pulse is approximately 40 mJ. The Nd:YAG is an acronym for neodymium-doped yttrium aluminum garnet ($\text{Nd:Y}_3\text{Al}_5\text{O}_{12}$).

The laser is comprised of three functional parts: (1) the master oscillator; (2) the regenerative amplifier; and (3) the power amplifier. The optical scheme of the Ekspla Nd:YAG laser is shown in Figure 2-5. The laser also includes a cooling unit, power supply and a remote control unit.

The master oscillator is a diode pumped passively mode-locked which uses an Nd:YVO₄ laser material. Mode-locking is achieved by means of a saturable absorber.

The master oscillator has two output beams. One of the output beams is employed for seeding of the regenerative amplifier. The second beam enters a photo-detector (labeled PHD1 in Figure 2-5). This photodetector transforms this light to electrical signal and delivers it to the synchronization card, producing synchronization pulses for the Pockels cell and TRAIN signals for system monitoring (i.e. energy stability). A Pockels cell is an electro-optical device in which the birefringence is modified under the influence of applied voltage. This allows for quick switching (nanosecond time scales) of the polarization state of the light in the cavity by applying voltage across a Pockels cell.

Regenerative amplifier is based on a diode pumped Nd:YAG rod (labeled R2). Mirrors M8 and M9 act as cavity mirrors of the regenerative amplifier while mirrors M10-M12 serve as retro-reflectors which improves the long-term stability of the cavity. The polarizer (P4) and Pockels cell (PC1) feeds the pulse output of the oscillator into regenerative amplifier cavity and also generates an amplified pulse out of regenerative amplifier cavity.

A quarter-wave plate (QWP1) prevents regenerative amplifier from free-running and input pulse injection. When the oscillator pulse is injected, the voltage on PC1 is switched on rapidly trapping the beam inside the cavity. After 25-28 round trips, when pulse is amplified to maximum level, voltage on the PC1 is switched off and amplified pulse is dumped out of the regenerative amplifier cavity. The Faraday rotator (FR1), half wave plate (HWP2) and polarizer (P1) are used to prevent the pulse to proceed from the regenerative amplifier into the master oscillator and sending the amplified pulse to the power amplifier.

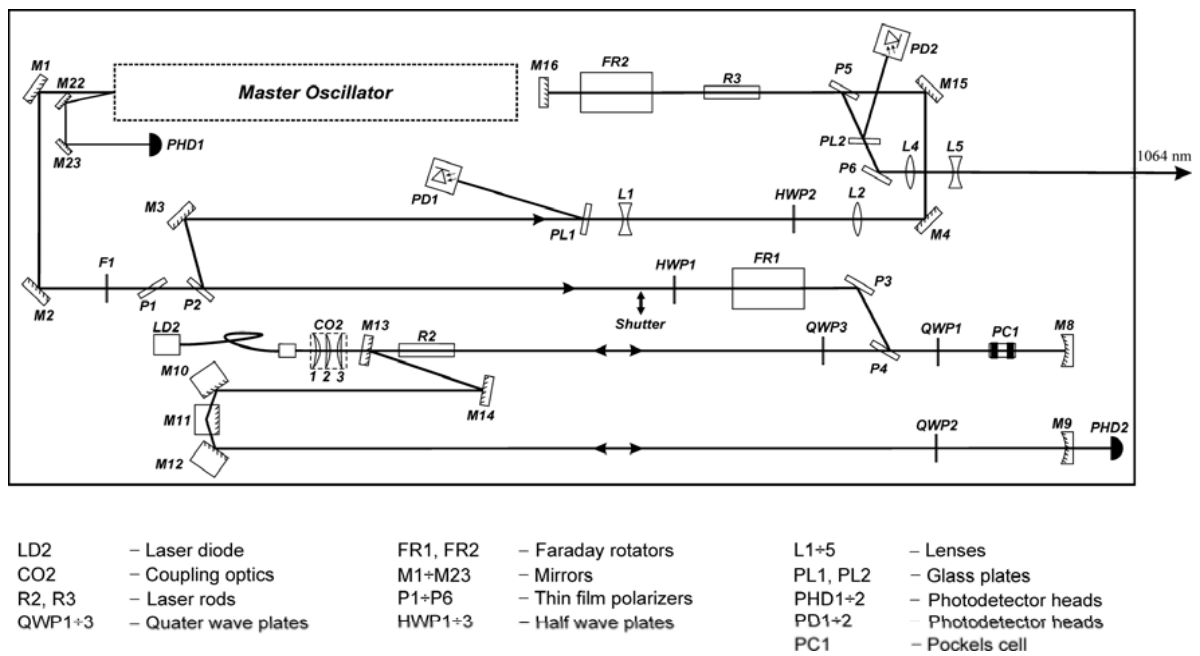
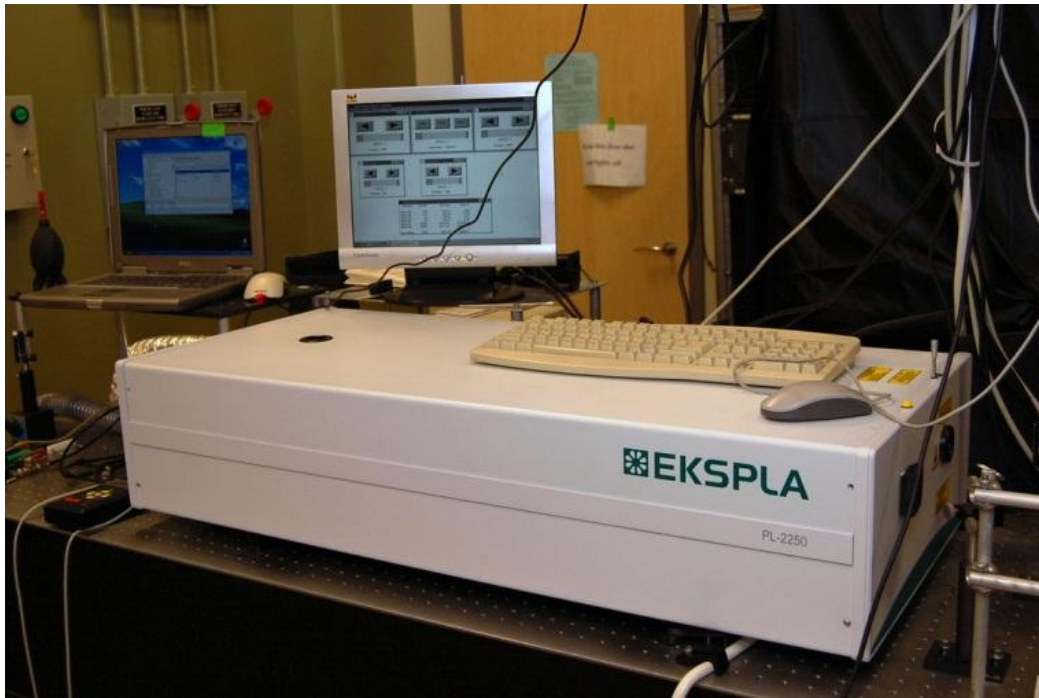


Figure 2-5. Photograph and optical scheme of the picosecond Nd:YAG laser.¹⁷

The power amplification stage makes use of a flash lamp pumped Nd:YAG rod (R3). To adjust the laser output energy without affecting the other radiation parameters, pulse amplification is controlled by varying the delay between the amplifier and regenerative amplifier flash lamps.

2.3.2. Optical Parametric Generator/Optical Parametric Amplifier

To convert the fundamental beam from the Nd:YAG laser to a fixed frequency visible beam and a tunable infrared beam, the optical parametric generator/optical parametric amplifier (OPG/OPA) is used.¹⁸ The OPG used in these experiments actually has two components, one which performs an optical parametric generation and an optical parametric amplification and another set of nonlinear crystals which performs another optical parametric generation (difference frequency generation). With optical parametric generation, the photon of an incident laser pulse (pump) is divided into two photons, the sum energy of which is equivalent to the energy of the pump photon, by a nonlinear optical crystal.

The photon of shorter wavelength generated by the down-conversion process is conventionally termed as the signal wave. The wavelengths of the two generated laser pulses, the signal and the idler, are determined by the phase matching condition, which is changed by the angle between the incident pump laser ray and the axes of the crystal. The wavelengths of the signal and the idler lights can, therefore, be tuned by changing the phase matching condition.¹⁸

If the created idler and signal passes back through the nonlinear crystals collinearly with the light of the same wavelength as the pump, a stronger output will be of the same wavelength as the signal and idler is acquired.¹⁸ This process is known as optical parametric amplification. A picture of the optical parametric generator/optical parametric amplifier is shown in Figure 2-16.

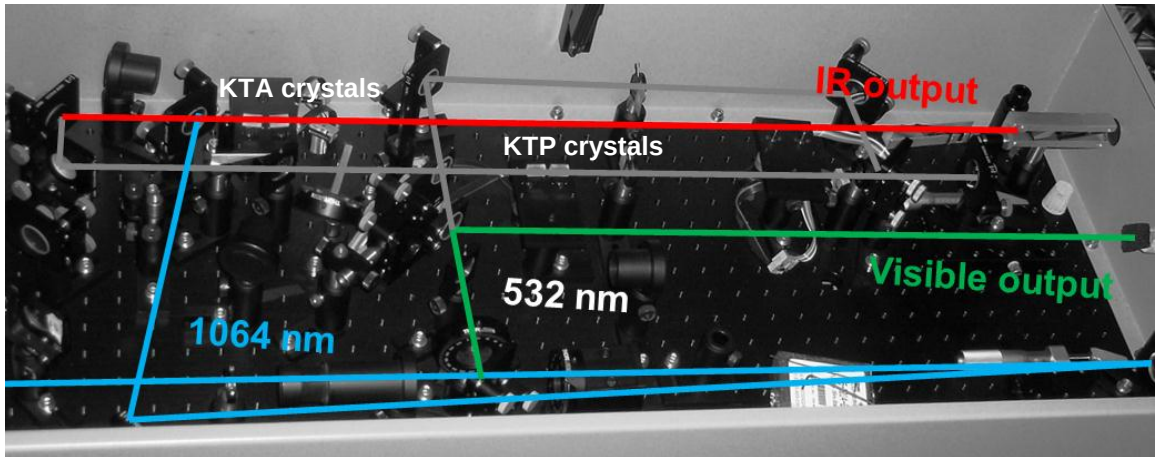


Figure 2-6. Photograph of optical parametric generator/amplifier

In the OPG, the fundamental is split into two separate beams using a beamsplitter. One of the beams is frequency doubled (2ω) in a nonlinear KTP crystal. Part of the frequency doubled beam (532nm) is used as the fixed visible component for conventional averaged SFG process (different from the 1064 nm used for the SFGIM setup). The other portion, the pump beam, is sent through two nonlinear KTP crystals (1 and 2) (Type II phasematching) whose angles are controlled by a set of dc motors. The resulting idler wave is amplified by an optical parametric amplification process. The resulting beam is combined with the original 1064 nm beam in two KTA crystals (3 and 4) (Type II phasematching) which are also controlled by dc motors. A difference frequency

conversion occurs which creates the mid-IR beam used for the SFG process. The mid-IR beam is filtered using germanium polarizers positioned at Brewster's angle to remove the idler and the 1064 nm beam. The resulting beam has a bandwidth of around 5 cm^{-1} and an average energy of 400-600 μJ per pulse ($2800\text{-}3300\text{ cm}^{-1}$). The frequency of the mid-IR beam is controlled by the position of the first KTP crystal. The position of the other three crystals is used to maximize the energy of the mid-IR beam in the frequency conversion process. All angle-tuned nonlinear crystals are moved independently by dc motors controlled by a computer program (LASERVISION).¹⁹

2.3.3. SFGIM Instrumentation

This section describes the sum frequency generation imaging microscope in terms of schematic diagrams as a general overview of its operation. A complete detailed list of the construction and development of SFGIM technique can be found from previous work by Cimatu.^{7, 20, 21} Figure 2-1 illustrates the basic diagram of the overlap of the fixed 1064 nm and tunable infrared beams at 60° and 70° , respectively, on the surface at the same time and space to generate the sum frequency generation (SFG) beam at 62.1° .

The schematic diagram of the general operation of the sum frequency generation imaging microscopy is shown in Figure 2-7. The Nd-YAG laser generates the fundamental 1064 nm beam while the OPG/OPA, which is also pumped by the 1064 nm beam, creates the tunable infrared beam. Then, both beams passed through two independent beam paths. The two beams overlapped at the surface and generated the coherent SFG beam. Then, the SFG beam passed through a 1:1 telescope and was

diffracted by the grating perpendicularly onto the plane of the microscope objective. Lastly, the SFG beam was imaged onto the Roper Scientific Intensified-CCD camera.

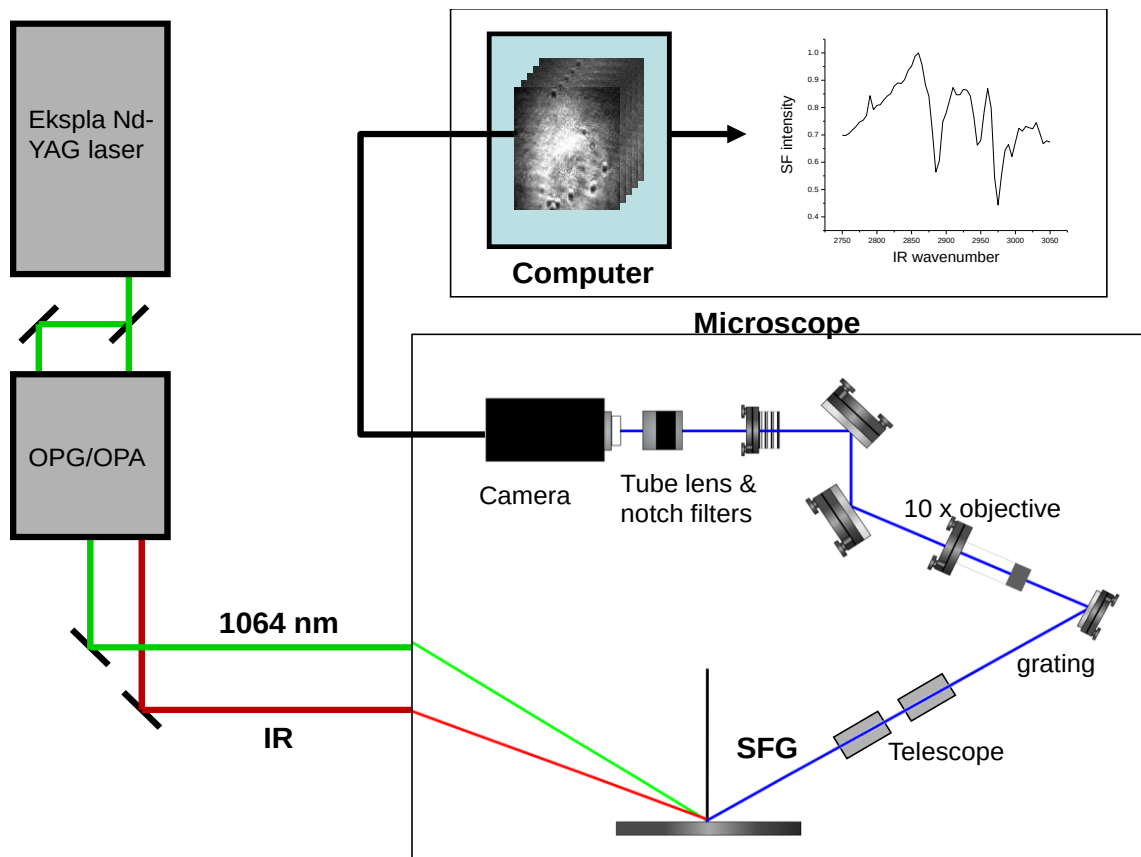


Figure 2-7. A schematic outline of the general operation of the sum frequency generation imaging microscopy

The controller attached to the PI-MAX CCD camera is also connected to the other three different attachments: 1) external triggering from the Laser, 2) power source, and 3) RS cable from the host computer. The controller was connected to the sync output of the laser as a source of external triggering, timing and gating. The gate width provided by the

CCD camera and the controller was adjusted according to the time delay of the sync by using the Winspec/32 software installed in the host computer.

The motors were tuned using the LaserVision control program in another computer. The base speed of the master control was adjusted depending on the acquisition time and speed of acquisition of the experiment. The rate of the motor was adjusted depending on the experiment to be performed or the number of accumulations to be acquired. Further details on experimental procedure can be found in the next section.

2.4. SFGIM Experimental Procedures

2.4.1. Alignment of the Samples

In aligning the sample with the microscope instrumentation, experimental goals such as good SFG signal, low noise, and minimal SFGIM image distortion are needed to be attained. Certain routine steps are needed to be kept in practice in order to have accurate and precise SFGIM measurements.

The alignment of the two input beams is of prime importance in order to obtain an optimal beam overlap on the surface and maintain the spectroscopic geometry of SFGIM. The probe beam 1064nm and the tunable IR beam are aligned towards the sample stage using an iris diaphragm that is attached on a magnetic base plate screwed onto the laser table. The SFG beam is aligned using a HeNe reference beam using the same iris diaphragm. Markings for all three beams are to be found on the table as references for two-point adjustments.

After the alignment of the beams, the sample stage is placed back to replace the iris diaphragm. A clean sample of evaporated gold on silicon wafer will be used as the reflective surface needed for alignment of the detection components of the SFGIM. Using the SFG HeNe reference beam, the gold film sample is aligned using the sample stage adjustments onto the two iris diaphragms directly after the 1:1 telescope. The diffraction grating is aligned towards beam axis of the 10x NIR objective.

After the proper alignment of the gold sample with the reference beam is achieved, the Pimax Controller and microchannel plate switches are both turned on. The Winspec program, a program that controls all the basic functions of the CCD camera, is launched from the host computer.

At the program prompt, the mode of operation is always set at Safe Mode to prevent oversaturation of the detector. The detector temperature is now then selected from the Setup tab with a temperature setting at -20° Celsius.

The overlap of the IR and 1064 beams is visually checked using the CCD detector as monitored from the Winspec program. By setting the mode of detection as spectroscopy mode, a Gaussian line profile will be the basis of alignment for the IR beam. From the setup pulser tab, the number of gates per exposure is set at 10 (see Figure 2-8). This means that accumulations of 10 per data acquisition will be employed while running in spectroscopy mode. From the main tab of the acquisition main menu, the CCD read-out needed to be changed in use region of interest (instead of use full chip). The gain settings in the intensifier tab needs to be set each time at 240 (see Figure 2-9).

The microscope is run using gate mode (instead of the shutter mode which is the initial setting at the startup of the program) for all SFGIM measurements.

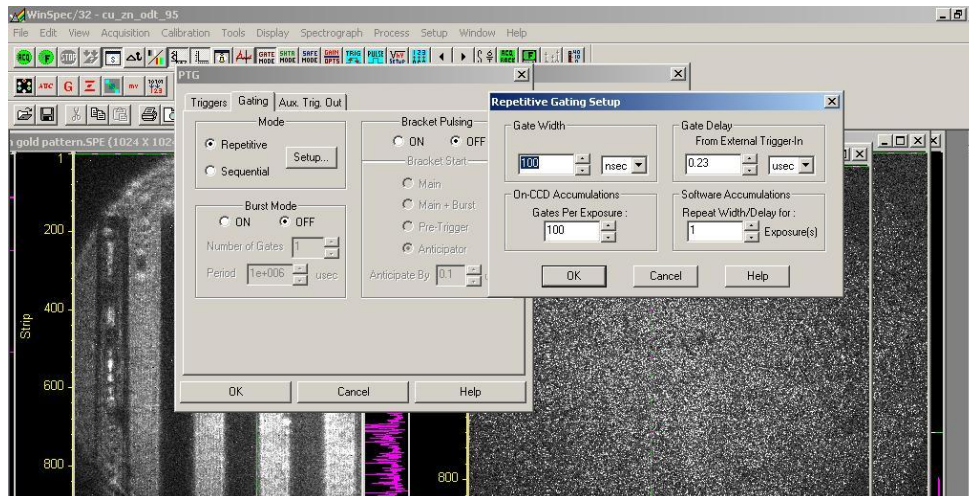


Figure 2-8. Repetitive gating setup at imaging mode for microscope alignment using gold film

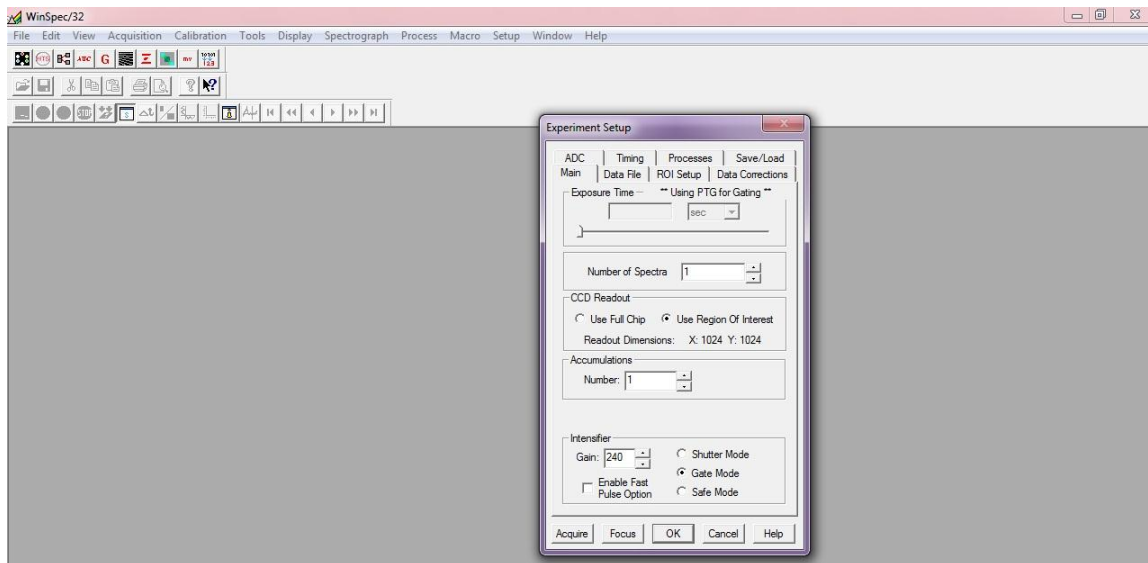


Figure 2-9. Main tab of the experiment setup dialog box where settings for CCD readout, gain and acquisition modes are located.

A file for the background signal corrections is required to be taken before any spectroscopic mode measurement. The acquire background tab from the acquisition main menu is used for this step. The IR beam mirror is adjusted to optimize the overlap of the input beams. While monitoring the Gaussian profile of the SFG output, signals are adjusted to reach its maximum intensity by slowly adjusting the knobs (both X and Y directions) of the IR beam mirror.

Once the overlap is optimized, the SFGIM setup is now ready to take images. The CCD read-out is now set to Use full chip and the mode of acquisition is now set to imaging. The On-CCD accumulations setting is changed from 10 to 100 for the first alignment with gold using Imaging mode. Another background correction is done by selecting acquire background tab at the acquisition main menu.

The focus tab is selected for a continuous acquisition at 10 accumulations. The beam profile is evaluated by performing necessary alignments of the 10x objective. This alignment is carried out by centering the beam spot onto the 1024 x 1024 CCD array which is closely monitored on the Winspec program of the host computer.

2.4.2. Procedures for SFGIM Measurements

When both spectroscopy and imaging mode alignments are done, the gold surface is now replaced with the actual sample. The actual sample can be aligned either by itself or with a SFG vacuum cell. The SFG cell (see Figure 2-10) is made partly of glass fittings and a metal case for optical windows (input side is a CaF_2 window and the output side is quartz window). The primary purpose of the cell is to protect reactive

samples (such Cu, Zn, Brass) from atmospheric conditions either by being purged with an inert gas (i.e. N₂) or by keeping it at high vacuum pressures (10^{-6} mm Hg) using a glass vacuum line that utilizes a thermal oil diffusion pump and mechanical backing pump.

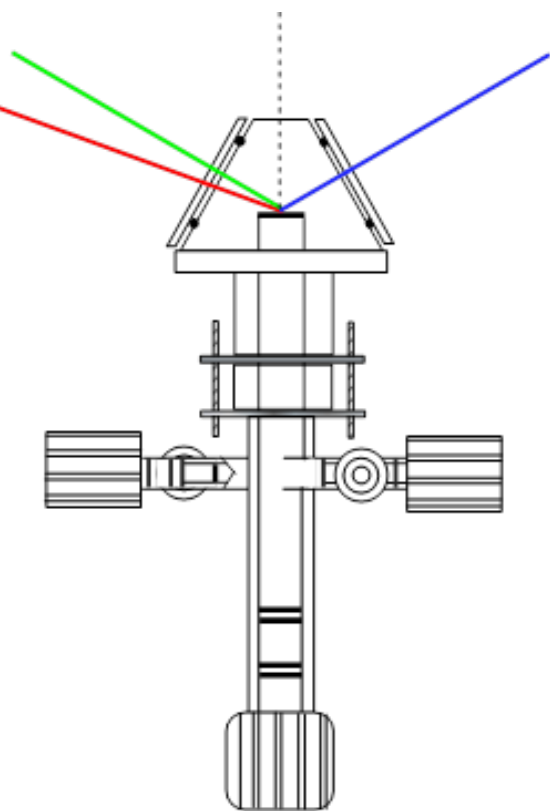


Figure 2-10. Photograph and schematic of the SFG vacuum cell

The sample stage was specifically designed to be able to hold the sample cell in place for convenient beam alignment. With the sample surface aligned with the SFG HeNe reference beam using the iris diaphragms located after the 10x objective, the microscope is now set for longer accumulation times. The number of accumulations is dependent on the SFG signal strengths of a particular sample. With low SFG signal

intensities, the accumulation time is made longer for each image acquisition. Typically for gold surfaces, an acquisition of 5000 accumulations per image is considered optimal to reach suitable spatial contrast.

When the gates per exposure is set at 5000 accumulations, images are needed to be collected every 5 cm^{-1} . For the case of octadecanethiol on metal surfaces, the typically IR frequency range is between 2750 and 3050 cm^{-1} which covers the methyl and methylene C-H vibrational modes.

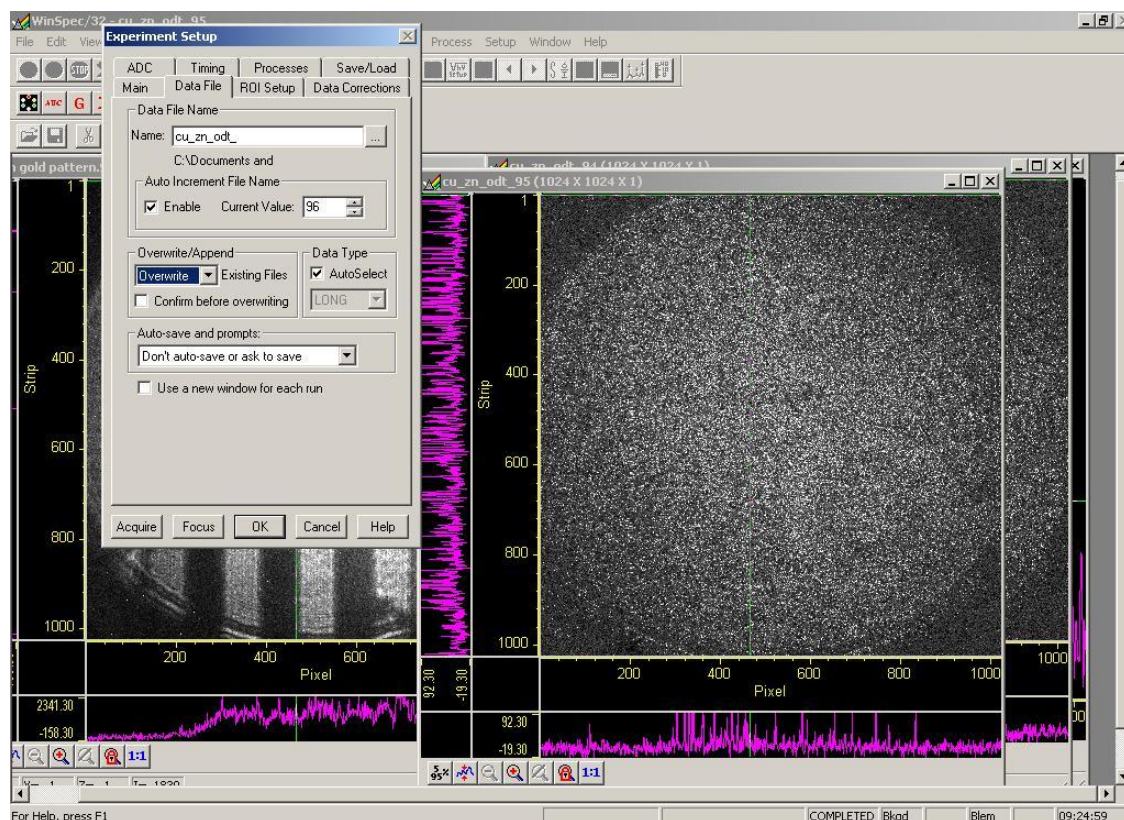


Figure 2-11. Winspec dialog box showing configurations for saving acquired images

From the acquisition tab of the main menu, the data file tab is accessed to enable saving of images with a corresponding file name. Using the auto increment file name (see Figure 2-11), a number can be assigned for each file. Numbering the files allows for the construction of an image stack using the ImageJ program after all sample measurements are collected.

A VisualBasic (VB) program named ProgNum is employed from the desktop of the host computer. This programs controls the number of images to be collected for a certain experiment. It automatically opens a Winspec acquisition window, saves the recorded image to a file with corresponding number assigned by auto increment, and closes the window to give way to the next image acquisition.

Using a LabView program on the LaserVision computer, the number of accumulations and range of IR frequencies are selected. This program controls the scan rate of the step motors of the LaserVision OPG/OPA system as the Winspec program simultaneously collect the images every 5 cm^{-1} .

2.4.3. Data Processing and Analysis

When all of the required images are collected for the entire IR frequency range, the images are stacked according to increasing frequency using the ImageJ program. Using a PlugIn called stack reverser, the order of the image stack is reversed. The image can be adjusted using the brightness/contrast tab.

In order to obtain an SFG spectra from certain ROIs on the SFGIM image, the PlugIn called spectral microscopy is utilized.²² A dialog box appears and asks for the

step size (5 cm^{-1}) and the upper limit of the frequency range (3050 cm^{-1}). By selecting an ROI on the image window, the SFG spectra can be obtained showing the averaged SFG intensities of the ROI for the range of IR frequencies. Using a macros program named JH.txt, spectral data from all ROIs of the entire SFGIM image stack are automatically saved. The length scale of the ROIs can be varied from 5×5 pixel to 100×100 pixel depending on the purpose of the data analysis. The macros program saves each spectral data into .txt files and can be accessed using a spectral fitting program written in Mathematica code. The spectral data are fitted using the Lorentzian form of equation 2-14. The fitted spectral parameters such as amplitudes, peak widths and phase can be used for surface mapping analysis such delta-function orientation analysis^{23, 24} or spatial mapping. The orientation analysis and mapping procedures are further discussed in Chapter 3. A schematic diagram of the spectrum extraction and surface mapping process is illustrated in Figure 2-12. Typical size of the SFGIM image being processed is 720×720 pixel. For ROIs with a size of 10×10 pixel each, a total of 5,184 SFG spectrum are needed to be fitted using the same initial values and constraints for all spectral parameters. Each vibrational assignment has three parameters: amplitude, peak width, and frequency. Hence for a spectrum that contains 6 resonant signals and 1 nonresonant signal (with magnitude and phase), a total of 20 parameters are to be obtained from each spectrum.

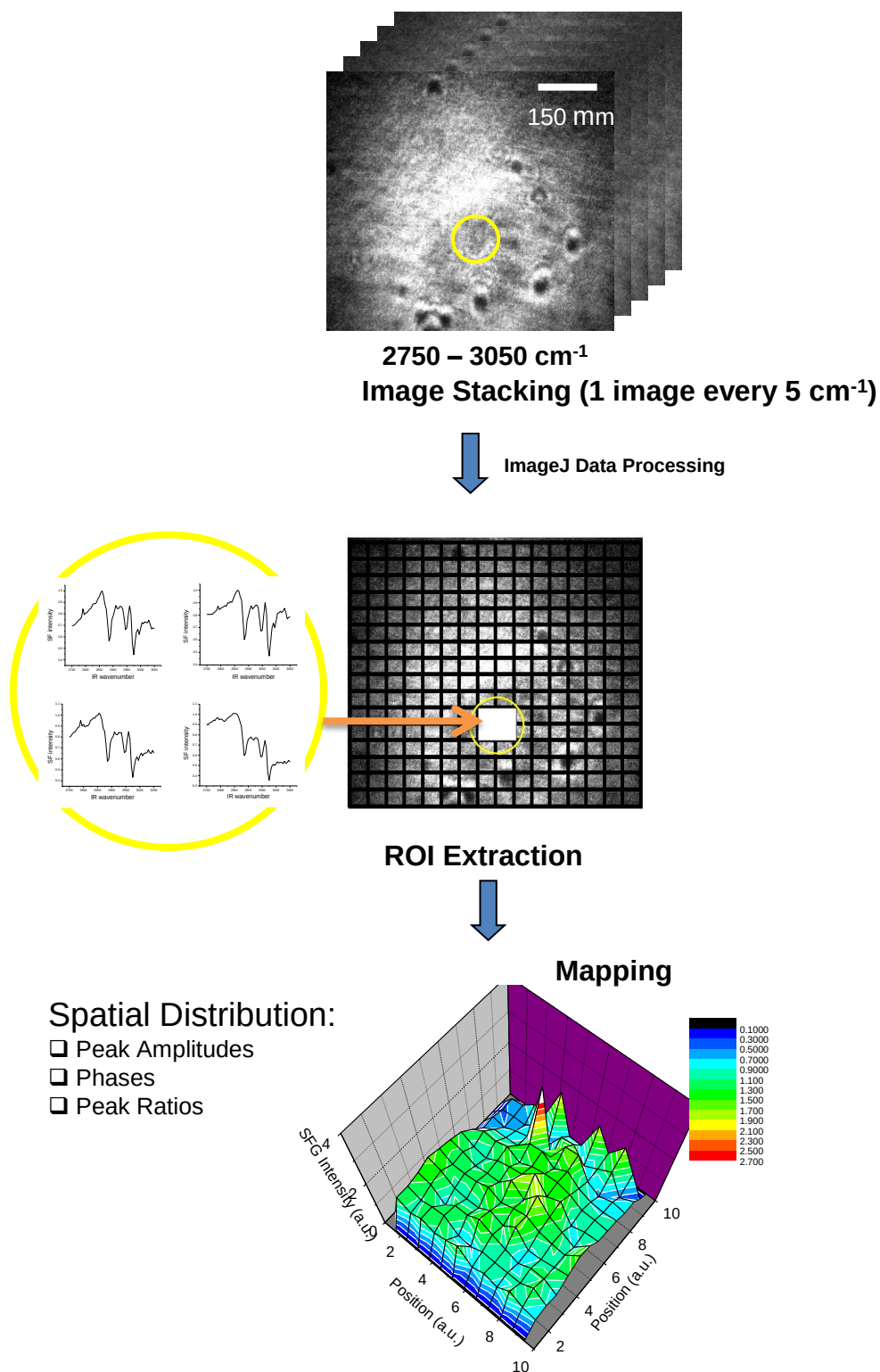


Figure 2-12. Schematic diagram of the data analysis and mapping procedure.

2.4.4. Resolution

The spatial resolution of the microscope was determined to be 2 microns.^{7, 20, 21, 25, 26} The routine calibration of spatial resolution of the camera is determined with the aid of striped patterns of microcontact-printed ODT on gold backfilled with methoxy-terminated thiols as shown in Figure 2-13.

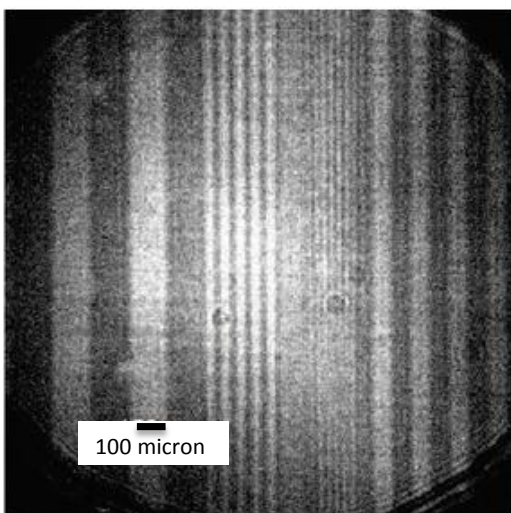
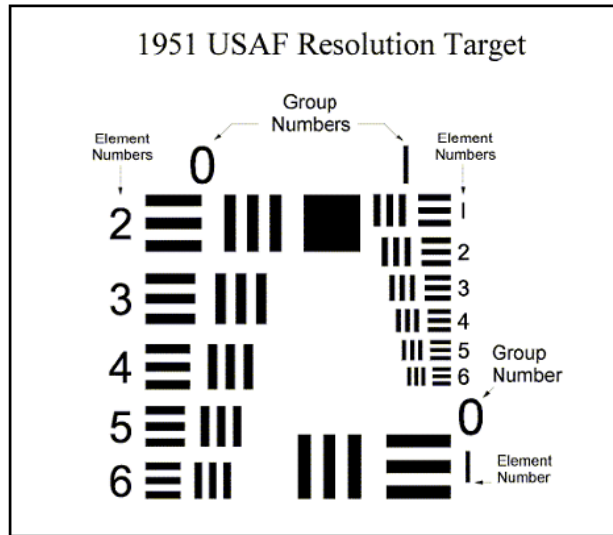


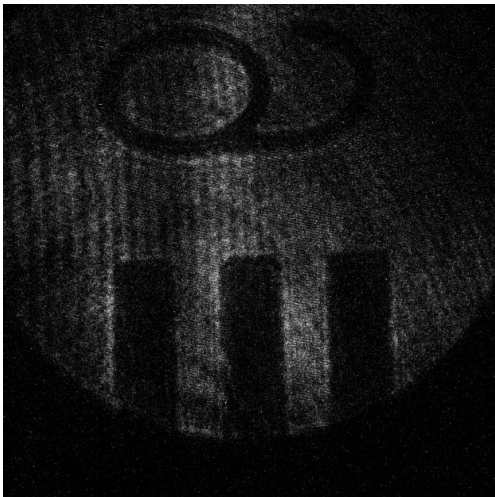
Figure 2-13. SFGIM image (showing features of 100 micron in length scale) of microcontact-printed ODT on gold with methoxy-terminated alkanethiol at 2875 cm^{-1} . Dark regions are ODT domains.

With the defined widths resolved using the microcontact-printed sample, the master pattern used for making the Polydimethylsiloxane (PDMS) stamps is compared side-to-side with the 1951 USAF Resolution target (Figure 2-14) using an optical microscope. Through this procedure, the field-of-view ($\sim 1\text{ mm}$) and length scale of the digital images can be calculated. The length scales of the striped patterns of the ODT

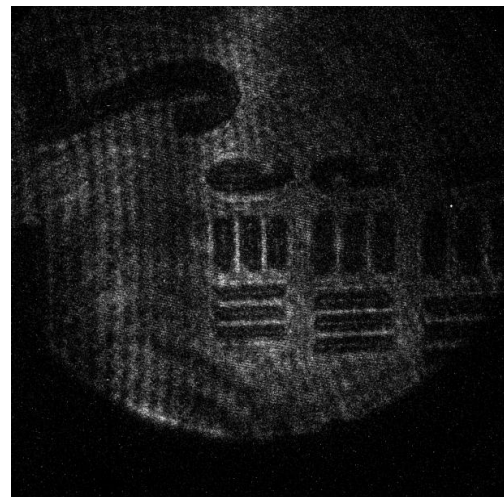
were determined showing that 1 pixel of the SFG image corresponds to 1.17 micron vertically and 0.92 micron horizontally.



1951 USAF Resolution Test Pattern - Group & Element Labels



Group 1 Element 6 (140 micron)



Group 3 Element 6 (35 micron)

Figure 2-14. Schematic (top) and SFGIM images (bottom) of 1951 USAF resolution test pattern

References

1. Superfine, R.; Huang, J. Y.; Shen, Y. R. *Phys. Rev. Lett.* **1991**, 66, 1066.
2. Shen, Y. R. *Nature (London)* **1989**, 337, 519-25.
3. Buck, M.; Himmelhaus, M. *J. Vac. Sci. Technol., A* **2001**, 19, 2717-2736.
4. Lambert, A. G.; Davies, P. B.; Neivandt, D. J. *Appl. Spectrosc. Rev.* **2005**, 40, 103-145.
5. Bain, C. D. *J. Chem. Soc., Faraday Trans.* **1995**, 91, 1281-96.
6. Shen, Y. R. *Annu. Rev. Phys. Chem.* **1989**, 40, 327-350.
7. Cimat, K. L. A., *Sum frequency generation imaging microscopy*. University of Houston: 2008.
8. Bain, C. D.; Davies, P. B.; Ong, T. H.; Ward, R. N.; Brown, M. A. *Langmuir* **1991**, 7, 1563-1566.
9. Himmelhaus, M.; Gauss, I.; Buck, M.; Eisert, F.; Woll, C.; Grunze, M. *J. Electron Spectrosc. Relat. Phenom.* **1998**, 92, 139-149.
10. Himmelhaus, M.; Eisert, F.; Buck, M.; Grunze, M. *J. Phys. Chem. B* **1999**, 104, 576-584.
11. Ward, R. N.; Duffy, D. C.; Davies, P. B.; Bain, C. D. *J. Phys. Chem.* **1994**, 98, 8536-8542.
12. Superfine, R.; Guyot-Sionnest, P.; Hunt, J. H.; Kao, C. T.; Shen, Y. R. *Surf. Sci.* **1988**, 200, L445-L450.
13. Wang, H.-F.; Gan, W.; Lu, R.; Rao, Y.; Wu, B.-H. *Int. Rev. Phys. Chem.* **2005**, 24, 191-256.

14. Demtroder, W., *Laser spectroscopy: basic concepts and instrumentation*. Springer: 2002.
15. Hecht, E.; Zajac, A. *Reading, Mass* **1974**, 301-305.
16. Hecht, E., *Optics*. Addison Wesley: 1987.
17. *Laser 2251A/20 Technical Description and User's Manual*. Ekspla: 2010.
18. Huang, J. Y.; Shen, Y. R., *Optical parametric generation and amplification*. CRC: 1995; Vol. 19.
19. *Operation and Maintenance Manual for Custom KTP/KTA/AgGaSe₂ OPG/OPA System*. LaserVision: 2001.
20. Cimatu, K.; Baldelli, S. *J. Am. Chem. Soc.* **2006**, *128*, 16016-16017.
21. Cimatu, K.; Baldelli, S. *J. Am. Chem. Soc.* **2008**, *130*, 8030-8037.
22. Daniels, M., Spectrum Extractor for Image J Program, 1.3. In National Institutes of Health: Bethesda, MD: 2004.
23. Rao, Y.; Tao, Y.-s.; Wang, H.-F. *J. Chem. Phys.* **2003**, *119*, 5226-5236.
24. Wang, J.; Paszti, Z.; Even, M. A.; Chen, Z. *J. Phys. Chem. B* **2004**, *108*, 3625-3632.
25. Cimatu, K.; Moore, H. J.; Lee, T. R.; Baldelli, S. *J. Phys. Chem. C* **2007**, *111*, 11751-11755.
26. Cimatu, K.; Moore, H. J.; Barriet, D.; Chinwangso, P.; Lee, T. R.; Baldelli, S. *J. Phys. Chem. C* **2008**, *112*, 14529-14537.

Chapter 3: Scale Dependence of the Orientation and Conformation Distribution Analysis of a Molecular Monolayer Using Sum Frequency Generation Imaging Microscopy

3.1. Introduction

Interfacial properties of thin organic films are of critical importance in many applications such as wettability, tribology, adhesion, and corrosion. These macroscopic physical processes are largely influenced by the molecular structure at the interface; hence, it is crucial to understand these interfacial materials at the molecular level. Spectroscopic determination of molecular order at surfaces provides abundant information into the nature and structure of surface systems. Most commonly used spectroscopic methods for orientation analysis include infrared absorption,¹⁻⁴ fluorescence,^{5, 6} linear dichroism using polarized infrared and UV-Vis light,⁷⁻⁹ second harmonic generation (SHG),^{10, 11} and sum frequency generation (SFG).^{12, 13} Connecting the relationship between the macroscopic orientation measurements and the molecular information by these spectroscopic techniques relies on averaged signal measurements over areas of a few hundred microns to a millimeter.

Conventional spectroscopic analysis of the surface monolayer lacks the measurement of two-dimensional information of the monolayer heterogeneity as defined by orientation distribution and structural defects. Self-assembled monolayers (SAMs) provide, in theory, convenient access to well-ordered organic interfaces whose molecular and aggregate structures can be specifically defined based on the numerous studies. Alkanethiol SAMs on gold, for example, has been the surface system of choice for

studying monolayer defects due to formation of ordered monolayers and the abundance of work on this system.¹⁴ SAMs structures on Au are generally regarded to have highly ordered arrangements compared to other metal substrates but their dynamic formation from the solution phase also results in structural complexities.¹⁵⁻¹⁷ External factors that cause monolayer defects include cleanliness of substrate, preparation method of the substrate, and composition and purity of the adsorbate solution, chemical nature of the adsorbate and substrate, reconstruction during assembly, and many others.^{14, 17-21} A major portion of these previous studies on gold focus on defects due to surface variations of the gold substrate examined typically by scanning probe microscopies (SPM) that explores the surface in the nanometer-scale.^{18, 22-24}

Different length scales of gold surface defects, which vary from 10 nm to 1mm, influence monolayer assembly.^{14, 25, 26} These substrate defects, that include gold steps and crystal edges, gold grain boundaries, and substrate impurities, result in domains representing regions of alkanethiol of diverse packing densities in different length scales.^{14, 27-30} SPM studies (i.e. AFM and STM) that investigated gold surfaces consistently agree that to form defect-free SAMs in the nanometer scale, the surface should have low microscopic roughness.³⁰⁻³⁴ Bulk gold and mica-annealed gold surfaces are rough on a macroscopic scale but contain nanometer-range atomic flatness.³¹ Losic *et al.* demonstrated the measurement of flat areas showing that flat gold made from the first gold atomic layer deposited directly on mica gave the largest flat surface areas (40-80 nm) per micron based on root-mean-squared AFM roughness scales compared to evaporated gold samples that have flat areas ranging between 2-5 nm.³⁰

However, this characteristic flatness in the nanometer scale is less important if micron-scaled images are needed to monitor macroscopic surface activity such as surface wetting or corrosion. Although macroscopically “smooth” evaporated gold film does not possess atomically flat regions, it offers varying roughness length scales (10 nm to 100 microns) which can be spatially imaged through spectromicroscopic techniques.²⁶⁻²⁹ This particular description of surface roughness makes thermally deposited gold films suitable for sum frequency generation imaging microscopy (SFGIM) measurements as a sample standard to compare with other metals of different surface reactivity.³⁵⁻³⁷ Furthermore, while SPM techniques (i.e. AFM, STM) deliver better lateral spatial resolution for surface imaging in the nanometer-scale, these are less sensitive to molecular information that describes defects based on the orientational order and packing density of the alkanethiol monolayers on metal substrates. In addition to its inherent micron-scale spatial resolution, the SFGIM technique takes advantage of the surface sensitivity to the C-H (methyl and methylene groups) stretching modes of alkanethiols that is typical of averaged-signal SFG spectroscopy.

A statistical analysis of sum frequency generation (SFG) spectra generated from the SFGIM images is performed by obtaining the symmetric and antisymmetric ratios of the CH₃ stretches that are used to determine the angular distribution of the terminal methyl group across the gold surface. In addition, the CH_{2-sym}/CH_{3-sym} peak intensity ratio is obtained to estimate the degree of conformational disorder of the ODT alkyl chains.^{36, 38-40} The orientation and conformation SFGIM maps constructed from these ratios are

used as a measure of surface defect concentration based on established structural information of the monolayer for gold.

The SFGIM maps are generated in different imaging length scales (5 to 720 μm) to illustrate the sensitivity of this technique in mapping out the spatial concentration of microscopic defects across the sample field-of-view (FOV). Distribution analysis suggests that the major contributions are efficiently accounted from micron to the sub-micron range which emphasize the relevance of scale of the imaging ROIs. Statistical analysis at different length scales reveals hidden areas of defects in smaller length scale that are obscured by average data. The capability of SFGIM in mapping domains of defect densities is utilized to illustrate the advantage of quantifying the surface defects in the macroscopic scale in terms of its relevance for imaging physical processes on metal such as localized corrosion and heterogeneous catalysis in the micron-scale.^{25, 41} By using the same method of processing imaging data and subsequent orientation analysis, comparison of monolayers of ODT on Au and Cu were done to test ability of statistical methods of evaluating monolayer order for different metal substrates. This is done to validate the feasibility of these statistical tools in evaluating heterogeneity of much more complex monolayers systems such as alloy substrates and corrosion-active surfaces.

3.2. Theoretical Basis

Relevant theoretical and experimental SFG concepts are reviewed here for better understanding of SFGIM. SFG is a nonlinear vibrational spectroscopic technique that

involves two input laser beams; visible and tunable IR that overlap in a medium to generate an output beam that has a frequency equal to the sum of the frequencies of the two incoming beams. It is a highly surface specific technique, since under the dipole approximation, it is forbidden in a medium with inversion symmetry.⁴²

$$I_{\text{SF}} \propto |P_{\text{SF}}^{(2)}|^2 \propto |\chi_{\text{eff}}^{(2)}|^2 I_{1064\text{nm}} I_{\text{IR}} \quad 3-1$$

$$\chi_{\text{eff}}^{(2)} = \chi_{\text{NR}}^{(2)} + \chi_{\text{R}}^{(2)} = \chi_{\text{NR}}^{(2)} + \sum_q \frac{N \langle \beta^{(2)} \rangle}{\omega_{\text{IR}} - \omega_q + i\Gamma_q} \quad 3-2$$

The intensity $I(\omega_{\text{SF}})$ of the generated sum frequency beam is proportional to the square of the induced polarization, $|P^{(2)}|^2$, on the surface introduced by the electric fields of the two incident beams (I_{IR} , $I_{1046 \text{ nm}}$). The term that relates the induced polarization response to the electric fields is called the second-order nonlinear susceptibility tensor $\chi_{\text{eff}}^{(2)}$. This has two components, the χ_{nr} coming from the nonresonant background of the surface and the resonant term χ_{r} , which contains the vibrational spectroscopic information. $\beta^{(2)}$ is the hyperpolarizability containing vibrational information averaged over all molecular orientation, which is composed of the Raman polarizability and the IR dipole transition moments. A_q , ω_{IR} , ω_q , and Γ_q are the amplitude, frequency of the IR beam, frequency of the normal mode and the damping constant of the q th vibrational mode, respectively.

$$\chi_{\text{eff}}^{(2)} = |\chi_{\text{NR}}^{(2)}| e^{i\phi} + |\chi_{\text{R}}^{(2)}| e^{i\delta(\omega_{\text{IR}})} \propto A_{\text{NR}} e^{i\phi} + \sum_q \frac{A_q}{\omega_{\text{IR}} - \omega_q + i\Gamma_q} \quad 3-3$$

The two laser beams are co-propagating and the emitted SFG signal at a specific angle is directional and coherent based on the conservation of momentum where the beams are aligned along the plane of incidence. In practice, the SFG spectra are complicated by the nonlinear optical response of the metal substrate. A striking characteristic of SFG spectra of metal surfaces is the wide variety of spectral lineshapes that arise from interference between the electric fields of the light emitted by the adsorbate (resonant) and the substrate (nonresonant). This is quantified by the relative phase shift, ϕ , which is the difference between the nonresonant(ϵ) and resonant(δ) phase as denoted in equation 3-3. The polar coordinate form of the SFG equation (equation 3-3) is the basis for the nonlinear model fitting to extract resonant amplitudes used for orientation analysis and mapping results.

3.3. Experimental Section

3.3.1. Sample Preparation

Gold substrates were prepared by thermally evaporating 100 nm of gold (Kurt-Lesker, 99.999%) onto chromium coated SiO₂ (100) wafers in 1×10^{-5} Torr pressure. The standard reagent of alkanethiol was used as received to prepare the SAMs on the metals (ODT, CH₃(CH₂)₁₇SH, 98%; EtOH, 200 Proof). The gold substrates were subjected to 2 hours of thiol solution deposition using 1mM ODT-ethanol solutions. The slides were rinsed with excess ethanol to remove weakly adsorbed thiol molecules. The samples were dried under a stream of N₂ gas. After the sample preparation, the gold slide was aligned for SFGIM data acquisition. Additional gold slides were overlaid with

evaporated copper metal to produce composite samples. These samples are used for the direct comparison of ODT formation on different metal substrates.

3.3.2. SFG Imaging Microscopy

A picosecond pulsed Nd:YAG laser (EKSPLA) with a 20 Hz repetition rate was used for the following experiments. The Nd:YAG laser provides the 1064 nm beam that pumps the optical parametric generator/amplifier (OPG/OPA) to generate the IR beam, which is tunable from 2000 to 4000 cm^{-1} . The polarization of the two incident beams and the SFG output were set to be p-polarized light (parallel to the plane of incidence) such that the polarization combination is set as ppp. The incidence angles of the IR and 1064 pump beams are set at 70° and 60°, respectively. The SFG microscope was set with a reflection configuration collecting the intermediate image from the grating by use of a 10x objective for magnification and tube lens for collimation. A Roper Scientific CCD camera with 1024 x 1024 pixel array was used for detection. By continuously scanning at fixed rates within the IR range of 2750-3050 cm^{-1} , one image is produced every 5 cm^{-1} . This IR frequency range captures the C-H vibrational frequencies for methyl and methylene groups in alkyl chains of ODT. The images were stacked using ImageJ and extraction through the stack generates the SFG spectrum. By selecting regions-of-interest (ROIs) from the image, spatial distribution of SFG spectra is demonstrated. With an FOV of 1mm², it has an approximated spatial resolution of 2 microns.^{43, 44}

3.4. Results and Discussion

3.4.1. Spatial Mapping and Orientation Analysis

Spectral assignments for the terminal methyl (CH_3) and methylene (CH_2) vibrational modes of ODT were determined based on previous works on alkanethiol-gold systems studied on the SFGIM instrument. The assigned peaks are the following: the terminal methyl symmetric ($\text{CH}_{3\text{-sym}}$) stretch at $\sim 2875\text{ cm}^{-1}$, methyl Fermi resonance ($\text{CH}_{3\text{-Fermi}}$) from the symmetric methyl stretch and methyl bending overtone at $\sim 2940\text{ cm}^{-1}$, and the CH_3 antisymmetric ($\text{CH}_{3\text{-asym}}$) stretch at $\sim 2965\text{ cm}^{-1}$. Weaker vibrational stretches present in the spectrum at 2850 and 2915 cm^{-1} are the methylene symmetric ($\text{CH}_{2\text{-sym}}$) and Fermi ($\text{CH}_{2\text{-Fermi}}$) vibrational modes, respectively, that are present due to gauche defects in the alkyl chains.

The ROI size typically used in previous studies performed on the SFGIM was 20×20 square pixel ROIs. One pixel is approximately equivalent to 1 micron based on conversion using the USAF pattern as standard test for spatial resolution.⁴⁴ The size of the ROIs was selected through a process that takes into account signal-to-noise ratios (SNR) of the SFG spectra. With ROI areas below 5×5 square pixel ROI, signal levels are too low to obtain quantitative fit for the resulting SFG spectra. Hence, maps of the same sample image stack with different length scales (based on pixel area) were constructed in sizes of 5, 10, 20, 45, 90, and 180 pixel square areas. The averaged orientation of the entire 720 pixel square image was also measured to compare with the orientation distribution of different length scales.

Orientation analysis of the SFG spectral data initiates with acquisition of the peak intensity ratios derived from curve fitting. The fitted intensity ratios in the ppp polarization of the symmetric and antisymmetric stretching modes of the terminal methyl groups were collected from each ROI extracted from the SFGIM image. The orientation equations relies on the summation of active tensor elements $\chi_{ijk,q}^{(2)}$ that makes use of constants such as $\beta^{(2)}$ -tensor elements and the depolarization ratio.^{38, 39, 45} Wang *et al.* emphasized that the measured tensor elements are linear combinations of $\langle \cos \theta \rangle$ and $\langle \cos^3 \theta \rangle$,⁴⁰ where θ is the tilt angle of the methyl C₃ axis to the surface normal, and the operator $\langle \rangle$ denotes the orientational ensemble average over different molecular orientations. It was assumed that the monolayer surface is azimuthally isotropic; such that the angle between the surface normal and the principal axis of the methyl group can represent the molecular orientation of the monolayer.

The orientation analysis involves the use of the δ -function distribution approximation where each ROI has a narrow molecular orientation distribution. Hence, the δ -function limit of $\langle \cos^n \theta \rangle$ is estimated as $\cos^n \theta$. Calculated orientation from this assumption will typically represent the favored molecular structures that give higher intensity contributions to the average SFG signal.

The conformational defects across the surface were measured by obtaining the intensity ratio of CH_{2-sym}/CH_{3-sym} from the curve fitting. Calculated ratios that deviate from zero define areas that contain varying concentrations of gauche defects. As a complement to the orientation distributions, the spatial maps of monolayer conformation provide additional information to the surface heterogeneity.

3.4.2. Orientation Distribution Analysis

The contour maps of intensity ratios ($\text{CH}_{3\text{-sym}}/\text{CH}_{3\text{-asym}}$) in Figure 3-1 (a-b) were used to generate the matrices of the methyl tilt angle θ that are presented as spatial maps in Figures 3-1c and 3-1e using the theoretical δ -function orientation curve of Au/ODT used in previous studies.^{36, 46} Histograms are constructed for extracting the overall statistical information of each ROI scale dataset used for the orientation analysis. The fitted parameters of these histograms are then used as quantitative measures of the experimental surface heterogeneity of the monolayer-metal system.

The heterogeneity of the imaged surface is visualized through the use of the orientation maps and histograms of the tilt angle of ODT as listed in Figure 3-2. Fitting the histogram curves allows for determining the angular distributions experimentally. As listed in Figure 3-3a, the mean orientation, θ , and distribution width, σ , were curve-fitted from the histograms in Figure 3-3 using two probability functions: Gaussian and Log-normal. The Gaussian distribution function has been used several times to describe molecular orientation on surfaces.⁴⁷⁻⁴⁹ Wang *et al.* demonstrated by comparing the Gaussian and Maximum Entropy Method (MEM) distributions in fitting distributions showing that the results deduced from both methods are good approximations for the angular distribution.⁴⁵ The Log-normal function distribution, a type of maximum entropy probability distribution, was tested for goodness of fit for orientation histograms as compared to the Gaussian function results. In Figure 3-3a, the calculated θ and σ from the two functions are comparably close as expected from fitting functions that are able to fit

the orientation distributions as linear combinations of the Legendre polynomials, $\langle P_n \rangle = \langle \cos^n \theta \rangle$ where $n=1,3$ for second-order nonlinear processes.

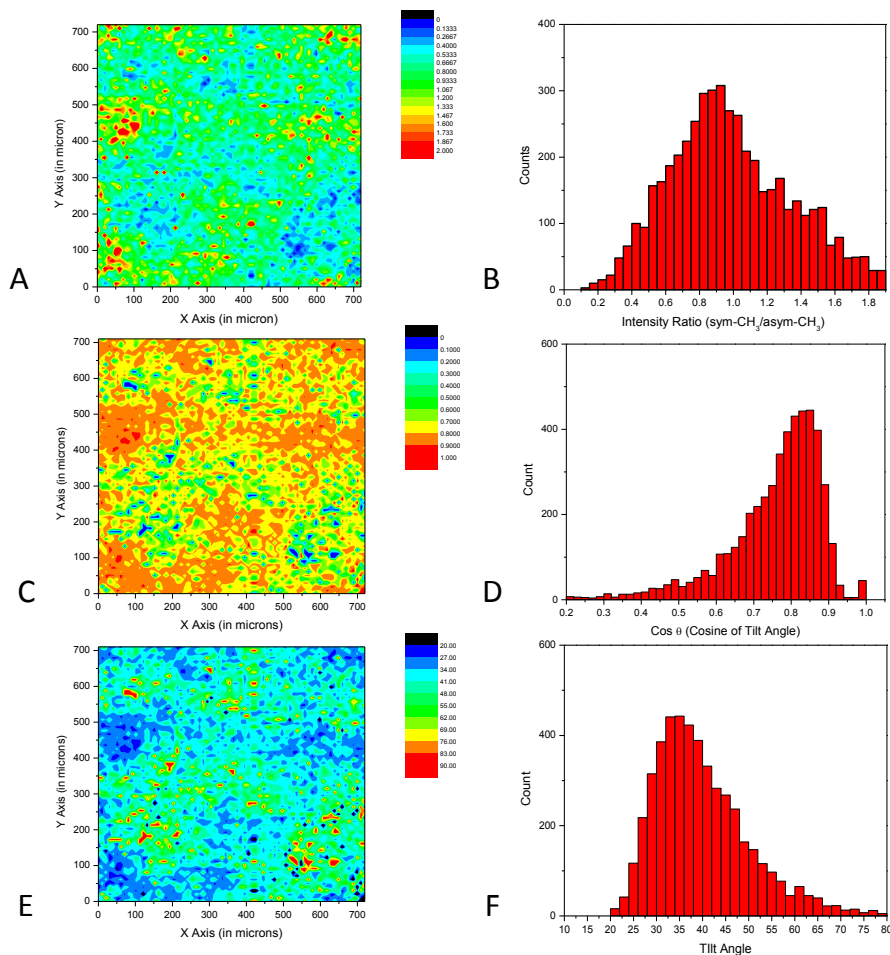


Figure 3-1. (A and B) Contour map and histogram, respectively, of the intensity ratio of the $\text{CH}_3\text{-sym}/\text{CH}_3\text{-asym}$ vibrational modes of the terminal methyl group, (C & D) Contour map and histogram, respectively, of the cosine of the tilt angle calculated from the δ -function approximation, and (E & F) Contour map and histogram, respectively, of the tilt angle of the C_3 axis of the terminal methyl group from the surface normal (ROI scale: 10 x 10 square pixel).

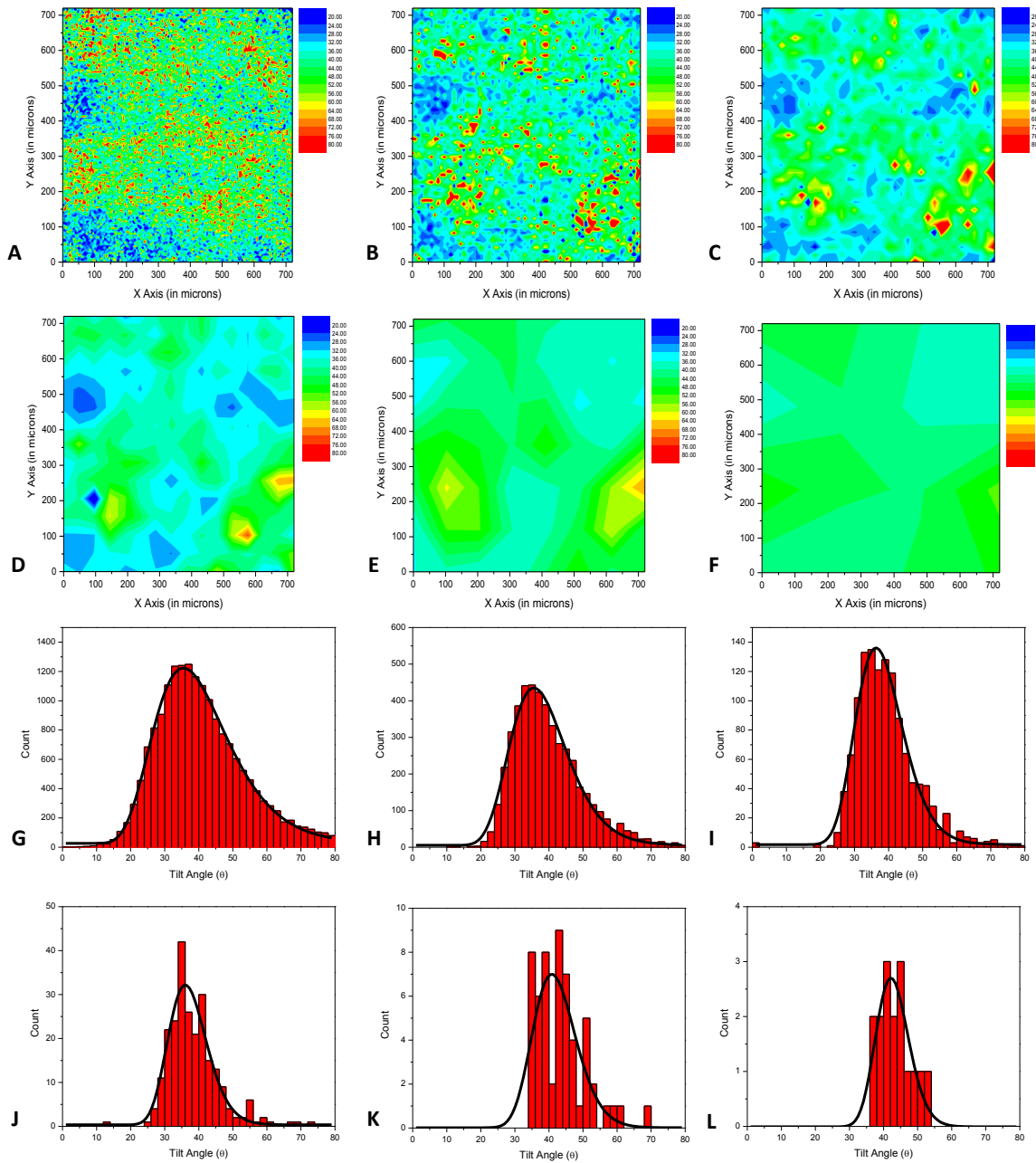


Figure 3-2. Contour maps of tilt angle distributions (in degrees) with different ROI sizes: (A) 5 x 5, (B) 10 x 10, (C) 20 x 20, (D) 45 x 45 and (E) 90 x 90 and (F) 180 x 180 square pixel areas; (G-L) are corresponding statistical histograms of the tilt angle distributions.

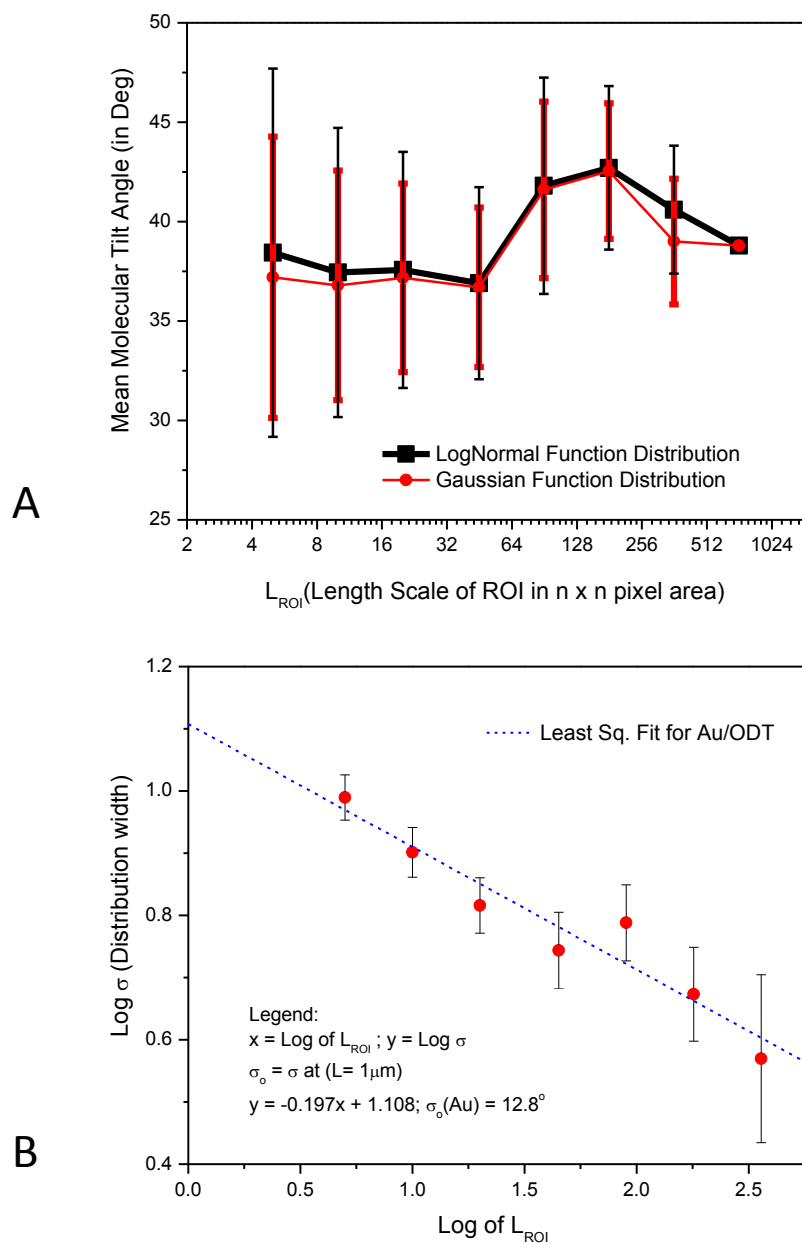


Figure 3-3. (A) Fitted mean methyl tilt angle (θ_{mean}) with distribution width ($\pm\sigma$) for each ROI-size dataset of different pixel scale areas for Au/ODT system (B) Distribution width versus length scale (for Au and Cu surface) fitted to determine the distribution width (σ_o) at $L=1\mu m$ as set by the SFGIM detection limit.

In Figure 3-4, two-dimensional maps involving signal intensities of the methylene stretch are used to interpret the alkyl chain defects of the SAMs film. The relative intensities of $\text{CH}_{2\text{-sym}}$ and $\text{CH}_{3\text{-sym}}$ modes had been often used as a useful measure of conformational order.^{36, 50, 51} In Figure 3-4, the maps of the fitted results for the $\text{CH}_{2\text{-sym}}/\text{CH}_{3\text{-sym}}$ intensity ratios reveal the relative amounts of alkyl backbone defects at the surface. As the ROI scale is decreased, hidden domains with high gauche defects appear from the contour maps. Averaging the $\text{CH}_{2\text{-sym}}/\text{CH}_{3\text{-sym}}$ intensity ratios over larger sample areas leads to loss of spatial conformational information.

The difference between the spectral information obtained from averaged SFG and SFGIM is experimentally demonstrated by the effect of changing the ROI scale to the orientation distribution. From Figure 3-2 (e-f), the data sets consist of large ROIs (at 90 to 180 microns) that make them similar to non-imaging SFG signal averaged over large areas of the sample. These ROIs are approximated by a narrow angular distribution that resembles a δ -function distribution. Hence, for large ROIs, even if these contain larger populations of defects, the calculated orientation represents the SFG favored structures (near 50°) as demonstrated in Figure 3-5. The sensitivity of the SFG technique to certain molecular orientations and distributions is directly linked to the experimental conditions of the SFG technique.

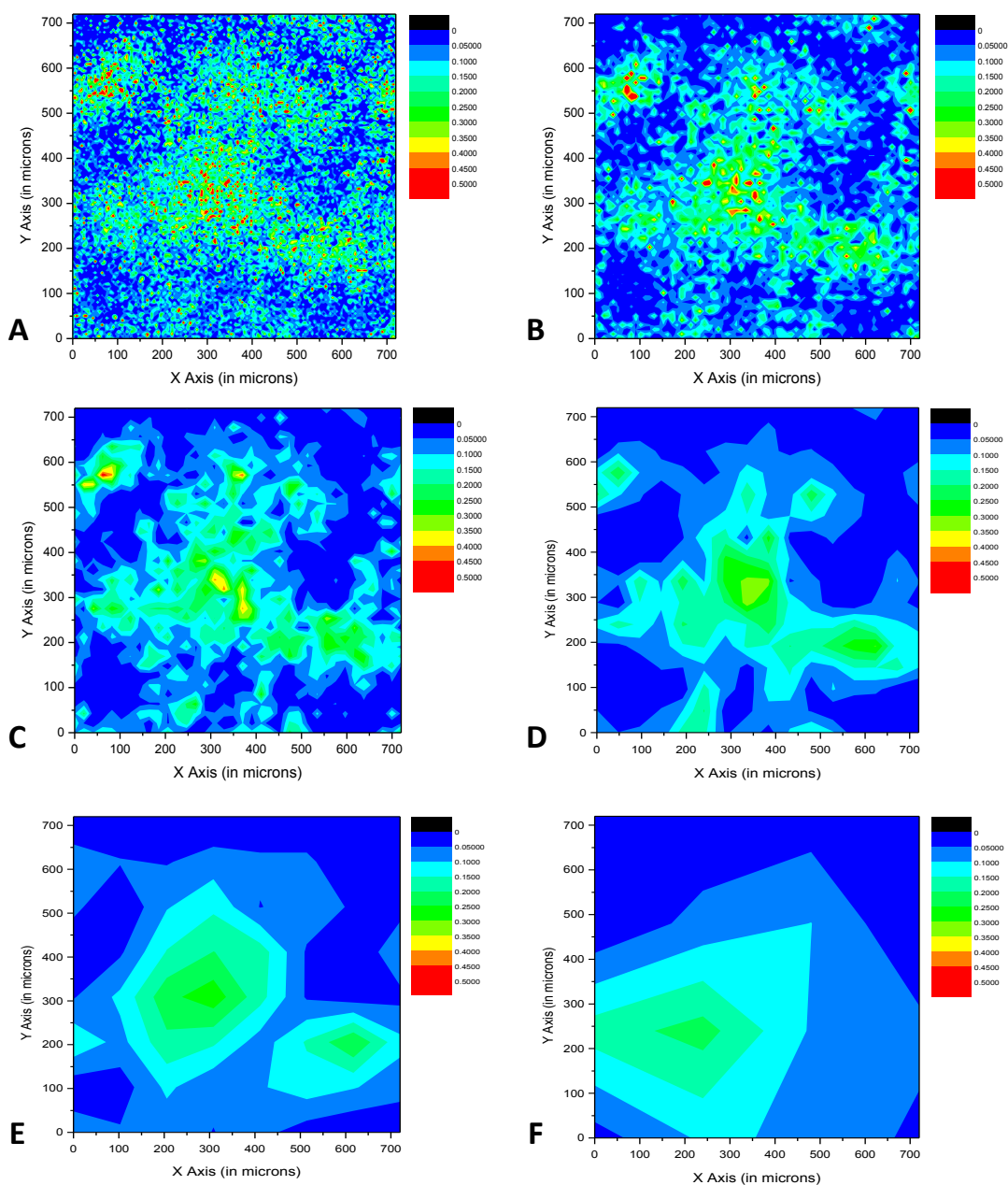


Figure 3-4. Contour maps of conformational defects from the fitted ratios of $\text{CH}_2\text{-sym}/\text{CH}_3\text{-sym}$ intensities in ppp polarization with different ROI scales of (A) 5 x 5, (B) 10 x 10, (C) 20 x 20, (D) 45 x 45 (E) 90 x 90, and (F) 180 x 180 square pixel areas.

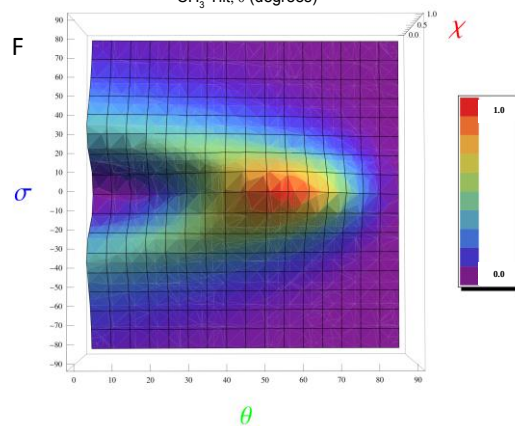
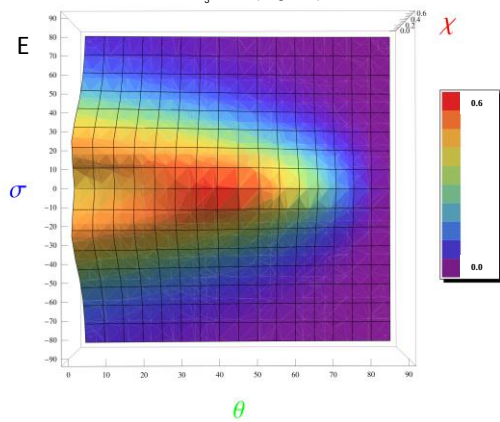
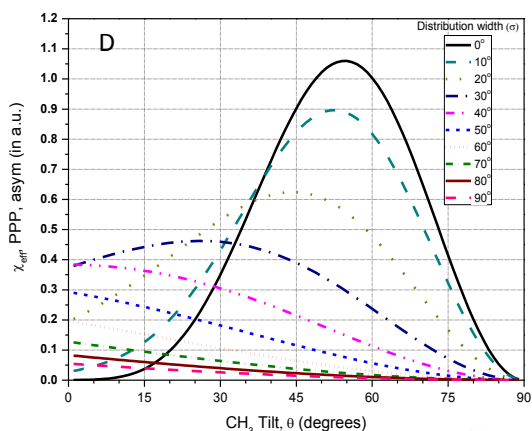
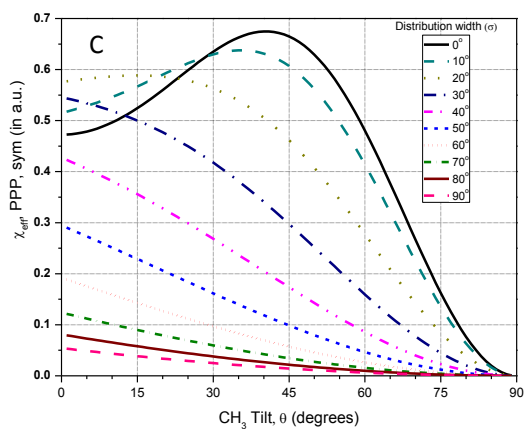
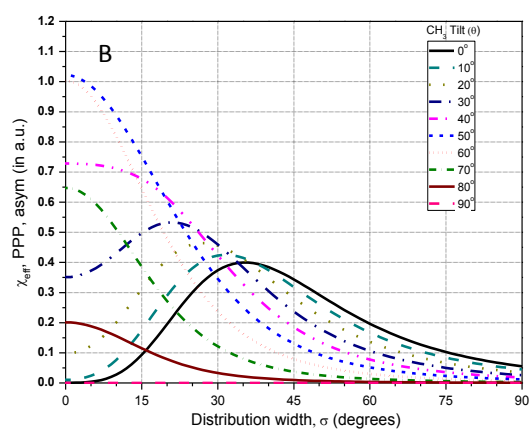
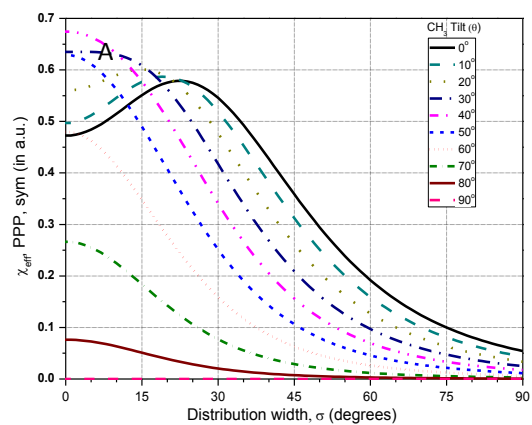


Figure 3-5. (A and B) The normalized effective susceptibility, $\chi_{\text{eff}}^{(2)}$, for the symmetric and antisymmetric CH₃ stretch, respectively, versus the distribution width, σ . Each curve represent each average molecular orientation from the surface normal; (C and D) The normalized effective susceptibility, $\chi_{\text{eff}}^{(2)}$, for the symmetric and antisymmetric CH₃ stretch, respectively, versus the molecular orientation, θ . Each curve represent each distribution width for a Gaussian function; (E and F) XYZ contour plot of normalized effective susceptibility, $\chi_{\text{eff}}^{(2)}(\text{CH}_3\text{-sym})$ and $\chi_{\text{eff}}^{(2)}(\text{CH}_3\text{-asym})$, respectively, vs. θ and σ . The polarization combination was set as ppp.

As discussed by Rao *et al.*, the $\chi_{\text{eff}}^{(2)}$, the nonlinear optical parameter directly proportional to the SFG signal, is simplified mathematically as a linear combination of $\langle \cos \theta \rangle$ and $\langle \cos^3 \theta \rangle$ such that:

$$I_{\text{SF}} \propto \left| \chi_{\text{eff}}^{(2)} \right|^2 = |N_s * d * (\langle \cos \theta \rangle - c * \langle \cos^3 \theta \rangle)|^2 \quad 3-4$$

The parameters c and d are functions that vary with particular experimental conditions such as molecular polarizability ratios, angular geometry of the SFG beams, dielectric constants of the two bulk media and the monolayer at the optical wavelength of the two input beams. The $\chi_{\text{eff}}^{(2)}$ as a measure of SFG detection sensitivity is related to the SFG experimental configuration through the c and d parameters. In Figure 3-5, the c and d parameters are used as experimental constants to generate the relationship of SFG intensity to the molecular orientation and its corresponding distribution width.

The SFGIM detection sensitivity is plotted (Figure 3-5 a-b) as a function of distribution width at different molecular orientations. Each curve represents a specific terminal methyl orientation (θ) subjected to a range of angular distributions. When the distribution width σ is zero (a delta distribution), the methyl tilt angles (θ) between 30° and 50° gives the strongest SFG intensities for the symmetric methyl stretch (ppp polarization). For the antisymmetric methyl stretch, SFG intensity for this mode is at maximum for orientations between 50° and 60° . Considering only the direction of the dipole transition moments with respect to the surface normal, the SFG intensity for orientations close along the surface normal ($\theta=0$) are, as expected, higher for the symmetric mode than the antisymmetric one. At $\theta=0$, the antisymmetric modes are perpendicular to the plane of incidence which results to a zero SFG signal in agreement with IR surface selection rules.⁵² This suggests that the SFGIM optical configuration for metal surfaces (i.e. Au, Cu, Ag) is suitable in detecting upright molecular orientations typical of well-oriented monolayers such as ODT. Figure 3-5 (e-f) shows the range for θ and σ with the best SFG signal contributions (red-colored region).

Certain ROIs with monolayer populations in the 40° - 60° angular interval highly contributes to the δ -average tilt. With average tilt angles at around 39° , the ODT/Au system produces fairly accurate estimates for the methyl orientation;^{36, 46, 53, 54} except for domains on the surface that contain higher concentration of defects. For large ROIs containing widely distributed orientation populations, the calculated δ -average tilt is dominated by signal-favored orientations. However, if the ROIs are small enough, it is possible to reveal areas of specific local orientations (with narrow tilt distributions) that are less-favored in the δ -function approximation (i.e. areas of defect). Hence, the tilt

angle histograms are wider for smaller ROI scales due to the inclusion of these less favored populations. As seen from Figure 3-2 (g-l), for the larger ROI scale, the tilt angle bias at 40° is noticeable with missing populations for $\theta < 35^\circ$ and $\theta > 55^\circ$ since these are the less favored orientations by SFG sensitivity.

From Figure 3-5, the SFGIM signal intensities converge at a minimum when σ approaches towards 90° at which the molecular distribution is considerably random. As the surface becomes less homogeneous, SFG becomes less sensitive. This description of sensitivity due to heterogeneity is consistent with the SFG signal being null in an isotropic medium. This limitation due to sample heterogeneity of SFG is similar to that of the SHG when describing an angular distribution for an inhomogeneous sample. Simpson and Rowlen^{9, 47, 55} proposed that the delta distribution approximation is specifically problematic for rough surfaces where adsorbed molecules are likely to have broader angular distributions.⁴⁵ In order to avoid an artificial convergence to a magic angle value, Simpson *et al.* complemented their SHG results with independent linear absorption measurements to simultaneously obtain both orientation angle and distribution. Other similar approaches involved various linear spectroscopic techniques to complement SHG and SFG.^{5, 56, 57} However, the key difficulty of these complementary approaches is that linear measurements lack the monolayer sensitivity required for orientation analysis. There were several SFG and SHG studies^{9, 40, 45, 47, 48, 55, 58, 59} that deduce the molecular orientation (θ) and its distribution (σ) but most them rely on the orientation parameter $D = \langle \cos \theta \rangle / \langle \cos^3 \theta \rangle$ with the assumption of a narrow distributions acquired through the average $\chi_{\text{eff}}^{(2)}$ over the whole sample area. These methods lack the ability of direct measurement of the experimental distribution.

Fortunately, SFGIM is capable of addressing this issue by treating equally all extracted regions as individual angular distributions that contribute to the global distribution of the sample. Each region is independently measured; hence, regions with less-favored molecular arrangements are better accounted for in the orientation analysis.

3.4.3. ROI Scale Analysis

As presented in the contour maps of the tilt angle in Figure 3-2 (a-f), the effect of reducing the ROI size from 720 to 5 microns reveals the heterogeneous features of the surface. As the ROI area is exponentially decreased, the domains of tilt deviations appear more distinct against the well-oriented portions (green). Since signal-favored orientations dominate the larger ROIs, the tilt angle values are typically close to the fitted normal distribution mean; orientations that are off the δ -function average are buried in the total $\chi_{\text{eff}}^{(2)}$ in the large ROI maps.

For the large ROI maps, the distributions widths calculated from the histograms are narrower in contrast to the smaller ROI maps. Clearly shown in Figure 3-2l, unaccounted populations appears to be “missing” on both sides of the distribution curve (tails), in contrast to the better fits of the wider distributions in Figure 3-2 (g-h). The orientation maps of smaller ROIs account for domains that contain molecules with lower SFG signal. When these smaller ROIs are counted into the statistical analysis of the entire data set, the distribution width increases and the obscured domains of less-favored molecular orientations appear in the spatial maps (Figure 3-2 a-f). Furthermore, the accuracy of calculated statistical parameters for small ROI scales is also demonstrated by projecting averaged orientation distribution of large ROI datasets (see Supporting

Information in Appendix A, Figure A-1). The calculated histograms resulted to narrow distribution widths and tilt angle spatial maps with angles that favored by the δ -function approximation.

As the ROI becomes smaller, the tilt angle θ and width σ converge to a finite value that are considered to be an indicator of the surface heterogeneity. Extrapolation of the measured values of the tilt and width (θ and σ) to “zero” scale provides a measure of the heterogeneity of the monolayer on the surface. The data in Figure 3-3b was fitted based on logarithm values ($\log \sigma$ vs. $\log$ of length scale L). The y-intercept of the fitted line for Au/ODT ($\sigma = 12.8^\circ$) is considered the marginal value for the distribution width corresponding to length scale of 1 μm , the resolution limit of the SFG microscope. This determination of absolute tilt distribution of the sample is subject to instrumental limitations and, hence, it is only suitable for the micron-scale ($>1 \mu\text{m}$) range approximations. Albeit, this demonstrates the significance of extracting tilt angle distributions at various ROI scales in revealing accurate statistical measures of molecular orientation.

Previous works on micron-scale AFM images of the evaporated gold substrates show a surface structure formed by large grains, with sizes from some tenths of a micron up to a few microns.^{23, 60} These substrate-induced heterogeneities lead to formation of domains with higher concentration of surface deformation. Furthermore, without any external influence from the substrate, it is also inherent for SAMs to incur defects upon formation to diverse dimensions: from nanoscale islands to micron-scale aggregates. Theoretical studies using molecular dynamic calculations confirms that for groups of

nanoscale islands of alkanethiol SAMs, appearance of well-differentiated domains are bordered by molecules that have higher-than-average number of conformational gauche defects which also possess preferred deviating tilt directions.⁶¹⁻⁶³ A combination of tilt and gauche defects, either induced by the substrate or adsorbate, defines the range of monolayer deformities present on the SAMs-Au system. Detection of these regions of deformed monolayer films is of prime importance to surface applications such as corrosion inhibition, adhesion, wetting, and lubrication.

3.4.4. Defect Correlation

There are a number of studies which relates the alkyl orientation to the conformational defects found in long-chain SAMs. Most of the assumptions are based on Euler transformation relationships that relate trans-gauche transitions and alkyl chain-twist to orientation of the alkyl chain obtained from simulations of experimental reflection absorption infrared spectroscopy (RAIRS) spectrum of monolayers.^{50, 64-66} In this method, only the tilt angle (Θ) of the chain axis with respect to the surface normal and the twist angle (Φ) about the chain axis are needed to characterize the whole molecular geometry (Figure 3-6). The geometrical description is determined through calculated hyperpolarizabilities as a function of the conformation. However, *ab initio* hyperpolarizabilities involve arbitrary initial parameter choices (i.e. local mode approximation, defect models) which may influence its precision in order to minimize computing complications required in a systematic survey of all possible molecular conformations.^{67, 68}

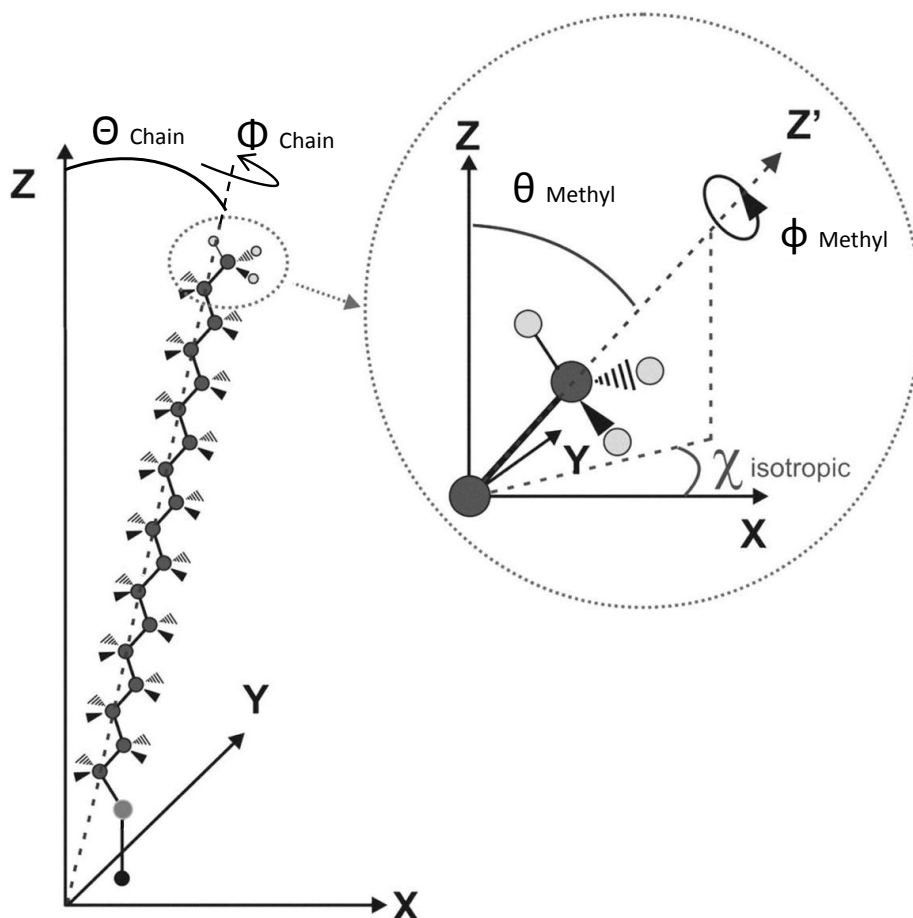


Figure 3-6. Geometric parameters that dictate relationship of CH_3 tilt angle (θ) to gauche defects: tilt angle (Θ) of the chain axis with respect to the surface normal and the twist Φ about the chain axis.

The geometric relationship of the terminal tilt angle (θ) to the chain orientation (Θ) was previously known to be influenced by the number of methylene groups (odd-even effect). From Figure 3-2, the range of θ ($\sim 39^\circ$) for Au/ODT is in agreement for alkanethiols with even number of carbon atoms in contrast to odd-numbered alkanethiols that typically have higher θ values at $\sim 60^\circ$.^{54, 69} Also, Au/ODT is known to have a chain tilt angle Θ at $\sim 30^\circ$ from RAIRS studies.^{53, 66} Both tilt angles θ and Θ are linked strongly

to represent the directionality of the monolayer chains. However, for the purpose of characterizing the monolayer orientation, the SFGIM orientation analysis is primarily concerned with the orientation of the methyl terminal group (θ).

Effects of the conformational change to the molecular geometry of the terminal CH_3 with respect to the surface normal had been demonstrated using averaged spectral information from linear and nonlinear spectroscopic techniques.^{50, 53, 64, 67, 68} In RAIRS, the spectra are averaged over all CH_2 groups (both cis and trans configurations), but, in SFG, all-trans portions of alkyl chains do not contribute to the spectra. Therefore, SFG in the CH_2 stretching region may reveal specifically chain defects that linear spectroscopies cannot uniquely detect.

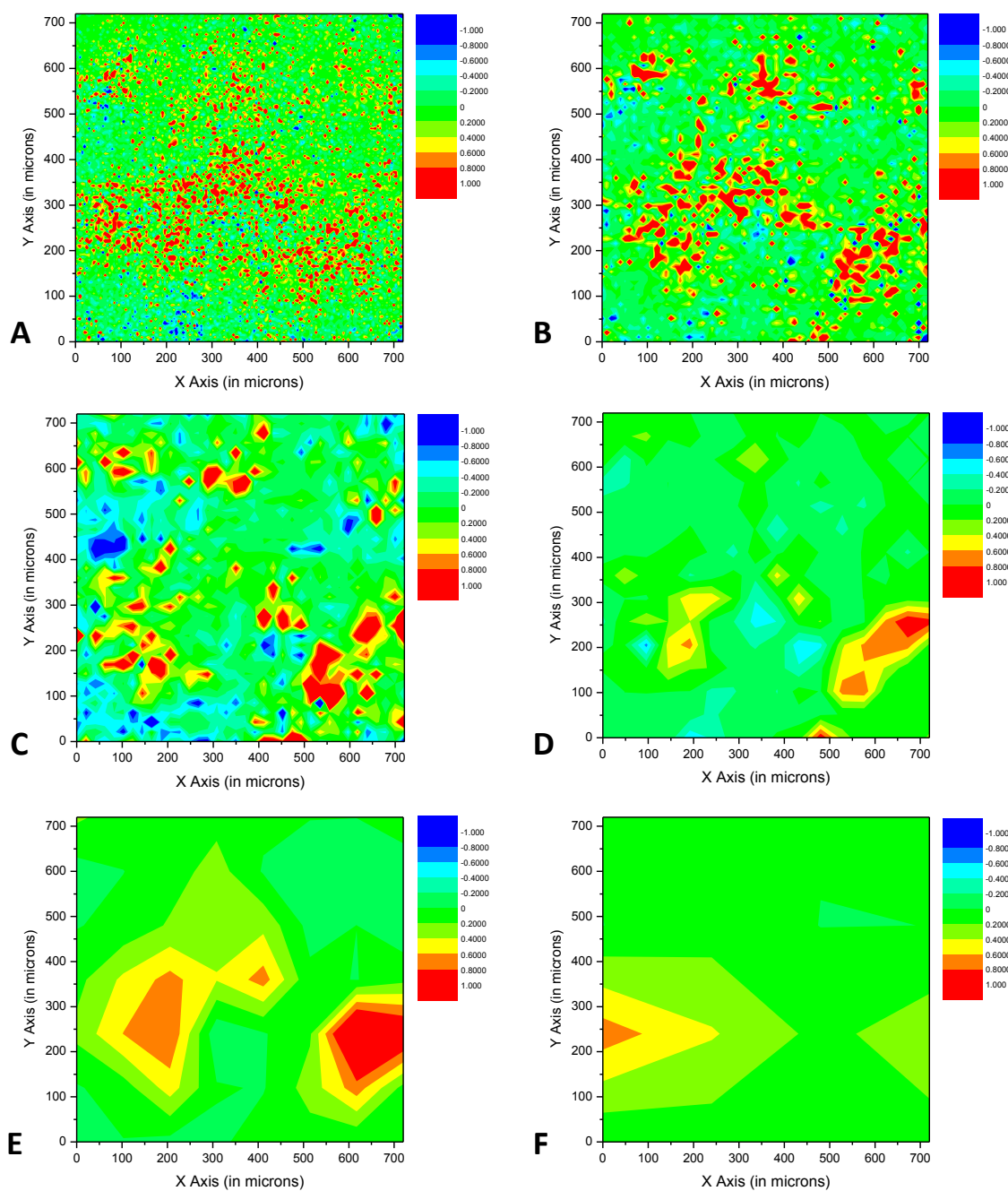
Providing that the orientations of CH_3 and all CH_2 groups are related geometrically using averaged spectroscopy, spatial conformational information can be extracted from SFGIM data by mapping the CH_3 and CH_2 band information in two-dimensions to see the direct relationship of local molecular tilt to gauche defects. The correlation function (CF) is estimated as a quantitative relationship between the average delta-function tilt angle and gauche defects such that

$$(\text{CF})_{i,j} = \left(\frac{\theta_{\delta} - \theta_{\text{mean}}}{\theta_{\text{mean}}} \right)_{i,j} \left(\frac{I_{\text{CH}_2\text{-sym}}}{I_{\text{CH}_2\text{-sym}} + I_{\text{CH}_3\text{-sym}}} \right)_{i,j} \quad 3-5$$

where θ_{δ} is the δ -function tilt angle at $(i,j)^{\text{th}}$ ROI position, θ_{mean} is the overall tilt average of the matrix dataset and the $I(\text{CH}_2\text{-sym})/I(\text{CH}_2\text{-sym}) + I(\text{CH}_3\text{-sym})$ is gauche defect ratio at position $[i,j]$ of the corresponding intensity map. The gauche term accounts for the ROIs

that contain significant $\text{CH}_{2\text{-sym}}$ signal intensities. As the CF value approaches zero, defect contributions, both orientation and conformational, goes to a minimum. It is either minimized by a well-oriented (near θ_{mean}) monolayer on a certain ROI (first term is zero) or the alkyl chains have all-trans configuration (second term is zero). Intuitively, both first and second terms could be either small or large. For example, a tilt deviation (first term is large) could be caused by a gauche defect (second term is large) on its alkyl chain.

Examining the maps of orientation (Figure 3-2 a-f) and conformation (Figure 3-4 a-f), similarities in the spatial domains are visible such that upon comparing it to the resulting CF maps (Figure 3-7 a-f), the familiar heterogeneous features are carried over as a mixture of orientation and gauche defect domains. ROIs that are green (minimum absolute CF values) represent areas that accommodate highly oriented monolayers with minimum gauche defects. As smaller ROIs are introduced, the scattered areas that have correlated defect contributions (less oriented and gauche chains) appear in the maps. By analyzing the spatial relationship between methyl tilts and gauche defects using smaller ROI scales, the correlated defects can be modeled as a continuous non-discrete type of distribution (Figure 3-7 g-l) wherein the maxima is at $\text{CF}=0$ (minimal defects).



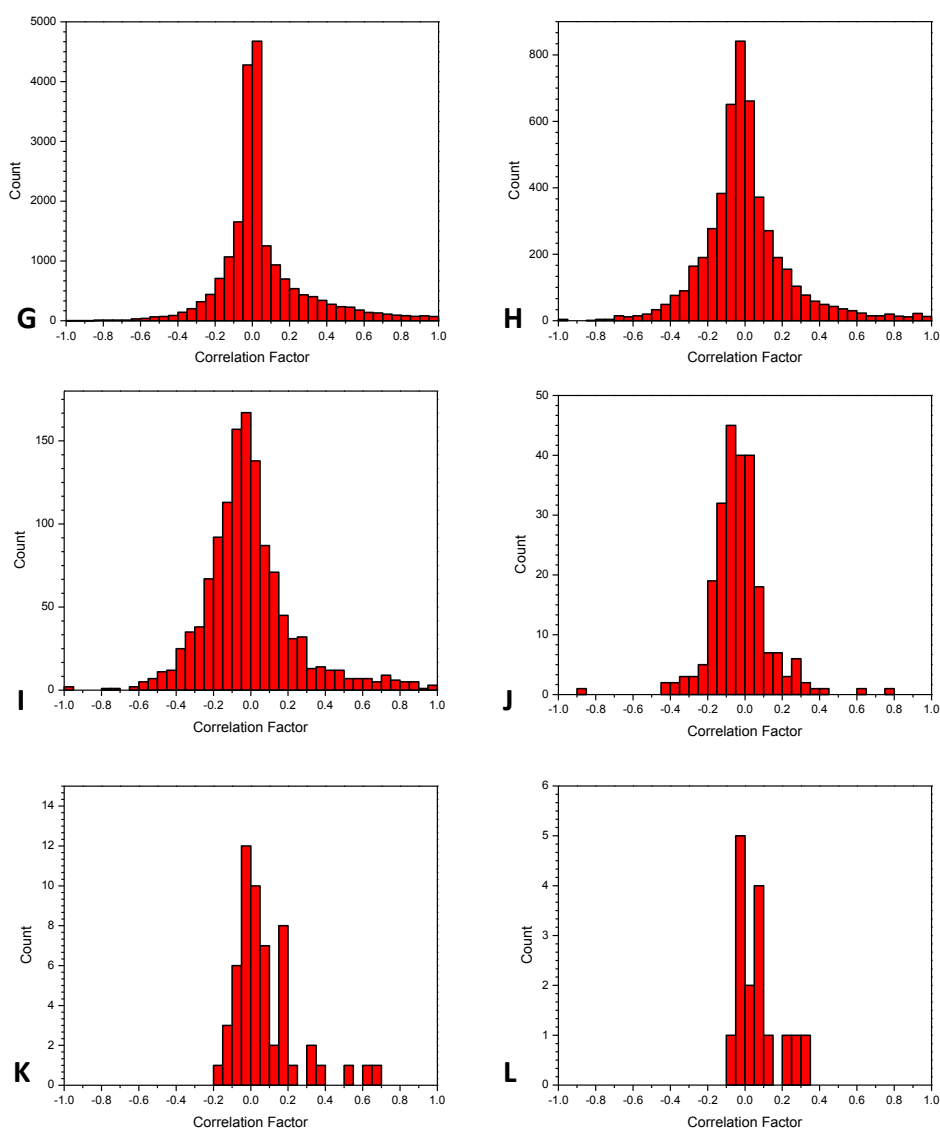


Figure 3-7. Correlation maps of the orientation and conformation distributions, wherein correlation function (CF) defines regions with minimal tilt angle deviations and CH₂ defects; different ROI scales: (A) 5 x 5, (B) 10 x 10, (C) 20 x 20, (D) 45 x 45 (E) 90 x 90 and (F) 180 x 180 square pixel areas. (G-L) Corresponding histograms of the correlation function (CF) wherein values close to 0 have minimal orientation and conformation defects.

For most of the ROI scales, the CF histograms are asymmetric (biased to positive values) due to the orientation distribution (Figure 3-2 e-f) are also biased to angles above the average. For large ROI scales (Figure 3-7 k-l), the defect population is not evenly distributed such that it appears mostly to have domains of ordered monolayers. The domains of higher defect concentration are not properly accounted as compared to the small ROI maps of Figure 3-7 a-b. This further validates that the δ -distribution approximations for large scale ROIs inhibit detection of defect domains.

However, ROIs with uncorrelated deviations are expected to arise. For example, gauche defects are minimum (second CF term is small) although orientation is off-average (first CF term is large). These uncorrelated ROIs with minimum CF values are difficult to locate spatially if not accounted for. These cases represent distinct populations that are intermediate states of orientation and conformation. These ROIs are classified in the scatter plot in Figure 3-8 as part of quadrants I and IV. Typically if the monolayer in an ROI is well-oriented and ordered, these ROIs are represented by quadrant III while ROIs with correlated tilt and gauche defects are in quadrant II.

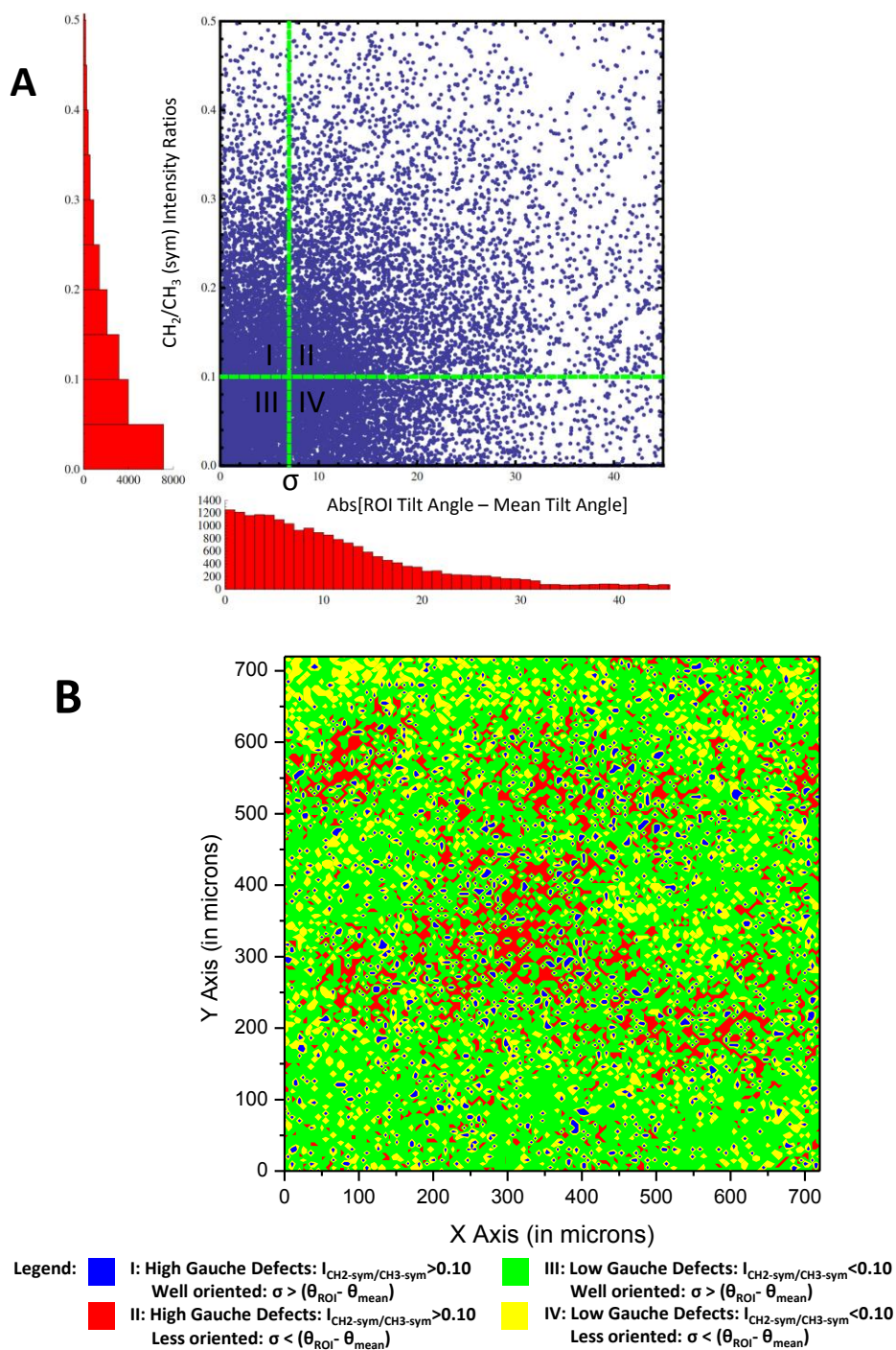


Figure 3-8. (A) Scatter plot of the gauche defect ratio against the absolute difference of the θ of each ROI to θ_{mean} where σ is the standard deviation for the orientation histogram from Figure 3-2 (ROI scale: 5 x 5 sq. pixel) (B) Spatial map of the four quadrants (I, II, III and IV) obtained from Figure 3-8a.

Although majority of the population is in quadrants III and II, the smaller populations in quadrants I and IV are existent based on the fact that not all of orientation and conformation parameters are correlated. Interestingly, ROIs in quadrant I are in close proximity to those in quadrant II. This suggests that ROIs of high gauche defect concentrations are grouped in micron-scale domains that exhibit a range of methyl tilt angles θ . Similarly, ROIs in quadrant III and IV are domains of tightly-packed monolayers with a range of θ values (mostly near θ_{mean}). Various length-scale models (i.e. single molecule, two-chain structure, nanoscale islands) were used to describe the relationship between the terminal CH_2 and CH_3 groups as a measure of the effect of gauche conformers to the terminal CH_3 orientation.^{54, 62, 66}

However, these correlation models do not account for the whole-chain conformation of the monolayer in specific length scales. Further spectroscopic analysis in spatial correlation of chain order to orientation, preferably towards more complex systems than Au/ODT (i.e. micropatterned samples, alloys), is needed to explain these uncorrelated defects.

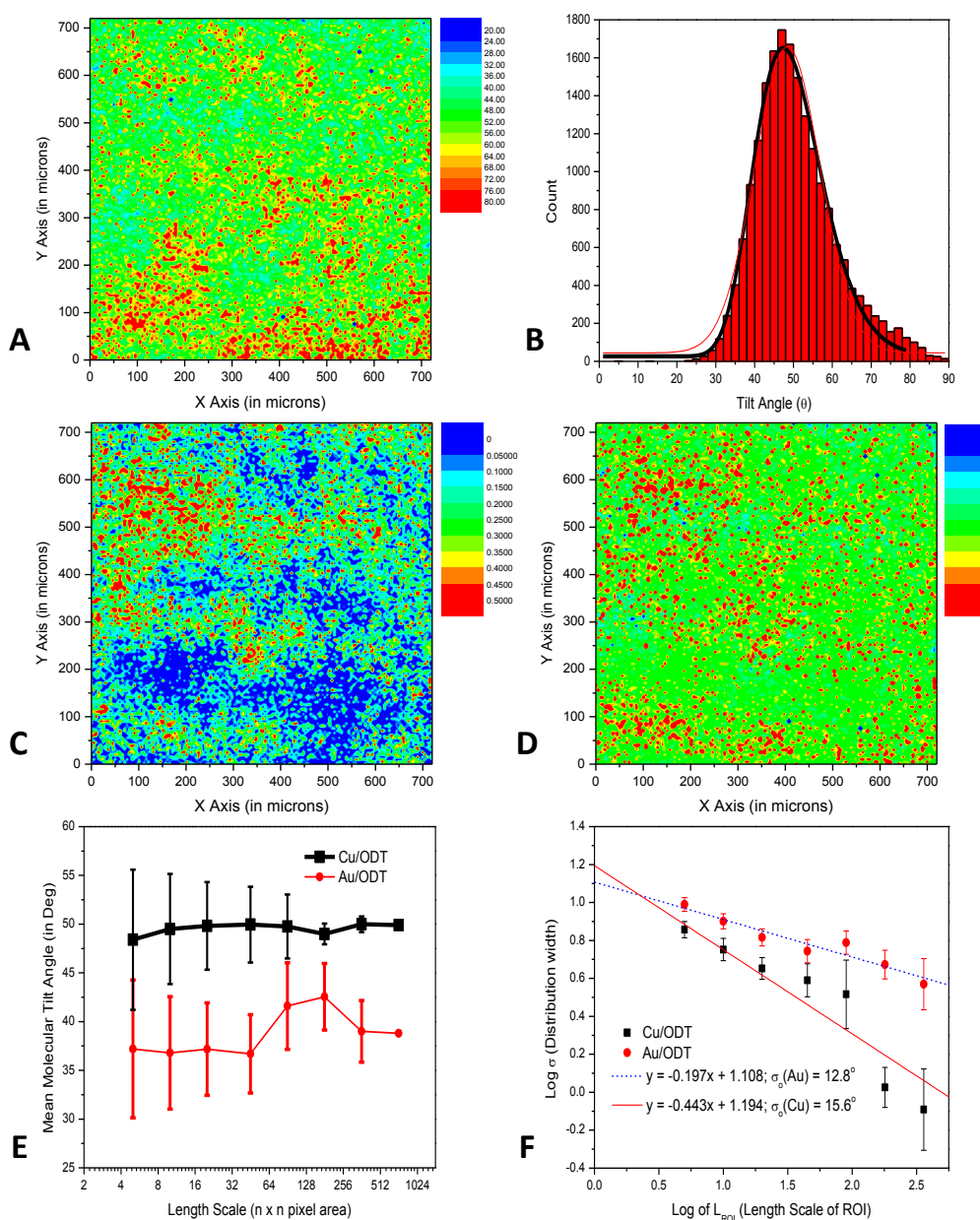


Figure 3-9. (A and B) Contour map (5 x 5 square pixel ROIs) and histogram for the tilt angle of terminal CH₃ group of the Cu/ODT film sample. (C) Contour map of CH₂-sym/CH₃-sym intensity ratios, (D) Contour map of CF values, (E) Comparison of the average methyl tilt angle (θ_{mean}) distributions, and (F) Distribution widths (σ_0) for Cu/ODT and Au/ODT sample systems.

3.4.5. Distribution Analysis of Cu/ODT

Although thiol adsorption on gold is the most widely studied system, copper has become the subject of increasing number of studies in relation with the formation of alkanethiol SAMs on its surface. Long carbon chain thiol SAMs has been repeatedly proven to inhibit oxidation of the surface of copper, and there had been numerous comparisons of the effective organization of different thiol varieties on copper for designing corrosion inhibiting molecular properties of these SAMs.⁷⁰⁻⁷⁵ SFGIM specifically provides a method to observe spatially the heterogeneity of SAMs on copper. This information is essential in examining the influence of the SAMs heterogeneity to the surface reactivity of copper (initial oxidation of Cu/ODT).⁷⁵

Using the same statistical approach, Au/ODT system was compared to that of Cu/ODT to provide insight in monolayer heterogeneity. The CF map was generated from tilt angle and gauche defect maps. In Figure 3-9, the difference in the mean orientation of ODT on Cu and Au are reported. The higher tilt angle range for Cu/ODT is in agreement to previous spectroscopic studies.^{66, 75} The histogram of terminal methyl orientation distribution showed that the Cu/ODT sample has a skewed distribution of tilt angles (Figure 3-9b) wherein there are more ROIs having tilts above the average. This orientation bias is also illustrated through the CF map wherein a higher population for positive CF values is observed. This suggests the preference of ODT monolayers on copper to lie flat closer to the substrate away from the surface normal (θ close to 90°). The positively skewed form of the CF distribution already demonstrates the tendency of Cu to produce less upright molecules that are correlated to inherent presence of CH_2

defects.^{76, 77} The apparent distribution width at 1 μm for Au and Cu were compared in Figure 3-9f showing that Cu has a slightly higher distribution width at $\sigma_0 = 15.6^\circ$. However, difference in the surface roughness, sample preparation and instrumental conditions affects the interpretation of the measured orientation distribution width.

By incorporating the evaporated films of Cu and Au together into one SFGIM image stack, difficulties in comparing of orientation distribution on Au and Cu surfaces brought about by sample preparation and instrumental conditions are minimized. In Figure 3-10a, the difference in the fitted ratios of the $\text{CH}_{3\text{-sym}}$ and $\text{CH}_{3\text{-asym}}$ intensities gave a bimodal curve resulting to two distinct ranges of different orientation distributions (Figures 10d and 10f). Similar with the former results on plain Cu substrate, the ODT chains on Cu lies ($\sim 50^\circ$) closer to the surface compared to that of the Au surface ($\sim 39^\circ$). This substantiates the claim that SFGIM has high sensitivity for distinct orientations due to signature molecular configurations of monolayers as an effect of substrate composition.

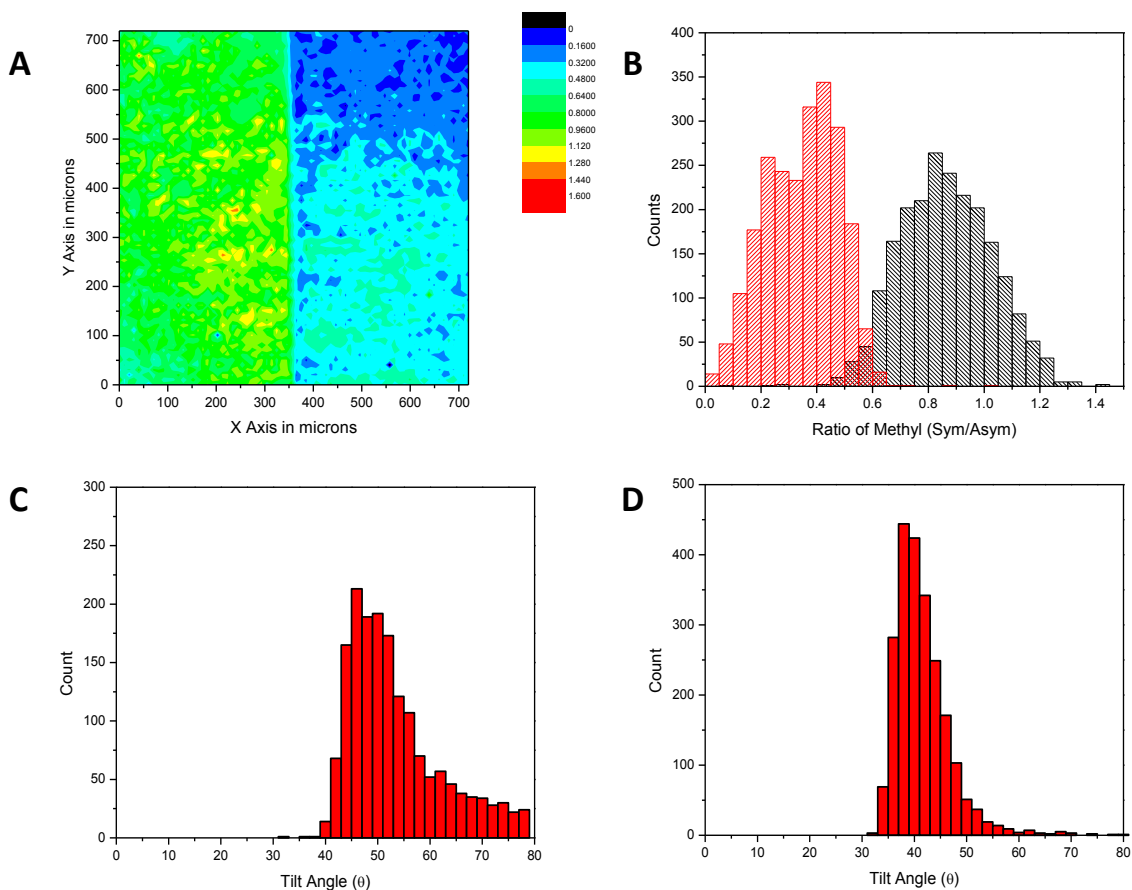


Figure 3-10. (A) Contour map of fitted ratios of the $\text{CH}_3\text{-sym}$ and $\text{CH}_3\text{-asym}$ intensities for ODT in Au (left) and Cu (right). (B) Combined distribution histograms of fitted ratios of the $\text{CH}_3\text{-sym}$ and $\text{CH}_3\text{-asym}$ intensities for Cu (red) and Au (black), and (C and D) tilt angle distributions for Cu and Au, respectively.

Comparing the tilt angle histograms of Cu and Au (Figures 3-10c and 3-10d), the distribution width is larger for Cu wherein it extends to angles closer to 90° . Alkanethiol monolayers on Cu had been widely known to be more heterogeneous compared to that of other coinage metals (i.e. Au, Ag, Pt) due to higher concentration of surface oxide.⁶⁶ Although thiol adsorption on gold is the most widely studied system, copper has become

the subject of increasing number of studies in relation with the formation of alkanethiol SAMs on its surface. Long carbon chain thiol SAMs has been repeatedly proven to inhibit oxidation of the surface of copper, and there had been numerous comparisons of the effective organization of different thiol varieties on copper for designing corrosion inhibiting molecular properties of these SAMs.⁷⁰⁻⁷⁵ However, there are no available spectroscopic studies that specifically provide a method to observe spatially the influence of the SAMs heterogeneity to surface corrosion on copper or similar metals. SFGIM can be used to probe air oxidation of Cu/ODT system to evaluate change in surface heterogeneity with exposure time.⁷⁵ The change in the substrate composition with metal oxidation has it direct effects on the monolayer distribution. The ability of SFGIM to profile orientation distribution based on substrate composition can be further tested on metal Cu alloy substrates (i.e. brass) that are expected to be more spatially heterogeneous than plain Cu.

3.5. Conclusion

This paper demonstrated the sensitivity of the SFGIM technique to measure the experimental orientation distribution of Au-ODT using the δ -function distribution approximation at different length scales. Factors such as instrumental configuration and surface properties have direct effects on the calculated methyl tilt angle and distribution width. The ODT monolayer that is oriented closer to the surface normal is a suitable chemical system to study based on the range of orientation angles the SFGIM is most sensitive.

Changing the length scale of the ROIs of the SFGIM image demonstrated the relationship of the resolution limit and signal sensitivity of the instrumentation in revealing hidden domains of monolayer defects across the surface. By using smaller ROI scales, buried information in averaged SFG signal as collected in conventional instrumentation can now be exploited as spatial maps to measure surface heterogeneity.

Based on the maps of CF distributions, orientation, and gauche defects can be correlated in defining the monolayer heterogeneity on gold through the use of varying length scales. Similarities in the domain patterns in the different maps (orientation, conformation and correlation) can be traced in each length scale, revealing smaller intricate defect-rich domains as the ROI scale is made smaller.

The statistical analysis made it possible to compare orientation distributions on Au and Cu. Using a composite sample, it was shown that monolayer orientations on Cu are less upright than on Au which indicates that SFGIM can distinguish and segregate monolayer populations based on substrate properties. Studying much more complex metal systems such as metal oxides and alloys are deemed possible within the scope of statistical analysis of SFGIM.

References

1. Johnson, C. M.; Tyrode, E.; Leygraf, C. *J. Electrochem. Soc.* **2006**, *153*, B113-B120.
2. MacPhail, R. A.; Strauss, H. L.; Snyder, R. G.; Elliger, C. A. *J. Phys. Chem.* **1984**, *88*, 334-41.
3. Persson, D.; Leygraf, C. *J. Electrochem. Soc.* **1993**, *140*, 1256-60.
4. Hollins, P. *Surf. Sci. Rep.* **1992**, *16*, 51-94.
5. Edmiston, P. L.; Lee, J. E.; Wood, L. L.; Saavedra, S. S. *J. Phys. Chem.* **1996**, *100*, 775-784.
6. Wirth, M. J.; Burbage, J. D. *J. Phys. Chem.* **1992**, *96*, 9022-9025.
7. Saavedra, S. S.; Reichert, W. M. *Langmuir* **1991**, *7*, 995-999.
8. Umemura, J.; Kamata, T.; Kawai, T.; Takenaka, T. *J. Phys. Chem.* **1990**, *94*, 62-67.
9. Simpson, G. J.; Rowlen, K. L. *J. Phys. Chem. B* **1999**, *103*, 3800-3811.
10. Heinz, T. F.; Tom, H. W. K.; Shen, Y. R. *Phys. Rev. A* **1983**, *28*, 1883.
11. Shen, Y. R. *Annu. Rev. Phys. Chem.* **1989**, *40*, 327-350.
12. Dick, B.; Gierulski, A.; Marowsky, G.; Reider, G. A. *Appl. Phys. B: Lasers Opt.* **1985**, *38*, 107-116.
13. Bain, C. D.; Troughton, E. B.; Tao, Y. T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. *G. J. Am. Chem. Soc.* **1989**, *111*, 321-35.
14. Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1103-1170.
15. Badia, A.; Lennox, R. B.; Reven, L. *Acc. Chem. Res.* **2000**, *33*, 475-481.

16. Poirier, G. E. *Chem. Rev.* **1997**, 97, 1117-1128.
17. Yang, G.; Liu, G.-y. *J. Phys. Chem. B* **2003**, 107, 8746-8759.
18. Poirier, G. E.; Tarlov, M. J. *J. Phys. Chem.* **1995**, 99, 10966-70.
19. Hautman, J.; Klein, M. L. *J. Chem. Phys.* **1990**, 93, 7483-7492.
20. Mar, W.; Klein, M. L. *Langmuir* **1994**, 10, 188-196.
21. Zhang, Z. S.; Wilson, O. M.; Efremov, M. Y.; Olson, E. A.; Braun, P. V.; Senaratne, W.; Ober, C. K.; Zhang, M.; Allen, L. H. *Appl. Phys. Lett.* **2004**, 84, 5198-5200.
22. Sun, L.; Crooks, R. M. *Langmuir* **1993**, 9, 1951-1954.
23. O'Dwyer, C.; Gay, G.; Viaris de Lesegno, B.; Weiner, J. *Langmuir* **2004**, 20, 8172-8182.
24. Stranick, S. J.; Parikh, A. N.; Tao, Y. T.; Allara, D. L.; Weiss, P. S. *J. Phys. Chem.* **1994**, 98, 7636-7646.
25. Zhao, X.-M.; Wilbur, J. L.; Whitesides, G. M. *Langmuir* **1996**, 12, 3257-3264.
26. Kuhnke, K.; Hoffmann, D. M. P.; Wu, X. C.; Bittner, A. M.; Kern, K. *Appl. Phys. Lett.* **2003**, 83, 3830-3832.
27. Vericat, C.; Vela, M. E.; Salvarezza, R. C. *Phys. Chem. Chem. Phys.* **2005**, 7, 3258-3268.
28. Strong, L.; Whitesides, G. M. *Langmuir* **1988**, 4, 546-558.
29. Rampi, M. A.; Schueller, O. J. A.; Whitesides, G. M. *Appl. Phys. Lett.* **1998**, 72, 1781-1783.
30. Losic, D.; Shapter, J. G.; Gooding, J. J. *Langmuir* **2001**, 17, 3307-3316.
31. Creager, S. E.; Hockett, L. A.; Rowe, G. K. *Langmuir* **1992**, 8, 854-861.

32. Guo, L.-H.; Facci, J. S.; McLendon, G.; Mosher, R. *Langmuir* **1994**, *10*, 4588-4593.
33. Hegner, M.; Wagner, P.; Semenza, G. *Surf. Sci.* **1993**, *291*, 39-46.
34. Wagner, P.; Hegner, M.; Guentherodt, H.-J.; Semenza, G. *Langmuir* **1995**, *11*, 3867-3875.
35. Zhang, H.; Romero, C.; Baldelli, S. *J. Phys. Chem. B* **2005**, *109*, 15520-15530.
36. Cimatu, K.; Baldelli, S. *J. Phys. Chem. C* **2007**, *111*, 7137-7143.
37. Hedberg, J.; Leygraf, C.; Cimatu, K.; Baldelli, S. *J. Phys. Chem. C* **2007**, *111*, 17587-17596.
38. Hirose, C.; Akamatsu, N.; Domen, K. *J. Chem. Phys.* **1992**, *96*, 997-1004.
39. Hirose, C.; Yamamoto, H.; Akamatsu, N.; Domen, K. *J. Phys. Chem.* **1993**, *97*, 10064-9.
40. Wang, H.-F.; Gan, W.; Lu, R.; Rao, Y.; Wu, B.-H. *Int. Rev. Phys. Chem.* **2005**, *24*, 191-256.
41. Preiner, M. J.; Melosh, N. A. *Langmuir* **2009**, *25*, 2585-2587.
42. Buck, M.; Himmelhaus, M. *J. Vac. Sci. Technol., A* **2001**, *19*, 2717-2736.
43. Cimatu, K.; Baldelli, S. *J. Am. Chem. Soc.* **2006**, *128*, 16016-16017.
44. Cimatu, K.; Baldelli, S. *J. Phys. Chem. B* **2006**, *110*, 1807-1813.
45. Wang, J.; Paszti, Z.; Even, M. A.; Chen, Z. *J. Am. Chem. Soc.* **2002**, *124*, 7016-7023.
46. Hernandez, M.; Chinwangso, P.; Cimatu, K.; Srisombat, L.-O.; Lee, T. R.; Baldelli, S. *J. Phys. Chem. C* **2011**, *115*, 4688-4695.
47. Simpson, G. J.; Rowlen, K. L. *J. Phys. Chem. B* **1999**, *103*, 1525-1531.

48. Simpson, G. J.; Westerbuhr, S. G.; Rowlen, K. L. *Anal. Chem.* **2000**, 72, 887-898.
49. Wei, X.; Zhuang, X.; Hong, S.-C.; Goto, T.; Shen, Y. R. *Phys. Rev. Lett.* **1999**, 82, 4256.
50. Chechik, V.; Schonherr, H.; Vancso, G. J.; Stirling, C. J. M. *Langmuir* **1998**, 14, 3003-3010.
51. Ward, R. N.; Duffy, D. C.; Davies, P. B.; Bain, C. D. *J. Phys. Chem.* **1994**, 98, 8536-42.
52. Greenler, R. G. *J. Chem. Phys.* **1969**, 50, 1963-8.
53. Nuzzo, R. G.; Fusco, F. A.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, 109, 2358-2368.
54. Nishi, N.; Hobara, D.; Yamamoto, M.; Kakiuchi, T. *The Journal of Chemical Physics* **2003**, 118, 1904-1911.
55. Simpson, G. J.; Rowlen, K. L. *Acc. Chem. Res.* **2000**, 33, 781-789.
56. Zakharov, A. V.; Iwamoto, M. *Phys. Rev. E* **2002**, 66, 061605.
57. Tronin, A.; Strzalka, J.; Chen, X.; Dutton, P. L.; Blasie, J. K. *Langmuir* **2000**, 16, 9878-9886.
58. Simpson, G. J.; Rowlen, K. L. *J. Am. Chem. Soc.* **1999**, 121, 2635-2636.
59. Rao, Y.; Tao, Y.-s.; Wang, H.-F. *J. Chem. Phys.* **2003**, 119, 5226-5236.
60. Casero, E.; Darder, M.; Pariente, F.; Lorenzo, E.; Martin-Benito, J.; Vazquez, L. *Nano Lett.* **2002**, 2, 577-582.
61. Siepmann, J. I.; McDonald, I. R. *Langmuir* **1993**, 9, 2351-2355.
62. Ahn, Y.; Saha, J. K.; Schatz, G. C.; Jang, J. *J. Phys. Chem. C* **2011**, 115, 10668-10674.

63. Saha, J. K.; Ahn, Y.; Kim, H.; Schatz, G. C.; Jang, J. *J. Phys. Chem. C* **2011**, *115*, 13193-13199.
64. Hore, D. K.; Beaman, D. K.; Parks, D. H.; Richmond, G. L. *J. Phys. Chem. B* **2005**, *109*, 16846-16851.
65. Evans, G. T. *J. Chem. Phys.* **1981**, *74*, 4621-4626.
66. Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y. T.; Parikh, A. N.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7152-7167.
67. Bourguignon, B.; Zheng, W.; Carrez, S.; Ouvrard, A.; Fournier, F.; Dubost, H. *Phys. Rev. B* **2009**, *79*, 125433.
68. Guo, Z.; Zheng, W.; Hamoudi, H.; Dablemont, C.; Esaulov, V. A.; Bourguignon, B. *Surf. Sci.* **2008**, *602*, 3551-3559.
69. Cimat, K.; Moore, H. J.; Lee, T. R.; Baldelli, S. *J. Phys. Chem. C* **2007**, *111*, 11751-11755.
70. Hutt, D. A.; Liu, C. *Appl. Surf. Sci.* **2005**, *252*, 400-411.
71. Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 9022-9028.
72. Denayer, J.; Delhalle, J.; Mekhalif, Z. *J. Electroanal. Chem.* **2009**, *637*, 43-49.
73. Chinwangso, P.; Jamison, A. C.; Lee, T. R. *Acc. Chem. Res.* **2011**, *44*, 511-519.
74. Jennings, G. K.; Yong, T.-H.; Munro, J. C.; Laibinis, P. E. *J. Am. Chem. Soc.* **2003**, *125*, 2950-2957.
75. Hosseinpour, S.; Hedberg, J.; Baldelli, S.; Leygraf, C.; Johnson, M. *J. Phys. Chem. C* **2011**, *115*, 23871-23879.
76. Dilimon, V. S.; Denayer, J.; Delhalle, J.; Mekhalif, Z. *Langmuir* **2012**, *28*, 6857-6865.

77. Fonder, G.; Cecchet, F.; Peremans, A.; Thiry, P. A.; Delhalle, J.; Mekhalif, Z. *Surf. Sci.* **2009**, *603*, 2276-2282.

Chapter 4: Monitoring Localized Initial Atmospheric Oxidation of Alkanethiol-covered Copper using Sum Frequency Generation Imaging Microscopy: Relation between Monolayer Properties and Cu₂O Formation

4.1. Introduction

Copper is widely utilized in a number of different industrial roles, which include acting as a major component in heat exchangers and electrical applications due to its high thermal and electrical conductivity. It has been proven that exposure to some constituents from the atmosphere (such as oxygen, water, and organic acids) are needed to be controlled to prevent formation of the oxides on copper surfaces. Localized types of corrosion attack on reactive metals and alloys have been studied intensively due to presence of susceptible domains that are associated with inherent surface defects of metals such as phase inclusions and grain boundary regions.¹ Since these vulnerable domains are generally smaller in area than the less reactive metal matrix, it is reasonable to make use of high resolution imaging techniques to reveal local chemical nature of these corrosion-initiating sites. Surface images that provide both spatial and chemical information on the surface will enable the identification of these sites and the possible chemical processes that initiate the corrosion.

There had been numerous studies to examine the chemical information of local corrosion sites on metal and alloy surfaces thru techniques such as x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and secondary-ion mass spectrometry (SIMS), while morphology and surface structure of corrosion sites was

surveyed through scanning probe microscopy (SPM) techniques such as AFM and STM.²⁻⁴ Vibrational spectroscopic techniques such as Raman and IR spectroscopy provide further chemical information through a more specific identification of chemical functionalities but enhancing it with spatial visualization across the surface of interest provide a more comprehensive description how local corrosion sites develop on the surface. Several methods such as photo-electron emission microscopy (PEEM), near edge X-ray absorption fine structure microscopy (micro-NEXAFS), surface probe microscopy (SPM), and miscellaneous microelectron and X-ray techniques have been developed that are capable of surface imaging which provide spatial, temporal, and chemical description in varying degrees but most require high vacuum conditions that limits the possibility of monitoring corrosion processes in ambient conditions.^{5, 6}

In contrast, Sum Frequency Generation Imaging Microscopy (SFGIM) provides the unique advantage of combining microscopy and spectroscopy into one surface-sensitive technique that operate at standard atmospheric conditions. In addition, it is suitable for monitoring interfacial chemical activity due to the inherent capabilities such as high surface specificity, submonolayer sensitivity, chemical selectivity, and a spatial resolution of approximately 1 μm .^{7, 8}

The ability of SFGIM as a spectroscopic imaging technique to characterize the local chemistry of oxidation sites is demonstrated by observing an alkanethiol-covered copper surface undergoing atmospheric oxidation. By modifying the surface properties of copper to increase its corrosion resistance, various organic and inorganic coatings have

been proposed. Among these coatings, self-assembled monolayers (SAMs) are found to be appropriate candidates as model systems for corrosion inhibitors due to their simple and spontaneous chemical adsorption, densely packed structure, and nanoscale thickness. The densely packed monolayer of alkanethiol self-assembled monolayers (SAMs) provides a low-permeability barrier that hinders access of oxidative elements in the air, specifically atmospheric oxygen and water, to metal surface.⁹ Previous studies suggest that alkanethiols are effective against atmospheric and aqueous oxidation of reactive substrates by forming thin (on the order of 2.0 nm thick), high-crystalline molecular barrier films on metals, alloys and semiconductors.¹⁰⁻¹² The SFGIM technique was involved in previous analyses making use of alkanethiol SAMs to study fundamental initial corrosion processes.^{7, 13-18} However, mapping the progression of initial corrosion on Cu-SAMs surface as measured by the SFG nonresonant phase shift and its spatial effect on monolayer order has not been explored with the SFGIM technique.

The susceptibility of metal-SAMs surfaces to localized oxide formation is largely dependent on the surface composition and monolayer integrity. These determining factors can be independently evaluated by constructing spatial maps and parameter distributions of nonresonant phase, monolayer orientation and packing defects extracted from fitted SFGIM spectral data. By chemically stripping the native oxide of the copper surface using amidosulfonic acid (ASA), the spontaneous atmospheric oxidation of Cu was observed as a change in the nonresonant phase response of SFG spectral lineshapes obtained from the SFGIM setup (1064 nm). In this study, the spatial correlations of monolayer order (in terms of conformation and orientation) are evaluated against the

two-dimensional distribution of the relative nonresonant phase which provides kinetic information of the oxide growth.

4.2. Background: SFG and the Nonresonant Signal Contribution

The definition of sum frequency generation (SFG) has been discussed in Chapters 2 and 3. The focus of the theoretical section is primarily on the convolution of the resonant signal with the nonresonant background in relation to a substrate that contains surface properties from Cu and its oxidized form, Cu₂O.

As seen from equation 4-1, the intensity $I(\omega_{\text{SF}})$ of the generated sum frequency beam is proportional to the square of the induced polarization $P^{(2)}$ on the surface due to the coming together of the electric fields of the two incident beams (E_{IR} , E_{vis}). The term that relates the induced polarization response to the electric fields is called the second order nonlinear susceptibility tensor $\chi_{\text{eff}}^{(2)}$. This has two components, the χ_{nr} coming from the nonresonant background of the surface and the resonant term χ_{r} , which contains the vibrational spectroscopic information. In equation 4-2, $\beta^{(2)}$ is the hyperpolarizability containing vibrational information averaged over all molecular orientation, which is composed of the Raman polarizability and the IR dipole transition. ω_{IR} , ω_{q} , and Γ_{q} are the frequency of the IR beam, frequency of the normal mode and the damping constant of the qth vibrational mode, respectively.

$$I_{\text{SF}} \propto |P_{\text{SF}}^{(2)}|^2 \propto |\chi_{\text{eff}}^{(2)}|^2 I_{1064\text{nm}} I_{\text{IR}} \quad 4-1$$

$$\chi_{\text{eff}}^{(2)} = \chi_{\text{NR}}^{(2)} + \chi_{\text{R}}^{(2)} = \chi_{\text{NR}}^{(2)} + \sum_{\text{q}} \frac{N \langle \beta^{(2)} \rangle}{\omega_{\text{q}} - \omega_{\text{IR}} - i\Gamma} \quad 4-2$$

It has to be noted that the two laser beams are co-propagating and the emitted SFG signal at a specific angle is directional and coherent based on the conservation of momentum where the beams are aligned along the plane of incidence. In polar coordinates, the susceptibility tensor $\chi_{\text{eff}}^{(2)}$ are described with magnitude and phase:

$$I_{\text{SFG}} \propto |\chi_{\text{eff}}^{(2)}|^2 = \left| \chi_{\text{R,ijk}}^{(2)} e^{i\delta(\omega_{\text{IR}})} + \chi_{\text{NR,ijk}}^{(2)} e^{i\epsilon} \right|^2 = |\chi_{\text{R,ijk}}^{(2)}|^2 + |\chi_{\text{NR,ijk}}^{(2)}|^2 + 2|\chi_{\text{R,ijk}}^{(2)}||\chi_{\text{NR,ijk}}^{(2)}|\cos(\epsilon - \delta(\omega_{\text{IR}})) \quad 4-3$$

$$I_{\text{SFG}} \propto \left| \chi_{\text{R,ijk}}^{(2)} e^{i\delta(\omega_{\text{IR}})} + \sum_{\text{q}} \frac{N \langle \beta^{(2)} \rangle}{\omega_{\text{q}} - \omega_{\text{IR}} - i\Gamma} e^{i\epsilon} \right|^2 \propto \left| \chi_{\text{R,ijk}}^{(2)} e^{i\phi} + \sum_{\text{q}} \frac{N \langle \beta^{(2)} \rangle}{\omega_{\text{q}} - \omega_{\text{IR}} - i\Gamma} \right|^2 \quad 4-4$$

The convolution of the resonant and nonresonant components of the susceptibility gives rise to the lineshape of the SFG spectrum. For a single molecular resonant response, a positive value of the cross term in equation 4-3 registers a peak in the spectrum; and a dip, if otherwise. For metals, the effect of the nonresonant component of the susceptibility is not negligible as compared to dielectric substrates such as glass. Hence, the effect on the cross-term of the $\chi_{\text{NR}}^{(2)}$ is more pronounced for molecule-metal systems. Here, $\phi = \epsilon - \delta$ is the difference between the phase of $\chi_{\text{NR}}^{(2)}$ and the part of the phase in $\chi_{\text{R}}^{(2)}$ that is independent of mid-IR frequency ($\omega_{\text{q}} - \omega_{\text{IR}} - i\Gamma$) contains a mid-IR frequency-dependent phase) and will be referred to hereafter as the phase shift. To obtain the absorbate parameters such as the resonant frequency, the vibrational amplitude, and phase shift, the experimental spectra are fitted to equation 4-4. When multiple vibrational modes are present, the second term in equation 4-4 becomes a summation over all modes.

The coherent nature of SFG introduces complications in the interpretation of the spectra as compared to linear vibrational spectroscopy, because there can be constructive and destructive interference between adjacent peaks as well as with the nonresonant background. This can especially be problematic when the nonresonant signal is strong, which is the case for most of metals.^{19, 20} The oxidation of the copper surface results to two oxidation states: Cu and Cu₂O. The surface electronic properties of these two surface components are different such that the nonresonant behavior of the surface is also more spatially heterogeneous. Previous SFG studies on the catalytic processes on pure copper surface suggest that copper oxide and adsorbed oxygen species on the copper surface affect the electronic structure of the subsurface atoms which directly affects the nonresonant background and the spectral shape of the SFG spectra.

4.3. Experimental Section

4.3.1. Sample Preparation and Exposure

Polycrystalline coupons (Goodfellow, 99.99%) of copper were used as sample material. The samples were rectangular with an area of 2 cm² and thickness of 1 mm. The samples were polished down to 0.25 μm using diamond compound, sonicated with ethanol for 5 min between each step. The standard reagent of alkanethiol was used as received to prepare the SAMs on the metals. (ODT, CH₃(CH₂)₁₇SH, 98%; anhydrous, 99% minimum; Ethanol, absolute-200 Proof, Aaper). Before the copper coupon was dipped for two hours in ODT-ethanol solution for SAMs deposition, the coupon was first chemically etched to remove native oxide using amidosulfonic acid (ASA, 99.5%, EMD) solution for 30 seconds and then rinsed with ethanol. After the SAMs deposition, the

metal sample is then washed with ethanol and dried with nitrogen gas stream before it was inserted into the sample cell.

The sample cell is made of glass and metal fittings that can maintain high vacuum pressures. The CaF_2 windows of the cell permit transmission of the input (1064 nm and IR) beams. A thinner quartz window was installed on the side of output beam of the SFG (~815 nm) due to space constraints on the detection side of the SFG microscope. The freshly polished sample is placed inside and the cell is evacuated down to pressures of 1×10^{-5} Torr to prevent atmospheric oxidation of the copper surface. The cell is then backfilled with inert N_2 gas before the SFGIM measurement. Oxidation of the copper sample was performed by opening the sample cell to the atmosphere for 10 hours while image acquisition is being performed.

4.3.2. SFGIM Data Analysis

The procedures on the image acquisition of SFGIM are discussed in Chapter 2 and 3. The IR frequency range used in the fitting analysis accommodates the C-H vibrational frequencies for the terminal methyl and chain methylene groups of the ODT alkanethiol. The images were processed using ImageJ and extraction through the SFGIM image stack generates the SFG spectrum. By dividing the SFGIM image into smaller regions-of-interests (ROIs) of at a length scale of 10×10 pixel, the spatial distribution of SFG spectral information is demonstrated for the alkanethiol-covered copper undergoing oxidation. The post-analysis was accomplished by stacking images from $2750\text{--}3050\text{ cm}^{-1}$ where the 61 images were processed by extracting the intensities from each region-of-

interest (ROI) and plotted as a function of the IR wavenumber using ImageJ and Mathematica.

The partitioning of one whole image to 10 x 10 pixel starts left to right and from top to bottom. After the fitting routine is finished, the corresponding data are collected as SFG intensity ratios which are used for further analysis of the orientation of the alkanethiols on the Cu sample.

4.4. Results and Discussion

4.4.1. Nonresonant Response of SAMs-Metal Systems

The transformation of the spectral lineshape of SAMs-metal samples as a function of the nonresonant phase of the SFG signal has been widely known to have a direct link to the surface electronic properties of the substrate at the interface. As presented in previous studies in SFG measurements of metal surfaces, factors that affect the nonresonant response include the experimental geometric configuration of the SFG setup,^{19, 21} the pump beam wavelength,^{22, 23} and the metal electronic structure.^{20, 24} The difficulty of SFG analysis on metals had led to studies that employ minimization of the nonresonant background using theoretical, such as maximum entropy method (MEM) analysis, and experimental methods (i.e. temporal delay).²⁵⁻³⁰

However, these methods prevent the acquisition of nonresonant information that describes changes in electronic properties of the metal surface undergoing oxidation. By employing these experimental methods an amount of spectral information is lost that prevent accurate SFG analysis to generate a reliable description of the molecular order.

Hence, the orientation and conformation analysis using SFG spectral data are carried out using fitting analysis that include change in nonresonant behavior as an effect of metal properties and pump beam wavelength.

The advantage of using SFGIM to reveal hidden domains of monolayer defects has been demonstrated previously using different length scales in surface dimensions.³¹ The systematic bias of conventional averaged SFG techniques towards monolayers with signal-favored orientation distributions is minimized in SFGIM wherein the spatial detection of localized defect sites is allowed. SFGIM brings to account regions that contain less signal-favored molecular structures to be included in the total distribution of monolayer order.

The spatial sensitivity of SFGIM is useful in monitoring change in monolayer order and nonresonant background during surface oxidation. As a direct method for identification of the anodic sites on surface, the regions that register a sizeable shift in nonresonant phase and increase in monolayer defect can be identified to have undergone atmospheric oxidation.

To produce a two-dimensional reference to which all spatial changes in SFG information can be correlated against, an initial homogeneous state for the sample surface is required. Hence, ASA, a chemical etchant, is used to remove the native oxide layer of the copper surface. This permits the initiation of the spontaneous atmospheric oxidation of the metal surface. These domains undergoing oxidation can be detected closely by

using the SFGIM technique through the use of spatial maps of orientational and conformational parameters gathered from fitted local spectra of the monolayer. By comparison between the change in CH_3 tilt angle and amount of CH_2 alkyl chain defects of prior and after images of the surface, the expected growth of the copper oxide film can be assessed effectively in the two-dimensional space of the substrate surface.

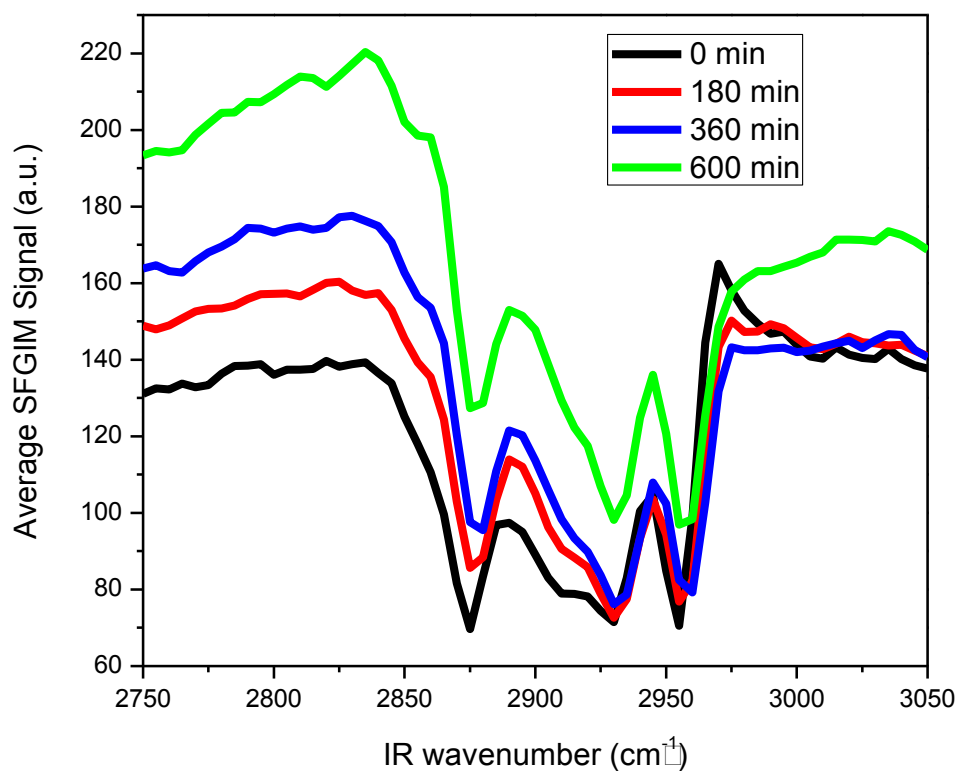


Figure 4-1. Spectral comparison of SFG lineshapes of Cu-ODT undergoing oxidation using averaged SFGIM data (1064 nm).

Figure 4-1 shows the SFG spectral response of ODT with the oxidation of the Cu substrate. The formation of thin oxide film beneath the ODT SAMs had been previously

studied using SFG spectroscopy complemented with reflection–absorption infrared spectroscopy (RAIRS), cathodic reduction and X-ray photoelectron spectroscopy (XPS).³² This study demonstrated sensitivity of SFG to detect the overall change in substrate composition by tracking the nonresonant response of the ODT-metal system when undergoing oxidation. The transformation of the spectral lineshape of the Cu-ODT using the 1064nm probe beam is much more subtle as compared to results from previous study³² which used 532 nm beam. At a certain wavelength of the probe, the optical properties of the metal (i.e. complex refractive index) surface will dictate the local field effects of the surface. The tensor elements of the effective susceptibility of the resonant SFG signal are dependent on these local fields and will have a direct influence on the convolution of the resonant and nonresonant signals which defines the spectral lineshape.

4.4.2. Relationship of the Relative Nonresonant Phase to the Oxidation Rate

As a source of important substrate information, the nonresonant SFG signal can be used as a measure of localized oxidation. Hosseinpour *et al.* were able to observe the effect of oxide formation to the nonresonant phase of Cu-ODT spectra using averaged SFG signal as a semi-quantitative measure of the oxidation kinetics.³² In Figure 4-2, the spatial maps and histograms of the nonresonant phase exhibited a shift from a distribution mean of ~1.5 to ~2.2 radians as an effect of surface oxidation. In table 4-1, based on listed values for the statistical mean and distribution width, a slight increase in the distribution width (coincides with the shift in the mean) was observed during exposure. These suggest that the distribution shift in the substrate signal as represented by the

nonresonant phase corresponds to the overall positive increase in concentration of oxidized Cu.

Table 4-1. Statistical parameters of the histogram distributions of the relative nonresonant phase (Gaussian fit).

Time (min)	<i>Relative nonresonant phase (rad)</i>	
	Mean	Distribution width (σ)
0	1.47	0.30
180	1.74	0.41
360	1.99	0.41
600	2.16	0.43

In Figure 4-3, the rate of the relative nonresonant phase shift of each imaging ROI were mapped spatially showing surface domains (in red) that registered the highest rates (calculated by using the least-squares method). These ROIs are identified as areas on the sample surface that had the most relative increase in Cu₂O concentration. However, different regions on the sample have different initial nonresonant relative phase values prior to air exposure. This demonstrates the ability of SFGIM to accurately define the spatial heterogeneity of the Cu surface using nonresonant phase that contains local information to the surface electronic structure of the oxidized metal substrate.³³⁻³⁵

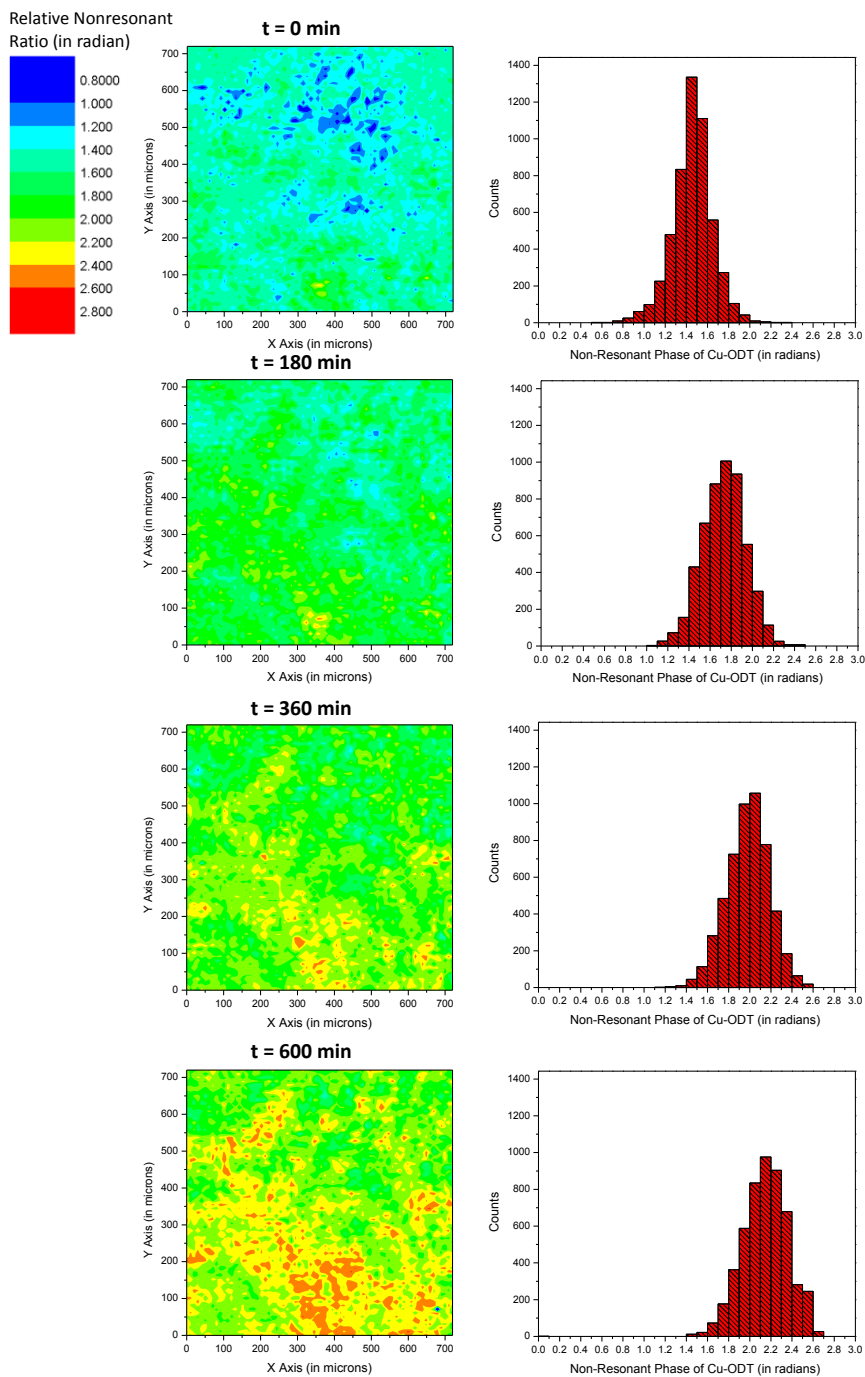


Figure 4-2. Maps and histograms of the relative nonresonant phase upon atmospheric oxidation. Regions in yellow represent substrate domains that contain higher concentration of Cu_2O .

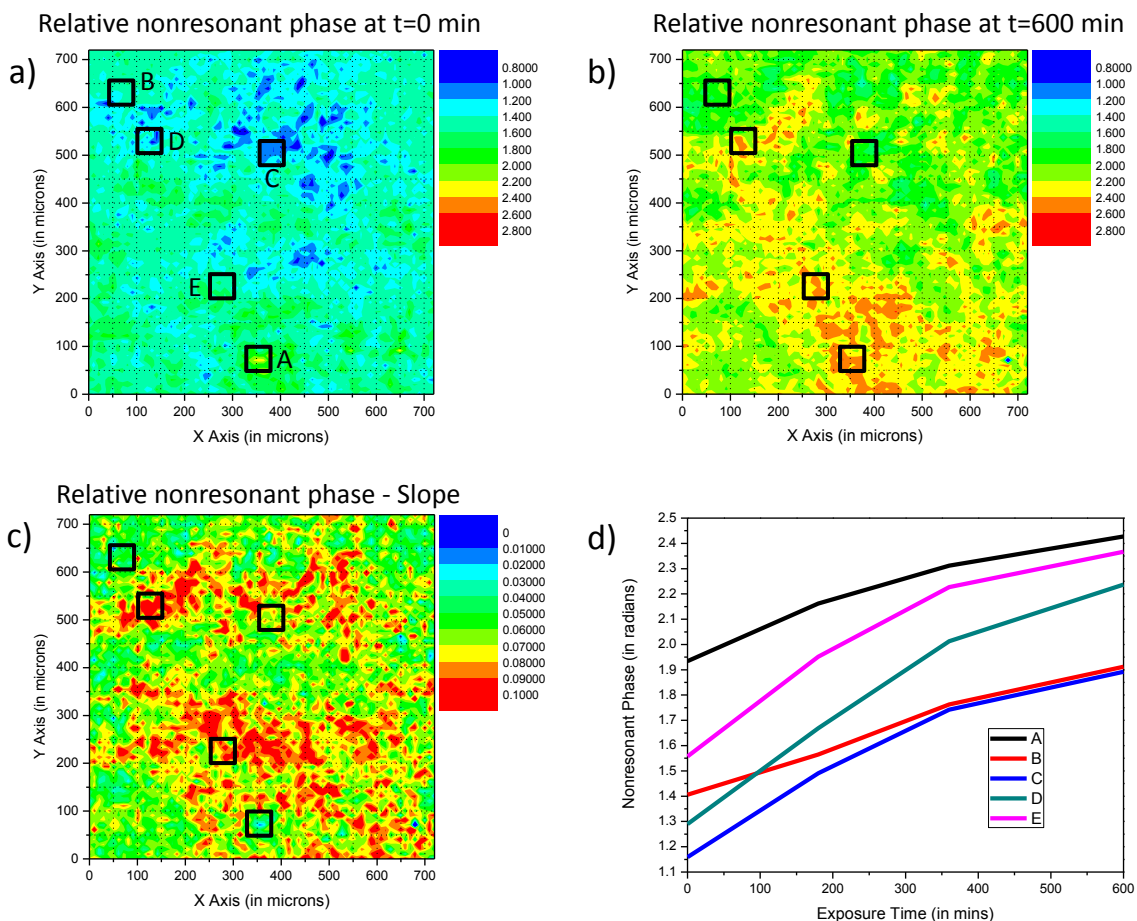


Figure 4-3. (a and b) Maps of relative nonresonant phase at $t = 0$ min and $t = 600$ mins, respectively; (c) Map of calculated slope (rate of change) of the relative nonresonant phase; (d) Scatter plot of the nonresonant phase as function of exposure from selected ROIs (size: 50 x 50 square pixels) labeled with a-e.

At different specified regions (regions A-E in Figure 4-3), it is shown that there is an overall increase in the nonresonant phase of the entire Cu surface with the individual initial phase values varying from 1 to 2 radians (~ 60 to 120 degrees). This initial state of heterogeneity can directly affect the progress of oxidation. Using the individual

nonresonant phase maps (from time 0 mins to 600mins), different regions on the surface have different initial oxide concentrations with varying local oxidation rates. Based on the local relative phase of regions C and D, these represent areas with low initial concentration of oxidized species that had high oxidation rates. These regions are relatively more reduced compared to the rest of the surface. The availability of oxidizable Cu resulted to higher occurrence of oxidation activity. As expected, region A contains a high level of oxidized species with low rates of oxidation. However, special cases such as region E also incurred a high rate of oxidation but started oxidizing at a higher initial nonresonant phase (high initial concentration of oxidized species).

At the length scale being probed by SFGIM, it can be proposed that the initial concentration of oxidized copper is not the only factor that influences the rate of localized oxidation. The initial state of SAM conformational and orientational order also contributes to the local oxidation kinetics. These effects of the monolayer order to the oxidation activity are efficiently evaluated using the corresponding spatial maps which are correlated with the surface properties represented by the local nonresonant signal.

4.4.3. Spatial Maps of Conformation and Orientation of Cu/ODT

As a measure the monolayer conformation of the ODT SAMs, the presence of gauche defects on alkanethiol chains was often estimated using the signal intensity of the symmetric methylene stretch.³⁶⁻³⁸ From the histograms of the intensity ratio of the symmetric modes of the methylene and methyl group in Figure 4-4, an overall increase in alkyl chain defects is observed as the distribution shifts towards higher methylene

intensities. Hence, the overall conformational disorder of the surface is increased as a result of the local oxidation.

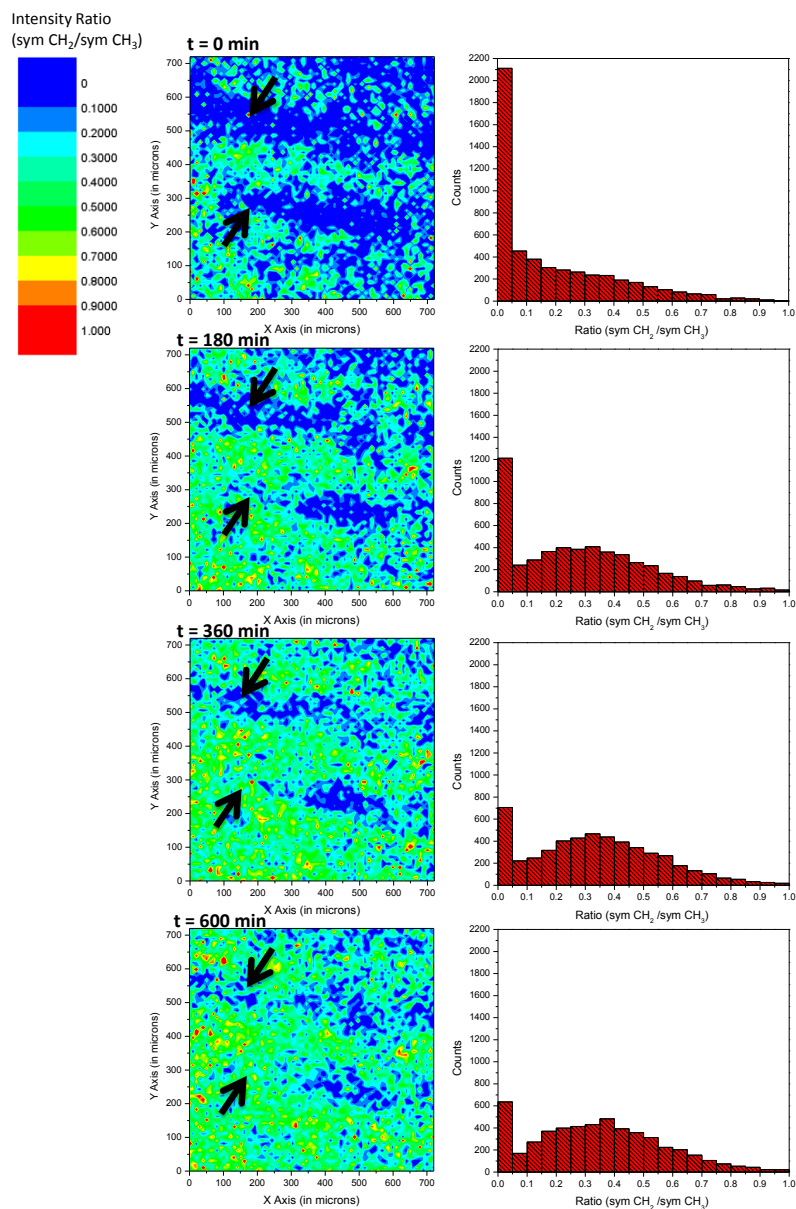


Figure 4-4. Maps and histograms of intensity ratios of CH₂-sym/CH₃-sym before and after air oxidation of the ODT-Cu samples (10x10 pixel ROI Maps). Arrows depicting areas that are well ordered (blue-colored regions) showing decrease in domain size as oxidation progresses from t = 0 min to t = 600 mins.

It also must be noted that the initial conformational state of the surface (at $t = 0$) is spatially heterogeneous such that the blue-colored ROIs represent regions with the least amount of gauche defects. As the surface is oxidized, the regions with high packing densities (less defect concentrations) becomes smaller suggesting that oxidation process perturb these regions of these well-ordered monolayers. By comparing the conformation map from $t = 0$ to $t = 180$ min, the well-ordered ROIs (blue) are gradually filled in (from the domain edges) with gauche defects.

By comparing the individual spatial maps of the nonresonant phase and conformation response (Figure 4-2 and 4-4), the shift in nonresonant signal is not specific to ROIs that undergo increase in gauche defects. The local nonresonant phase is linked directly to the oxidation of Cu and, hence, any change in its value is caused by the formation of Cu_2O . The gauche defects are not locally correlated with the magnitude of the nonresonant phase, however, both of these parameters resulted to shifted distributions wherein there is an overall increase in the phase and chain disorder.

To fully picture the correlation of the nonresonant effect to the monolayer order in terms of conformation and orientation, the spatial effects of oxidation on the local monolayer orientations are presented in Figure 4-5. During the oxidation, the monolayer orientation evolved such that it shows regions with C_3 axis of the terminal methyl groups being more upright towards the surface normal. In table 4-2, the calculated distribution mean and width for the orientation intensity ratio demonstrates the shift and broadening of the overall orientation. Based on literature of studies on alkanethiol-gold systems using

SFG spectroscopy,³⁹⁻⁴¹ spectral assignments for the terminal methyl (CH₃) and methylene (CH₂) vibrational modes of ODT were determined. The assigned peaks are the following: the terminal methyl symmetric (CH_{3-sym}) stretch at 2875 cm⁻¹, methyl Fermi resonance(CH_{3-Fermi}) at 2940 cm⁻¹, and the CH₃ antisymmetric (CH_{3-asy}) stretch modes: out-of-plane (CH_{3-asy(op)} at 2950 cm⁻¹) and in-plane (CH_{3-asy(ip)} at 2965 cm⁻¹). Weaker vibrational stretches present in the spectrum at 2850 and 2915 cm⁻¹ are the methylene symmetric (CH_{2-sym}) and Fermi resonance (CH_{2-Fermi}) vibrational modes, respectively, that are present due to gauche defects in the alkyl chains.

Table 4-2. Statistical parameters of the histogram distributions of the orientation intensity ratio of CH_{3-sym}/CH_{3-asy(ip)} and methyl tilt angle (deg).

Time (min)	Intensity Ratio (CH_{3-sym}/CH_{3-asy(ip)})		Methyl Tilt Angles (deg)	
	Mean	Distribution width (σ)	Mean	Distribution width (σ)
0	0.76	0.51	37.0	11.4
180	0.93	0.54	34.1	9.5
360	1.10	0.60	31.8	8.1
600	1.13	0.65	31.6	8.0

By using the bond polarizability model and the formulas presented by Wang *et al.* and Hirose *et al.*, the orientation analysis from SFG spectral data is performed by recovering the fitted results of the peak intensity ratios of symmetric and antisymmetric (in-plane) stretches of the terminal methyl.⁴²⁻⁴⁵ The intensity ratio is plotted against the

tilt angle (θ) of the C_3 axis from the surface normal wherein a delta function distribution approximation is used to deduce the ensemble average orientation for each ROI. In Figure 4-6, the tilt angle results were already corrected with the appropriate refractive indices for Cu and Cu_2O by individually matching the intensity ratio to the corresponding nonresonant phase (Cu and Cu_2O) of each ROI to ensure reliability of tilt angle calculations.

As seen from Figure 4-5, there is a notable shift in the ROI distribution of the average intensity ratio and the calculated delta-function tilt angle wherein an overall decrease in the methyl tilt angle is observed. The average orientation shift towards a more upright terminal methyl group as an effect of oxidation on Cu-ODT was also confirmed previously by averaged SFG signals employing 532 nm pump beams.³²

Interestingly, the ROIs with high occurrence of tilt angle shifts are also the same regions that incurred highest amounts of Cu_2O as measured by the relative nonresonant phase (comparing Figures 4-2 and 4-5). These changes are consistent with the evolution of a more heterogeneous methyl environment at the surface as a result of exposure to corrosive conditions. It has been often demonstrated in previous studies (specifically using RAIRS) that both orientation and conformation of alkanethiols are typically altered (into a more disordered state) by the introduction of oxides to metal surfaces of coinage metals (such as Pt and Cu).^{9, 46-48} However, the spatial relationship of orientation and conformation to oxide formation could not be deduced using the RAIRS technique. From Figures 4-2 and 4-5, it is inferred from the individual parameter maps that the spatial change of the nonresonant phase and orientation are locally similar with exposure time.

This demonstrates that the monolayer orientation is sensitive to the local surface modification by oxide formation.

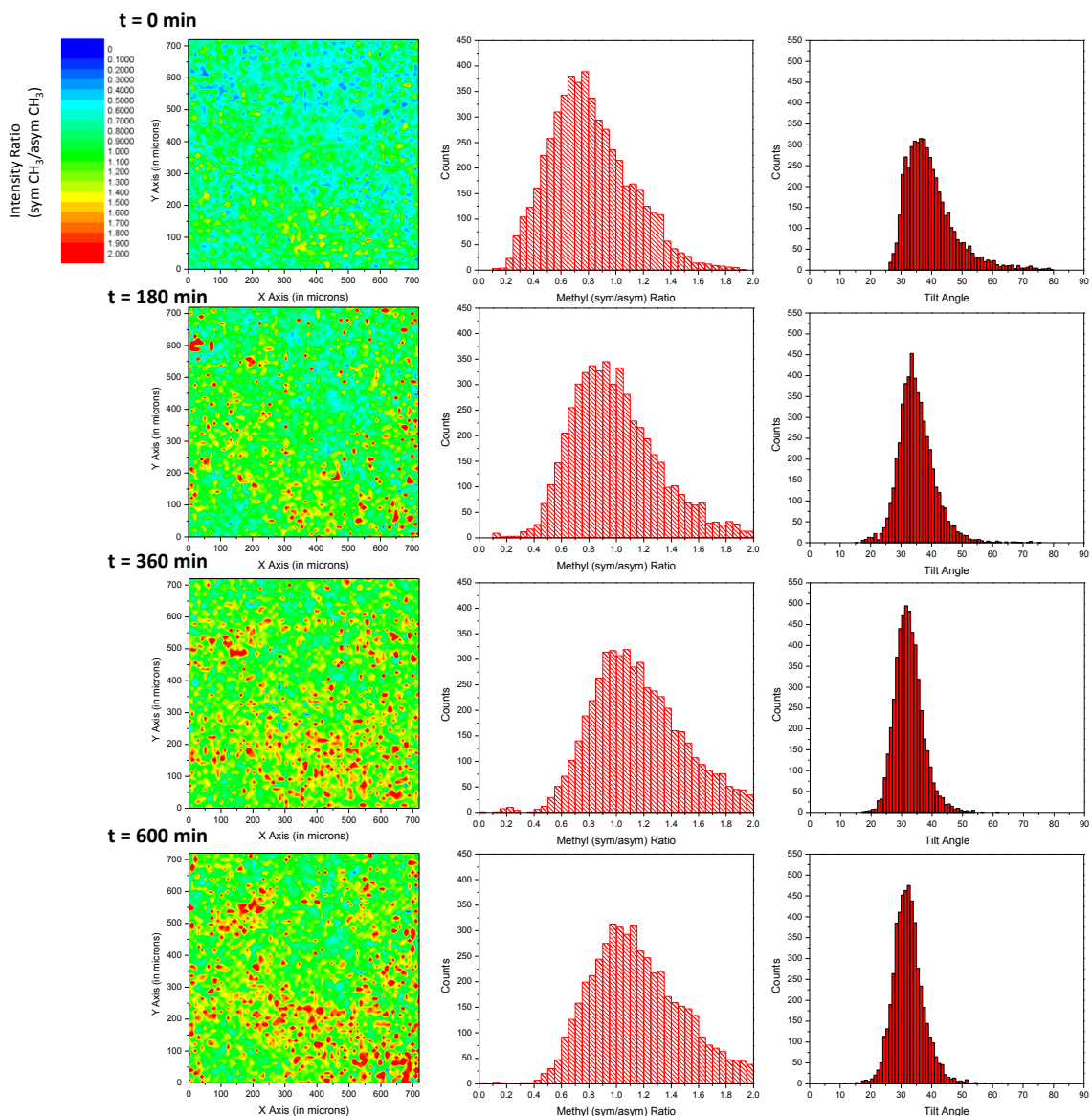


Figure 4-5. Maps and histograms of intensity ratios of $\text{CH}_3\text{-sym}/\text{CH}_3\text{-asym(ip)}$ before and after air oxidation of the ODT-Cu samples. Corresponding histograms of calculated methyl tilt angles.

4.4.4. Spatial Correlation of the Nonresonant Phase to the Monolayer Order

In Figure 4-6, a scatter plot is constructed to correlate two spectral parameters: nonresonant phase and $\text{CH}_3\text{-sym}/\text{CH}_3\text{-asym(ip)}$ intensity ratio. With exposure time, the correlated distributions (surrounded by an ellipsoid quantile to represent the distribution at 90 % confidence interval) shifts as an effect of oxide formation. From $t=0$ min to 600 mins, the increase in the distribution width of the correlated distribution (larger area for the ellipsoid quantile) suggest the disruption in the overall orientation of the alkanethiol.

However, by obtaining the terminal methyl tilt angles using the delta-function distribution approximation for each ROI from the experimental $\text{CH}_3\text{-sym}/\text{CH}_3\text{-asym(ip)}$ ratio, a narrower tilt angle distribution is recovered after the surface exposure. In Figure 4-6, the distribution shift shows a decrease in the average tilt angle towards 20° with a smaller distribution width.

It must be noted however that the range of calculated methyl tilt angles for the oxidized Cu is subject to the mathematical limit of the delta-function orientation curve. In Figure 4-7, it is demonstrated that at higher values of methyl intensity ratios (>1.0), the range of possible methyl tilt angles is narrower. For the range of ratios between 1.0 and 1.5, this corresponds to a narrow set of tilt angles (compare the angle distributions of A and B). As observed from the shift of the methyl ratios as the Cu surface is oxidized (histograms in Figure 4-5), the calculated methyl tilt angles becomes smaller (more upright) but also the distribution becomes narrower due to intrinsic nature of the delta-function orientation curve.

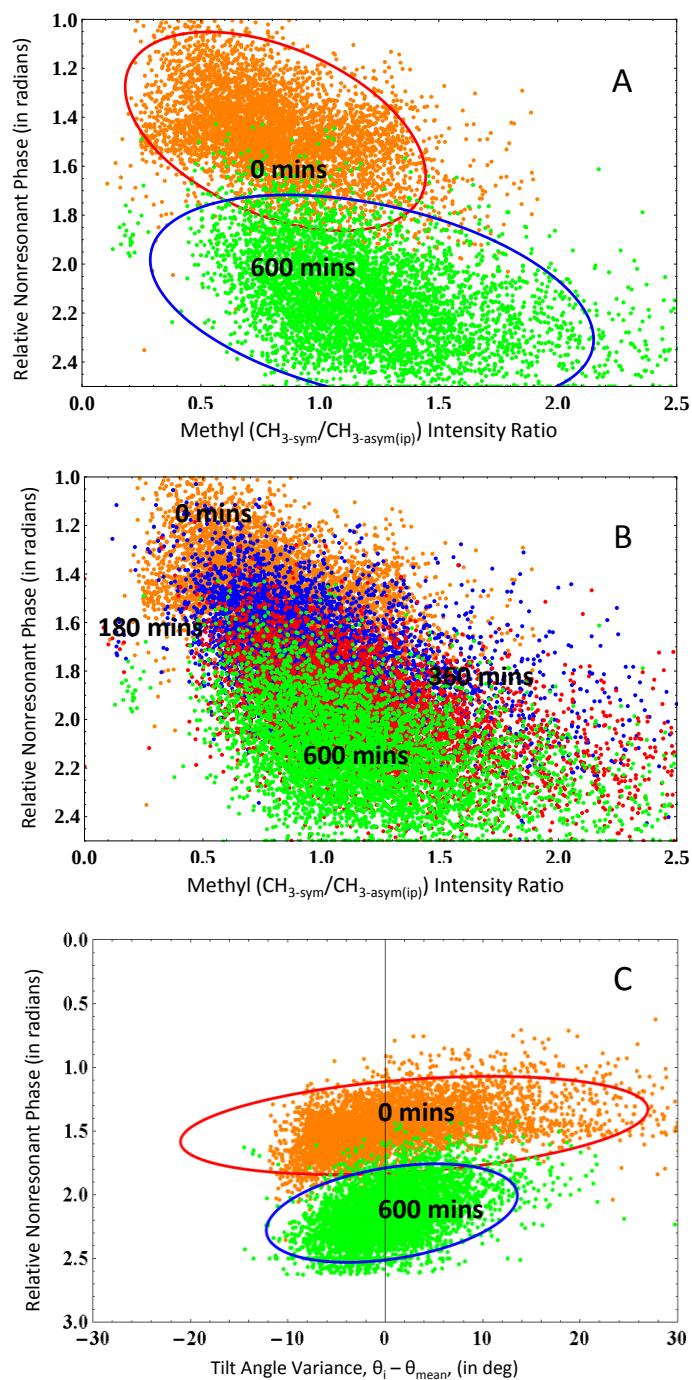


Figure 4-6. (A) Scatter plot of nonresonant phase vs. $\text{CH}_{3\text{-sym}}/\text{CH}_{3\text{-asym(ip)}}$ ratio for $t = 0$ min and $t = 600$ mins; (B) Scatter plot of nonresonant phase vs. $\text{CH}_{3\text{-sym}}/\text{CH}_{3\text{-asym(ip)}}$ ratio at different times (0, 180, 360, 600 mins) of sample exposure; (C) Scatter plot of nonresonant phase vs. tilt angle variance for $t = 0$ min and $t = 600$ mins.

It was demonstrated that the tilt angle calculated by the delta-function orientation analysis of an ROI is biased towards signals of molecules with favored structures as dictated by sensitivity of the SFG technique.³¹ Ideally, if a Gaussian distribution correction is applied, this artificial narrowing of orientation distribution at higher methyl ratios can be corrected. However, the actual Gaussian distribution widths of each ROI are unknown. Hence, there is need for further evaluation on how to acquire the individual orientation distributions of each ROI. In the future, this problem can be resolved by changing the experimental configuration of SFGIM using different polarizations and beam geometries.

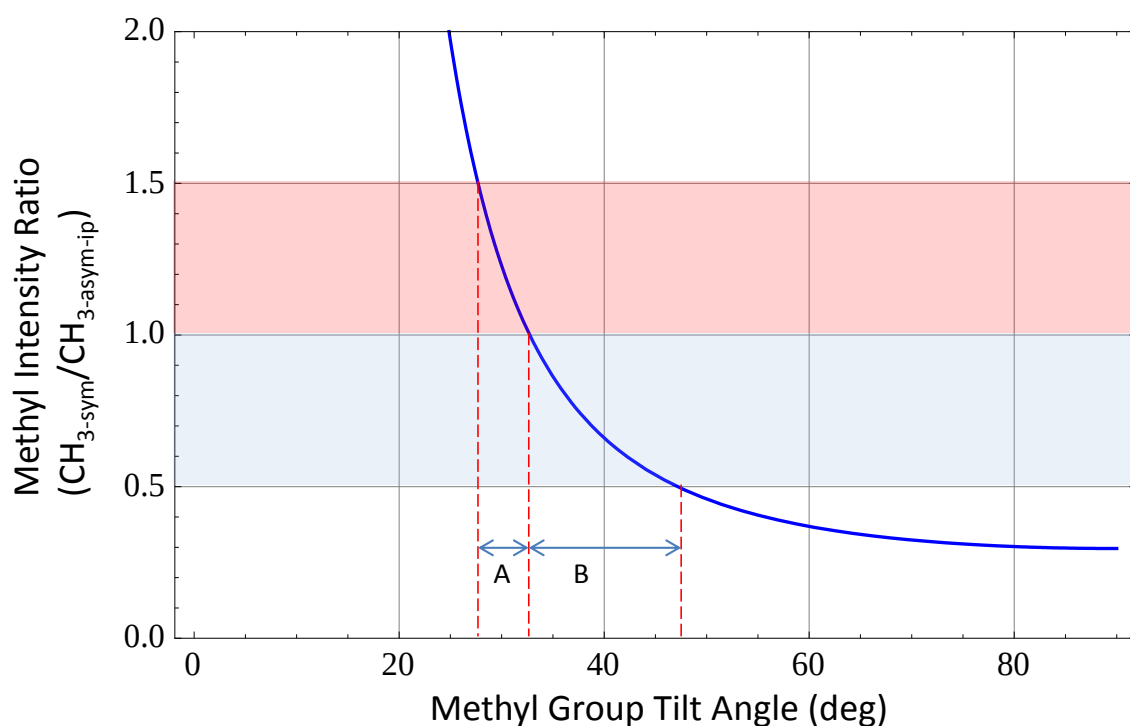


Figure 4-7. The orientation curve calculated by using the delta-function distribution approximation.

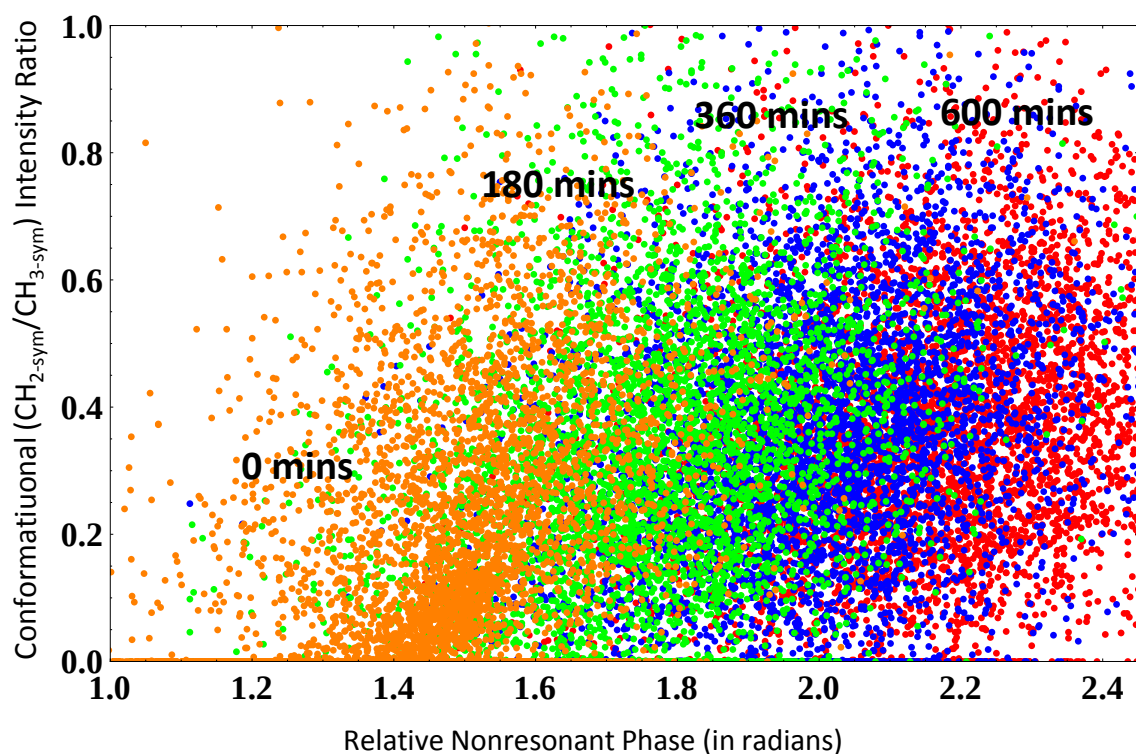


Figure 4-8. (Left) Scatter plot of conformation ratio vs. nonresonant phase; (right) contour plot of conformation ratio vs. nonresonant phase at different times (data points colored orange, green, blue, and red are for exposure times of 0, 180, 360, 600 mins, respectively) of sample exposure.

The individual maps of intensity ratios of $\text{CH}_{3\text{-sym}}/\text{CH}_{3\text{-asym(ip)}}$ is spatially correlated to the amount of local oxide as measured by the relative nonresonant phase. However, the spatial maps of gauche defects do not correlate locally with the change in nonresonant background (see Figures 4-2 and 4-4). In Figure 4-8, the correlated distributions of gauche defects and nonresonant phase incur overall shift towards a more disordered monolayer with exposure the shift in the nonresonant phase distribution corresponds to a shift in the distribution of gauche defects. This suggests that with the

introduction of Cu oxidation underneath the SAMs, the amount of chain disorder is increased in the overall conformational distribution of the sample as demonstrated by the deviation of the gauche ratio away from zero with exposure time. The correlation distribution (Figure 4-8) of conformational order and nonresonant phase also show increase in the distribution width (larger scatter of points) which further proves that the surface becomes more heterogeneous with oxide formation as a function of these two parameters.

In contrast to orientation order, the spatial maps of chain order do not correlate to the local oxide concentration. The conformation maps show a different spatial behaviour (compared to its nonresonant and orientation counterparts) due to the tendency of gauche defects to grow inward from the edges of surface domains with good crystallinity. The overall distribution of both monolayer tilt angles and chain conformation are collectively affected by the formation of oxide but the localized changes of these parameters behave differently.

In Figure 4-9, the map for the least-squares slope of nonresonant phase which represent the spatial distribution of the local oxidation rates is spatially correlated to the initial conformational order ($\text{CH}_{2\text{-sym}}/\text{CH}_{3\text{-sym}}$ intensity ratio). Based on the map of conformational order at $t = 0$ min, regions enclosed in boxes suggest that areas with well-ordered monolayers matches the areas with the highest change in nonresonant phase (as measured by the slope). Although the individual gauche maps do not follow the same spatial changes as compared to the orientation and nonresonant background, the highest

rates occurred on the more crystalline monolayer domains. This is an indication that the presence of well-ordered monolayers has a direct relation on the susceptibility of surface towards oxygen transport.

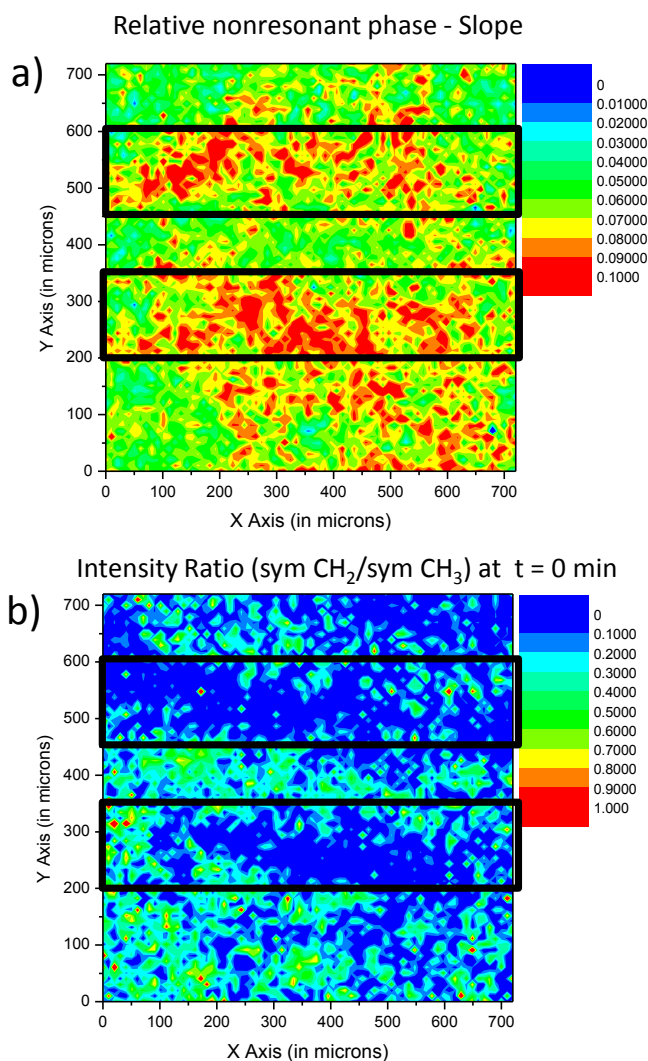


Figure 4-9. (a) Map of calculated slope (rate of change) of the relative nonresonant phase; (b) Map of the gauche ratio at t = 0 min.

Intuitively, areas with well-ordered monolayers are expected to have slower rates of oxidation since higher surface coverage inhibits oxygen transport.^{2, 9, 47, 48} It is

important to note, however, these molecules are not absolute surface barriers that completely inhibits oxygen transport from atmosphere into the alkyl chains and finally to the underlying Cu atoms. Various studies (both experimental and theoretical) have shown that the barrier properties of alkanethiols depend strongly on its molecular order.^{9, 10, 47, 49,}
⁵⁰ Molecular dynamic simulations of the oxygen transport through alkanethiols on Cu suggests that barrier resistances were a function of crystallinity, density and chain length of the SAMs.⁵⁰ Even highly ordered SAMs contain isolated populations of defect formations which are prone to local oxidation.

If the conformational maps at t=0 min and at t=600 mins are compared, the surface area of the domains that contain highly ordered monolayers becomes smaller during the exposure which shows that there is a localized increase in gauche defects that resulted from surface oxidation. By assuming that the Cu surface is spatially heterogeneous in terms of oxidation species (Cu and Cu₂O) prior to alkanethiol adsorption, it is implicit that assembly of monolayers that are free of defects are expected to appear on less oxidized areas (due to lower surface defects). As the alkanethiol-covered surface was exposed to air, there is a general increase in gauche defects on the entire surface. At t=600 mins the areas with low gauche defects decreased in surface area but these regions persisted to contain domains with the least amount of chain defects over the entire sample surface. These domains of well-ordered monolayers at the upper half of the surface area persisted to have the least amount of underlying oxidized Cu as observed from the nonresonant phase map at these regions (with phase values at <1.8 radians) at 600 mins of exposure.

These domains with ordered monolayers had the most concentration of reduced Cu species. In effect, these areas would have the most concentration of Cu to undergo oxidation. This explains why these areas would register higher rates of oxidation and, also, the highest amounts of orientation change (as seen from Figure 4-9). Hence, these are the important surface descriptions of Cu-ODT that can affect the oxidation kinetics of Cu-ODT: (1) initial state of surface oxide heterogeneity; (2) initial state of conformational order.

Thus, while the overall gauche defects increase as the signal (relative nonresonant phase) of the Cu_2O increases showing a positive correlation in the distribution, the local surface concentration of each ROI is not the cause of the presence of CH_2 defects; but the oxidation rate, $d[\text{Cu}_2\text{O}]/dt$, of Cu is the spatial cause of the gauche defect formation. The surface in this way is spatio-kinetically heterogeneous where different regions are in different stages of oxidation (Figure 4-3). Some regions are reduced while some are more oxidized. Those regions with higher concentration of reduced Cu (low relative nonresonant phase) will have higher oxidation rates while those regions with higher concentration of oxidized species will have lower oxidation rates. The oxidation rates are spatially varied, affecting the local formation of gauche defects.

4.5. Conclusion

The spontaneous atmospheric oxidation of Cu was observed as a change in the nonresonant phase response of SFG spectral lineshapes using the SFGIM setup which

employs a 1064 nm probe beam. Results from a recent study that utilized a 532-nm beam showed similar findings on the effect of Cu oxidation on the nonresonant signal. Hence, surface reactions such as surface oxidation can be monitored as an effect of the local electronic properties of the metal using nonlinear optical spectroscopy.

Results from the spatial distributional analysis shows that there is an overall decrease in the mean tilt angle and an increase in the amount of alkyl gauche defects as a result of the oxidation of the metal surface. There was a definite increase in the overall monolayer disorder as result of the surface oxidation. Spatial correlations between the orientation order and the relative nonresonant phase were monitored suggesting that the formation of the oxide induces orientation disorder in the localized regions of the surface. On the other hand, the changes in the conformational order were rather spatio-kinetically correlated with respect to the local oxidation rates.

We have demonstrated that SFGIM can be used to examine atmospheric corrosion processes when ODT on copper is exposed to atmosphere, to in situ monitor oxide growth with a significantly higher sensitivity to monolayer order (both orientation and conformation) than any other commonly used techniques in surface science.

REFERENCES

1. Roberge, P. R., *Corrosion Engineering: Principles and Practice*. McGraw-Hill: 2008.
2. Hutt, D. A.; Liu, C. *Appl. Surf. Sci.* **2005**, 252, 400-411.

3. Abe, Y.; Komatsu, M.; Okuhira, H. *Appl. Surf. Sci.* **2003**, 203-204, 859-862.
4. Kleber, C.; Hilfrich, U.; Schreiner, M. *Appl. Surf. Sci.* **2007**, 253, 3712-3721.
5. Vickerman, J. C., In *Surface Analysis – The Principal Techniques*, John Wiley & Sons, Ltd: 2009.
6. Lipkowski, J., Ross, P. N., Eds., *Imaging of Surfaces and Interfaces*. Wiley-VCH: New York, 1999.
7. Cimatu, K.; Baldelli, S. *J. Phys. Chem. B* **2006**, 110, 1807-1813.
8. Kuhnke, K.; Hoffmann, D. M. P.; Wu, X. C.; Bittner, A. M.; Kern, K. *Appl. Phys. Lett.* **2003**, 83, 3830-3832.
9. Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, 114, 9022-9028.
10. Zamborini, F. P.; Crooks, R. M. *Langmuir* **1998**, 14, 3279-3286.
11. Sheen, C. W.; Shi, J. X.; Maartensson, J.; Parikh, A. N.; Allara, D. L. *J. Am. Chem. Soc.* **1992**, 114, 1514-1515.
12. Schoer, J. K.; Ross, C. B.; Crooks, R. M.; Corbitt, T. S.; Hampden-Smith, M. J. *Langmuir* **2002**, 10, 615-618.
13. Cimatu, K.; Baldelli, S. *J. Am. Chem. Soc.* **2006**, 128, 16016-16017.
14. Cimatu, K.; Baldelli, S. *J. Phys. Chem. C* **2007**, 111, 7137-7143.
15. Cimatu, K.; Baldelli, S. *J. Am. Chem. Soc.* **2008**, 130, 8030-8037.
16. Cimatu, K.; Moore, H. J.; Barriet, D.; Chinwangso, P.; Lee, T. R.; Baldelli, S. *J. Phys. Chem. C* **2008**, 112, 14529-14537.
17. Cimatu, K.; Moore, H. J.; Lee, T. R.; Baldelli, S. *J. Phys. Chem. C* **2007**, 111, 11751-11755.

18. Hedberg, J.; Leygraf, C.; Cimat, K.; Baldelli, S. *J. Phys. Chem. C* **2007**, *111*, 17587-17596.
19. Tanaka, Y.; Lin, S.; Aono, M.; Suzuki, T. *Applied Physics B* **1999**, *68*, 713-718.
20. Harris, A. L.; Chidsey, C. E. D.; Levinos, N. J.; Loiacono, D. N. *Chem. Phys. Lett.* **1987**, *141*, 350-6.
21. Holman, J.; Davies, P. B.; Nishida, T.; Ye, S.; Neivandt, D. J. *J. Phys. Chem. B* **2005**, *109*, 18723-18732.
22. Dreesen, L.; Humbert, C.; Celebi, M.; Lemaire, J. J.; Mani, A. A.; Thiry, P. A.; Peremans, A. *Applied Physics B: Lasers & Optics* **2002**, *74*, 621.
23. Braun, R.; Casson, B. D.; Bain, C. D.; van der Ham, E. W. M.; Vreken, Q. H. F.; Eliel, E. R.; Briggs, A. M.; Davies, P. B. *J. Chem. Phys.* **1999**, *110*, 4634-4640.
24. Superfine, R.; Guyot-Sionnest, P.; Hunt, J. H.; Kao, C. T.; Shen, Y. R. *Surf. Sci.* **1988**, *200*, L445-L450.
25. Lagutchev, A.; Hambir, S. A.; Dlott, D. D. *J. Phys. Chem. C* **2007**, *111*, 13645-13647.
26. Shalhout, F. Y.; Malyk, S.; Benderskii, A. V. *The Journal of Physical Chemistry Letters* **2012**, 3493-3497.
27. Stiopkin, I. V.; Jayatilake, H. D.; Weeraman, C.; Benderskii, A. V. *The Journal of Chemical Physics* **2010**, *132*, 234503-9.
28. Sovago, M.; Vartiainen, E.; Bonn, M. *J. Phys. Chem. C* **2009**, *113*, 6100-6106.
29. Busson, B.; Tadjeddine, A. *J. Phys. Chem. C* **2009**, *113*, 21895-21902.
30. Curtis, A. D.; Reynolds, S. B.; Calchera, A. R.; Patterson, J. E. *The Journal of Physical Chemistry Letters*, *1*, 2435-2439.

31. Santos, G.; Baldelli, S. *J. Phys. Chem. C* **2012**, *116*, 25874-25887.
32. Hosseinpour, S.; Hedberg, J.; Baldelli, S.; Leygraf, C.; Johnson, M. *J. Phys. Chem. C* **2011**, *115*, 23871-23879.
33. Westerberg, S.; Wang, C.; Chou, K.; Somorjai, G. A. *J. Phys. Chem. B* **2004**, *108*, 6374-6380.
34. Lin, S.; Oldfield, A.; Klenerman, D. *Surf. Sci.* **2000**, *464*, 1-7.
35. Yamamoto, H.; Watanabe, N.; Wada, A.; Domen, K.; Hirose, C. *The Journal of Chemical Physics* **1997**, *106*, 4734-4744.
36. Ward, R. N.; Duffy, D. C.; Davies, P. B.; Bain, C. D. *J. Phys. Chem.* **1994**, *98*, 8536-8542.
37. Chechik, V.; Schonherr, H.; Vancso, G. J.; Stirling, C. J. M. *Langmuir* **1998**, *14*, 3003-3010.
38. Cimatu, K.; Baldelli, S. *J. Phys. Chem. C* **2007**, *111*, 7137-7143.
39. Bain, C. D. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1281-96.
40. Lambert, A. G.; Davies, P. B.; Neivandt, D. J. *Appl. Spectrosc. Rev.* **2005**, *40*, 103-145.
41. Buck, M.; Himmelhaus, M. *J. Vac. Sci. Technol., A* **2001**, *19*, 2717-2736.
42. Hirose, C.; Yamamoto, H.; Akamatsu, N.; Domen, K. *J. Phys. Chem.* **1993**, *97*, 10064-9.
43. Lu, R.; Gan, W.; Wu, B.-h.; Zhang, Z.; Guo, Y.; Wang, H.-f. *J. Phys. Chem. B* **2005**, *109*, 14118-14129.
44. Hirose, C.; Akamatsu, N.; Domen, K. *J. Chem. Phys.* **1992**, *96*, 997-1004.

45. Wang, H.-F.; Gan, W.; Lu, R.; Rao, Y.; Wu, B.-H. *Int. Rev. Phys. Chem.* **2005**, *24*, 191-256.
46. Li, Z.; Chang, S.-C.; Williams, R. S. *Langmuir* **2003**, *19*, 6744-6749.
47. Jennings, G. K.; Munro, J. C.; Yong, T.-H.; Laibinis, P. E. *Langmuir* **1998**, *14*, 6130-6139.
48. Jennings, G. K.; Yong, T.-H.; Munro, J. C.; Laibinis, P. E. *J. Am. Chem. Soc.* **2003**, *125*, 2950-2957.
49. Ishibashi, M.; Itoh, M.; Nishihara, H.; Aramaki, K. *Electrochim. Acta* **1996**, *41*, 241-248.
50. Srivastava, P.; Chapman, W. G.; Laibinis, P. E. *J. Phys. Chem. B* **2008**, *113*, 456-464.

Chapter 5: Orientation and Conformation Distribution Analysis of Alkanethiol on Cu-Ag, Patterned Cu-Zn and Brass Surfaces

5.1. Introduction

Brass is an alloy (Cu–Zn) widely used in the manufacture of various types of products across many industries. The corrosion behavior of Cu–Zn alloys has been extensively studied for a wide range of surface conditions with specific interest in preferential dissolution of zinc, stress corrosion cracking and pitting corrosion, when exposed to aggressive aqueous environments.¹⁻⁴

Different techniques have been proposed and applied to protect brass from corrosion and, among them, the chemical versatility of coating techniques are very interesting. Self-assembled monolayers (SAMs) are formed through a simple chemisorption process wherein an ultra-thin hydrophobic film prevents transport of oxidative agents such as atmospheric water and oxygen. It offers a great prospect to protect metal substrate from corrosive elements from the atmosphere. In this context, the application of organic monolayers on brass through self-assembly has been investigated to test its chemical barrier properties against surface oxidation.⁵⁻⁷ In the last 20 years, this approach has been used to modify a variety of metals and oxide surfaces. The most studied self-assembled monolayers (SAMs) are the alkanethiol ($\text{HS}-(\text{CH}_2)_x\text{-X}$) chemisorbed on surfaces of noble metals like gold.⁸⁻¹⁰ Most recently, studies the properties of alkanethiols as barrier films on oxidisable metals such Cu, Zn, and Ni have been reported.¹⁰⁻¹⁶

The monolayer order of adsorbed thiol molecules on different metal substrates were studied using SFGIM.^{14, 17-22} The results demonstrated that the presence of assembly defects and inhomogeneity of the monolayer on reactive metal surfaces influence the surface reactivity of the metal substrate such as atmospheric oxidation.

Over the past several years, it has always been assumed that a surface is homogenous based on the averaging of the acquired signal. By only considering the average signal, many local features of the surface are overlooked and thus, leading to an inaccurate understanding of the system. Due to development of various microscopic techniques that have atomic resolution of the surface, it has been demonstrated that the surface was spatially heterogeneous at different length scales: from atomic scale to micronscale. However, most of these microscopic techniques are incapable of detecting surface domains based on their chemical nature, specifically, the molecular order on the surface.

SFG imaging permits two-dimensional visualization of the surface structure and the relation of molecular environment to the surface physical properties. For example, it is known that physical properties such as surface wetting, friction, adhesion, and corrosion inhibition of the SAMs are influenced by the degree of molecular order of the film. Therefore, the ability of imaging spectroscopy to evaluate the quality and the structure of the monolayer films based on their inherent vibrational spectrum is beneficial in understanding localized chemical reactivity.

In this work, surface modification of the surface of the brass surface with an alkanethiol thin film were analyzed using spatial distribution analysis using the SFGIM

technique. Motivation for this work stems from the successful spectroscopic imaging using sum frequency generation (SFG) nonlinear technique on polycrystalline surfaces of copper undergoing initial atmospheric oxidation.¹⁶ In order to characterize the surface properties of chemically heterogeneous metal surfaces, a patterned metal surface comprising of copper islands deposited on bulk zinc was used to show spatial contrast of alkanethiols on a heterogeneous and reactive sample. By using this model surface, the capability of SFGIM to describe the monolayer order on brass alloy surfaces is evaluated for suitability in monitoring surface reactions on these complex surfaces.

5.2. Theory

SFG spectroscopy has been described thoroughly in Chapters 2 and 3. Also, the importance of the signal interference of the nonresonant background was discussed previously in the earlier chapters.

Several important advantages that makes SFG suitable for studying monolayers on metals include submonolayer detection limit, inherent surface sensitivity, and its capability to deduce orientational information of the surface molecules. The SFG signal depends on such diverse parameters as the number density and the average orientation of interfacial species, the phase and amplitude of the nonresonant contribution from the metal substrate compared to that of the adsorbate, the Fresnel factors, and possible resonances of the probe beam with optical transitions in the interfacial region.²³⁻²⁷ Another factor that may complicate interpretation of SFG signals is the possible enhancement of the SFG signal due to surface plasmons, similar to surface-enhanced Raman scattering on structured surfaces.²⁷ Thus, all of these factors are needed to be

taken into account in the accurate interpretation of SFG signals for the orientational analysis of the molecules. For this analysis, molecular hyperpolarizabilities are calculated using bond additivity models and Raman depolarization ratios. This analysis assumes free rotation about the C_3 symmetry axis for the methyl groups, an isotropic plane, and a delta-function distribution of tilt angle from the surface normal.²⁸⁻³³

5.3. Experimental Section

5.3.1. Sample Preparation and Exposure

The polycrystalline samples (zinc, copper and brass coupons) were polished with SiC grit paper, from 600 mesh in steps down to 2000 mesh, in water. Diamond paste with particle sizes 3 μm , 1 μm , and, finally, 0.25 μm was used as the final polishing steps, with ethanol used as lubricant. In order to remove residual diamond particles, each sample was sonicated in ethanol for 5 min between each step. After being polished, the sample was quickly rinsed with ethanol to remove residues of the electrolyte and then immediately immersed in the ODT/ethanol (20 mM) solution, dried with nitrogen gas, and placed into the sample cell. There it was kept in dry $\text{N}_2(\text{g})$, and aligned with the SFGIM instrumentation for image collection. All water used was obtained from a Millipore RiOs-8 and Milli-Q PLUS purification system, filtered through a 0.2 μm Millipak filter.

5.3.2. SFG Microscope and Data Analysis

The basic procedures for the SFG microscopy was discussed in full detail in Chapters 2 and 3. In this experiment, however, since the metal surfaces are reactive to the atmosphere, persistent use of the sample cell filled with inert nitrogen gas was employed in order to prevent atmospheric oxidation of the surface.

The intensity, I_{SFG} , of the SFG spectra was fitted to a Lorentzian function with Mathematica software. All experiment performed with the two input beams set to p polarization, where the output beam is also p-polarized (p-polarized 1064 nm beam, and p-polarized IR beam). p-polarized light refers to the light with polarization parallel to the plane of incidence as opposed to s-polarized light, which is light polarized perpendicular to the plane of incidence.

Images were continuously scanned the infrared frequency at every 5 cm^{-1} . Each image acquisition was 5000 shots per image from $2750\text{-}3050 \text{ cm}^{-1}$. Local spectra were obtained by averaging local regions of the surface with an approximate area of $10 \times 10 \text{ }\mu\text{m}^2$. Vibrational spectra were acquired by extracting the signal intensity from the images and plotting it as a function of the infrared frequency using a fitting program written in Mathematica.

5.4. Results and Discussion

5.4.1. Rationale for using Cu-Ag Binary Surface

A recent study involving SFGIM observed the growth of a metal oxide on an alkanethiol covered copper substrate.^{16, 22} This demonstrated the capability of SFGIM to interpret the monolayer order of the SAMs on a metal substrate susceptible to atmospheric oxidation. The analysis was made possible by constructing spatial maps of orientation and conformation parameters recovered from spectral fitting of 5×5 micron ROIs of the sample field-of-view (FOV). From the results of spatial correlations of these parameters, it was found that the nonresonant signal changes locally with the formation

of the oxide and has a direct effect on the local orientation and conformation of the copper surface.

To evaluate the reliability of the spatial analysis of monolayer order on alloy samples, metals surfaces with known domain patterns of heterogeneous compositions are initially investigated. By employing this method, the ability of SFGIM in defining monolayer orders as a function of composition heterogeneity can be compared between a surface with controlled (patterned) heterogeneity and a surface with random (naturally occurring) heterogeneity such as alloys.

Since there is recent established SFGIM information on Cu surfaces of extensively heterogeneous character (oxidized Cu surface), brass, which is largely composed of Cu (major component) and Zn (minor component), is chosen as the most viable surface that is closest in SGIM signal signatures that can be easily studied with SFGIM.

The first steps in accurately evaluating random heterogeneous features of brass starts with the use of a well-defined surface with large surface composition domains. A surface that contains a large region of Cu surrounded by Ag was utilized to provide a suitable flat sample that contained two specific surface regions of different elemental compositions.

Copper-Silver (binary surface)

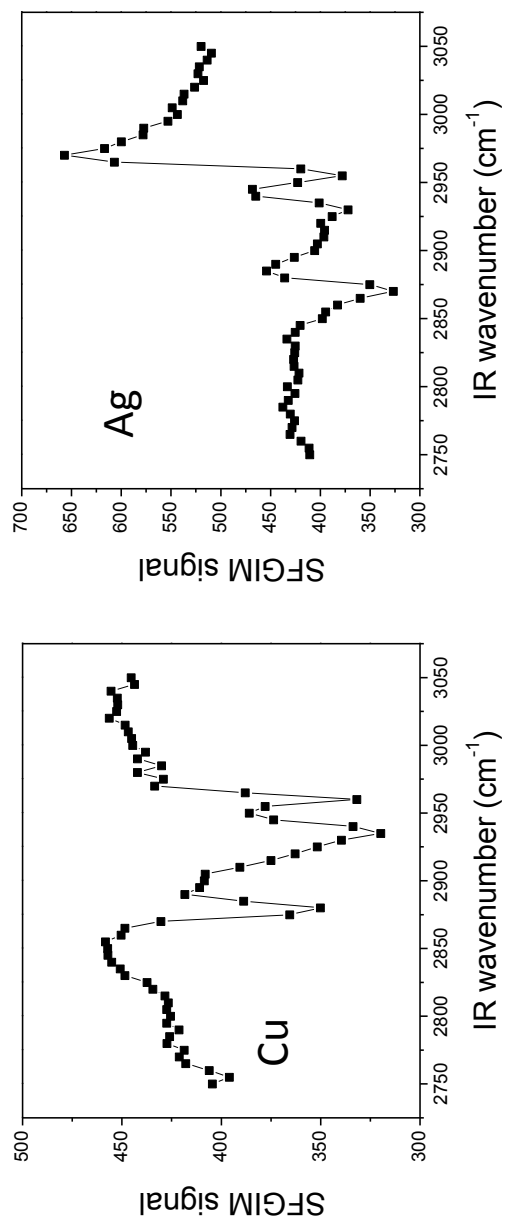
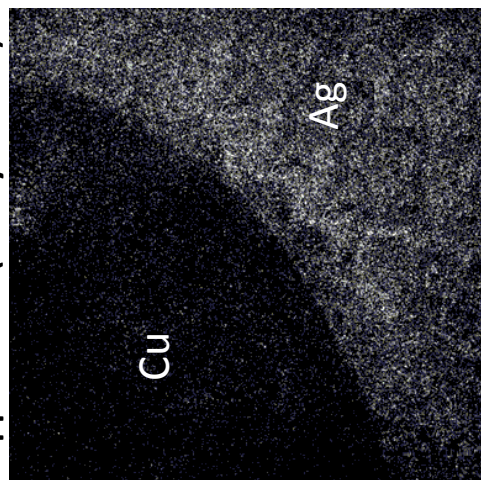


Figure 5-1. SFGIM image of Cu-Ag binary surface at 2875 cm⁻¹. Average SFGIM spectra of Cu and Ag grain domains. (720 x 720 pixel)

As seen in Figure 5-1, the SFGIM image at 2875 cm^{-1} is shown to have a Cu domain (darker region) and an Ag domain (lighter region) which is characterized by the image contrast, as a result in the difference in the baseline SFG nonresonant background signal of these surfaces. A similar image contrast is observed from the optical microscope image (Figure 5-2). From the results of the spectral-fitted nonresonant phase of the Cu-Ag surface, the two regions, that are clearly resolved in the spatial map of the relative nonresonant phase (see Figure 5-2), possess distinct spectral lineshapes (see SFG spectra in Figure 5-1). The distinct spectral signatures of Ag and Cu resulted in a visibly sharp boundary due to the image contrast induced by the difference of the phase of the two regions.

The sharp boundary as result of the predefined heterogeneity of the of the Cu-Ag surface is clearly demonstrated, not only through the relative nonresonant phase signal, but also through the maps of the fitted intensity ratio of the symmetric and anti-symmetric stretching modes of the terminal methyl group of ODT. The extracted intensity ratios represent the local monolayer orientation through the calculation angle of the C_3 axis of the terminal methyl group against the surface normal using the delta-function approximation.

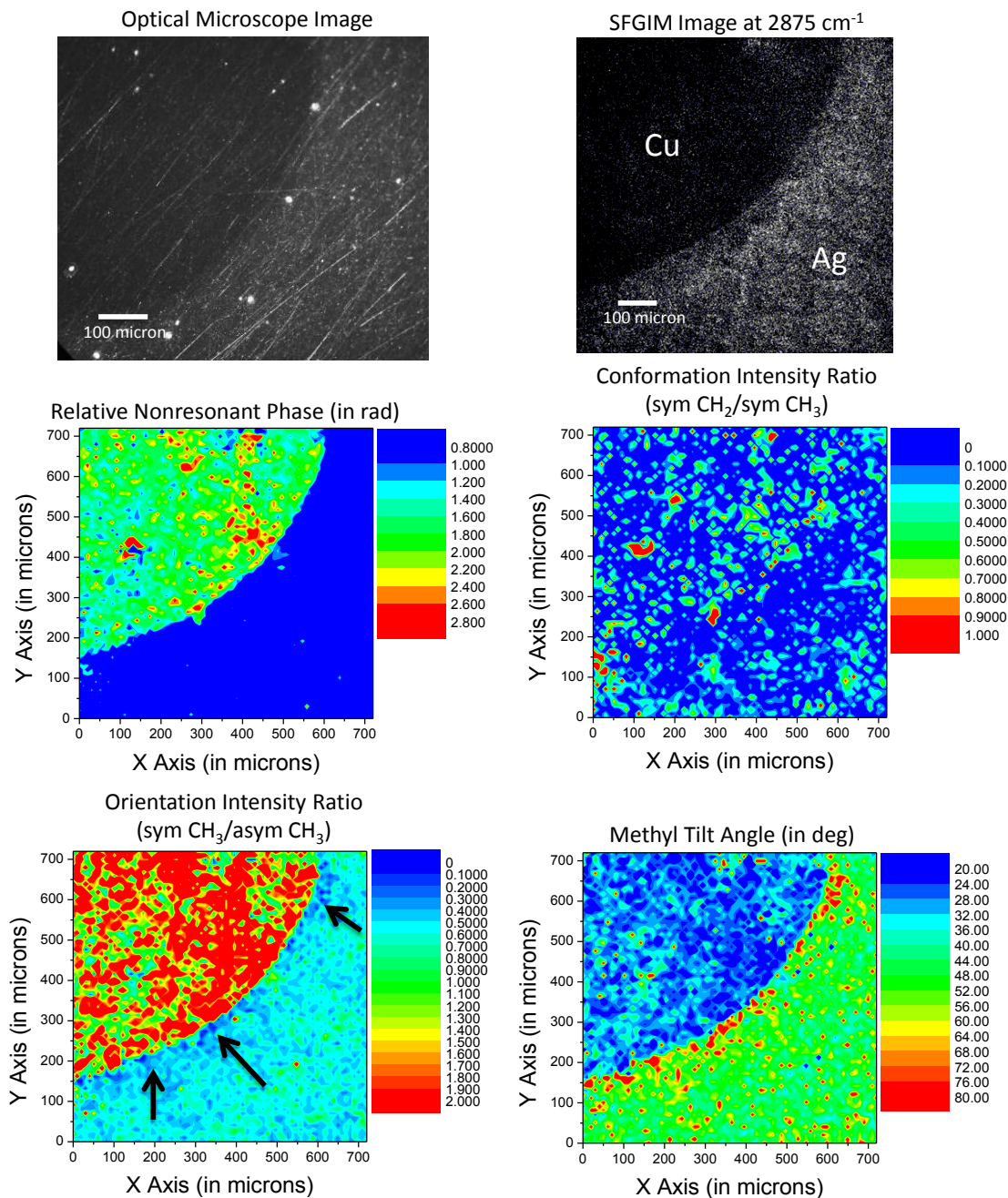


Figure 5-2. Optical and SFGIM image (at 2875 cm⁻¹) of the Cu-Ag binary surface. Spatial maps of the nonresonant phase, conformation intensity ratio, orientation intensity ratio, and terminal methyl tilt angle. (Total surface scale: 720 x 720 pixel; ROI scale: 10 x 10 pixel)

In the spatial map of the orientation intensity ratio (Figure 5-2), there is localized deviation in the orientation ratio (less upright in terms of methyl orientation) of the monolayer domains located close to the binary boundary. Arrows (on spatial of the orientation intensity ratio) point to the particular region of the boundary. On the surface of the boundary region, the possibility of localized heterogeneity in terms of surface composition is possible such that mixing of the electronic properties of the two metals resulted to an intermediate nonresonant background signal for the domains on the boundary. A previous observation in the atmospheric oxidation of Cu suggests that the monolayer orientation is sensitive towards changes in substrate properties due to atmospheric oxidation. At the boundary of the Cu-Ag sample, the local surface composition could have caused structural effects to the adsorbed monolayer such that it induced isolated domains of altered orientations.

Clearly, the presence of these two regions resulted to a bimodal distribution for both nonresonant phase and monolayer orientation (see histograms in Figure 5-3). However, this is not the case for the monolayer conformation of the surface. As observed from the spatial map (Figure 5-2) and histogram (Figure 5-3) of the methylene intensity ratios which serves as a representation of gauche defect concentration of the surface, there is no marked distinction in monolayer conformation between the Ag and Cu domains. In this sample the difference in composition of the two domains did not have a direct effect on the amount of local gauche defects on the surface. Hence, the two parameters spatially correlated for the Cu-Ag surface are: nonresonant phase and terminal methyl intensity ratio.

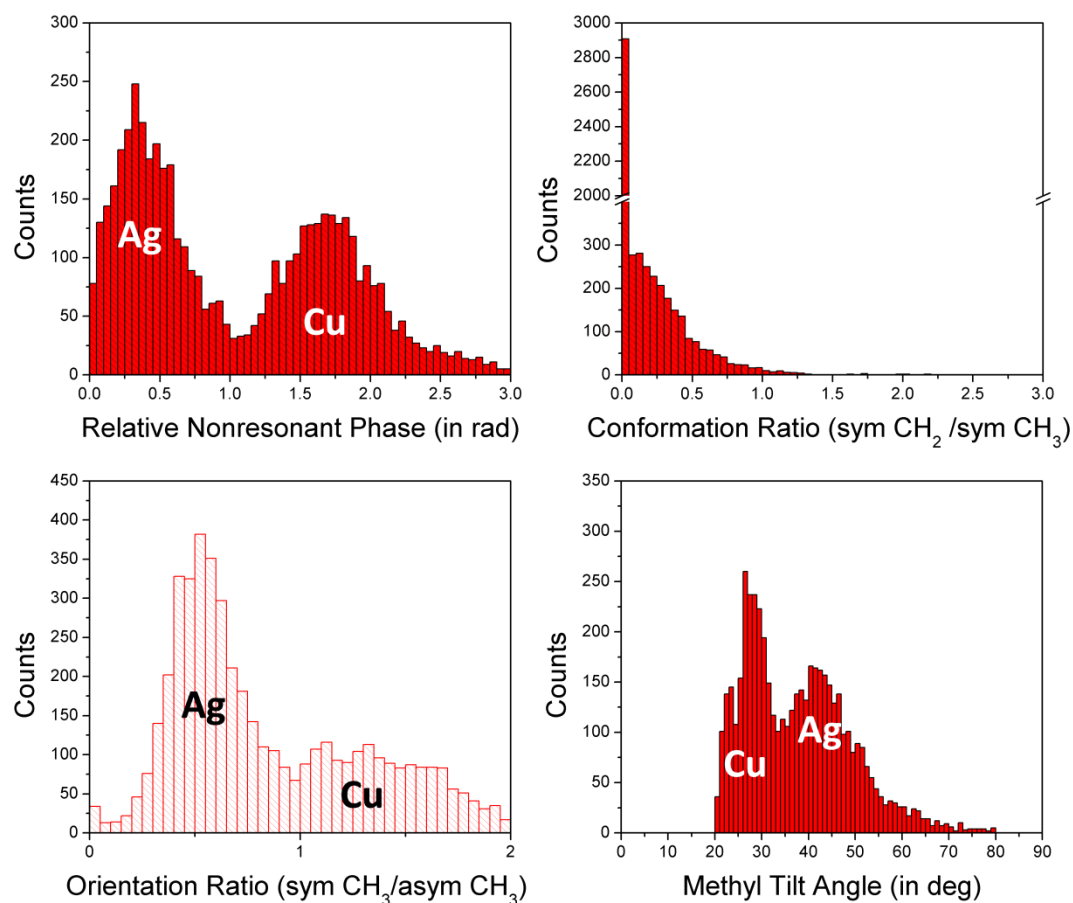


Figure 5-3. Histograms for the spatial distribution of relative nonresonant phase (in radians), conformation ratio, orientation ratio, and methyl tilt angle (in deg) for Cu-Ag binary surface.

5.4.2. Rationale for using Cu-Zn Checkerboard Samples

Since it was already understood that to accurately describe the monolayer order on a randomly heterogeneous (in terms of composition) surface of brass, the system being studied should closely resemble the brass surface in composition (its chemical components – Cu and Zn) with well-defined domains (spatially patterned) such that a reliable correlation of the spectral parameters between patterned Cu-Zn and actual brass

samples can be carried out. Hence, a patterned surface comprised of deposited-Cu islands on polished Zn was devised as a model binary surface to contain separate Cu and Zn components. Unlike the Cu-Ag surface, the patterned Cu-Zn surface is more spatially heterogeneous in terms of surface composition. As seen in the schematic diagram in Figure 5-4, copper islands (100-nm thick) of different length scales (from 50 microns to 25 microns) were deposited on the polished zinc. The length scales of the surface domains aids in the evaluation of the SFGIM spatial analysis in accurately describing the sample surface at different length scales. However, it must be emphasized that there are critical differences in the length scales of composition domains between patterned binary surfaces and real alloy surfaces. This is further explained in the spatial analysis of the brass surface.

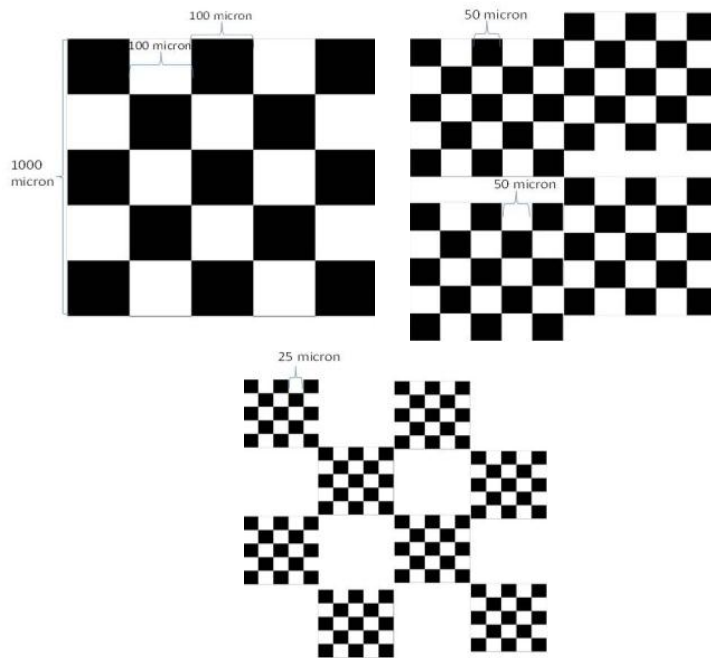


Figure 5-4. Schematic Diagram of the Cu-Zn checkerboard patterned sample.

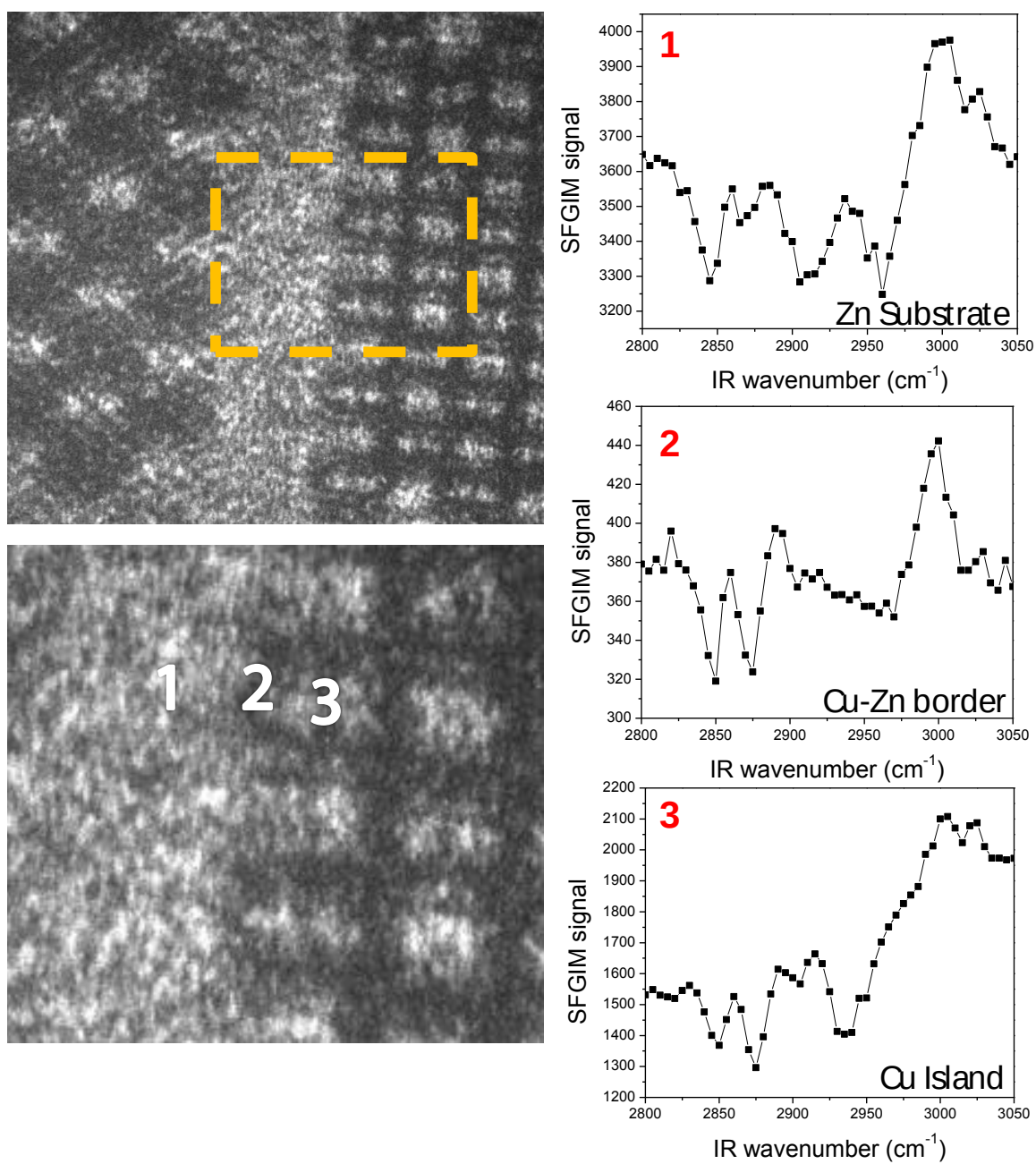


Figure 5-5. SFGIM image of Cu-Zn checkerboard patterned surface at 2875 cm⁻¹. Average SFGIM spectra of Zn, Cu-Zn, and Cu-grain domains.

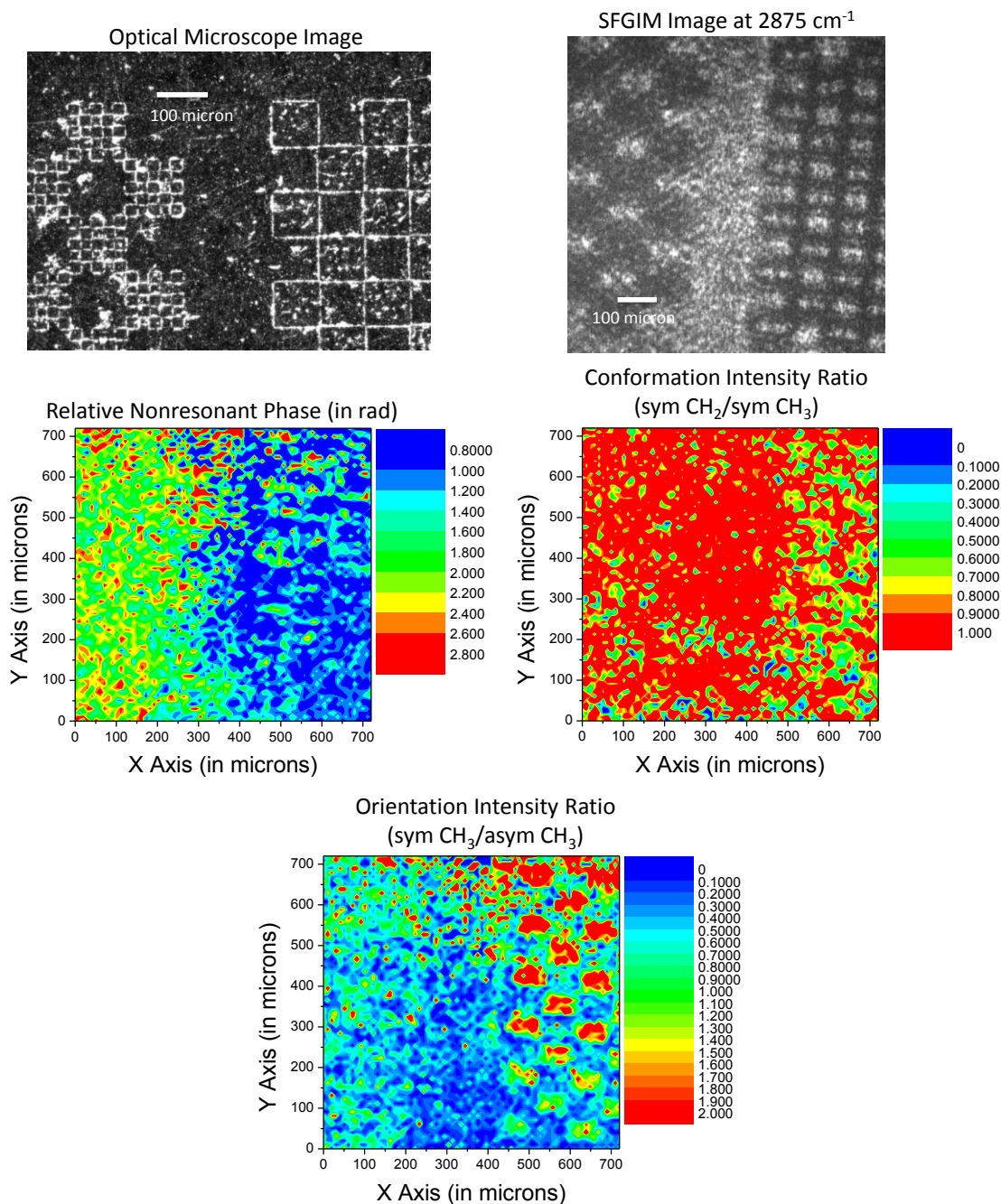


Figure 5-6. Optical and SFGIM image (at 2875 cm^{-1}) of the Cu-Zn checkerboard patterned surface. Spatial maps of the nonresonant phase, conformation intensity ratio, and orientation intensity ratio. (Total surface scale: 720×720 pixel; ROI scale: 10×10 pixel).

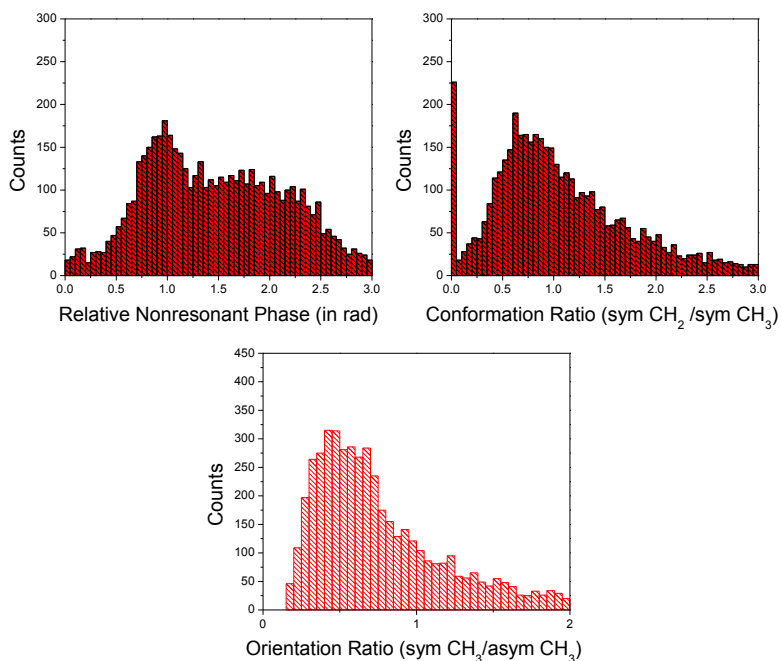


Figure 5-7. Histograms for the spatial distribution of relative nonresonant phase (in radians), conformation ratio, and orientation ratio for Cu-Zn checkerboard patterned surface.

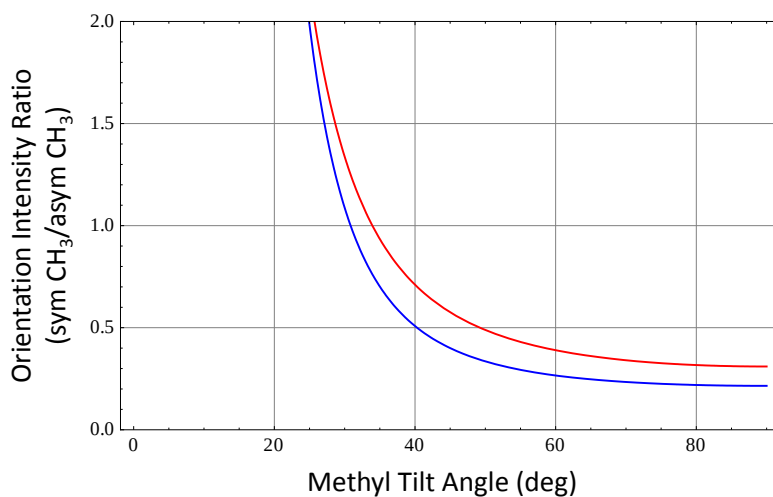


Figure 5-8. SFGIM orientation curve (delta-function approximation) for Cu (red) and Zn (blue) surfaces.

In Figure 5-6, the SFGIM image at 2875 cm^{-1} is presented wherein the checkerboard pattern layout is clearly visible as an effect of the nonresonant signal intensity differences between the Cu and Zn domains. Zn generally has a higher nonresonant background signal compared to Cu in the C-H vibrational frequency range. This nonresonant background effect is not observed in the optical microscope image.

Although the nonresonant signal magnitudes (background intensity) are different from the Cu and Zn domains, the spatial map of the fitted relative nonresonant phase (Figure 5-6) did not show a close resemblance to the checkerboard patterns as seen from the optical and SFGIM images. Based from the corresponding SFG spectra for the Cu and Zn domains, the spectral lineshapes are not as distinct as compared to the Cu-Ag surface. However, the SFG intensities in the C-H vibrational frequency range are, indeed, higher for the Zn domains when compared Cu domains and Cu-Zn boundary.

Based from the histogram of the nonresonant phase in Figure 5-7, there is a considerable overlap in the phase distributions (compare this to the sharp bimodal distributions of Cu-Ag nonresonant phase). The nonresonant response from the ROIs right side of the checkerboard pattern had values close to 1.0 radian while the left side had values closer to 2.0 radian. This is one major difference of the Cu-Zn with the Cu-Ag surface wherein there is a better local spatial correlation between the nonresonant phase and the methyl intensity ratios. For the Cu-Zn surface, the distributions for the monolayer orientation are statistically wider compared to the bimodal orientation distribution of Cu-Ag surface. Since the phase was used before as a guide in determining the surface composition, the lack of spatial correlation of the phase to the orientation ratio led to

inability to segregate the domains into separate Cu and Zn domains for proper conversion of the orientation ratio to tilt angles using the corresponding orientation curves (see Figure 5-8). Hence, in the future the magnitude of the nonresonant signal can be a possible alternative to replace the nonresonant phase.

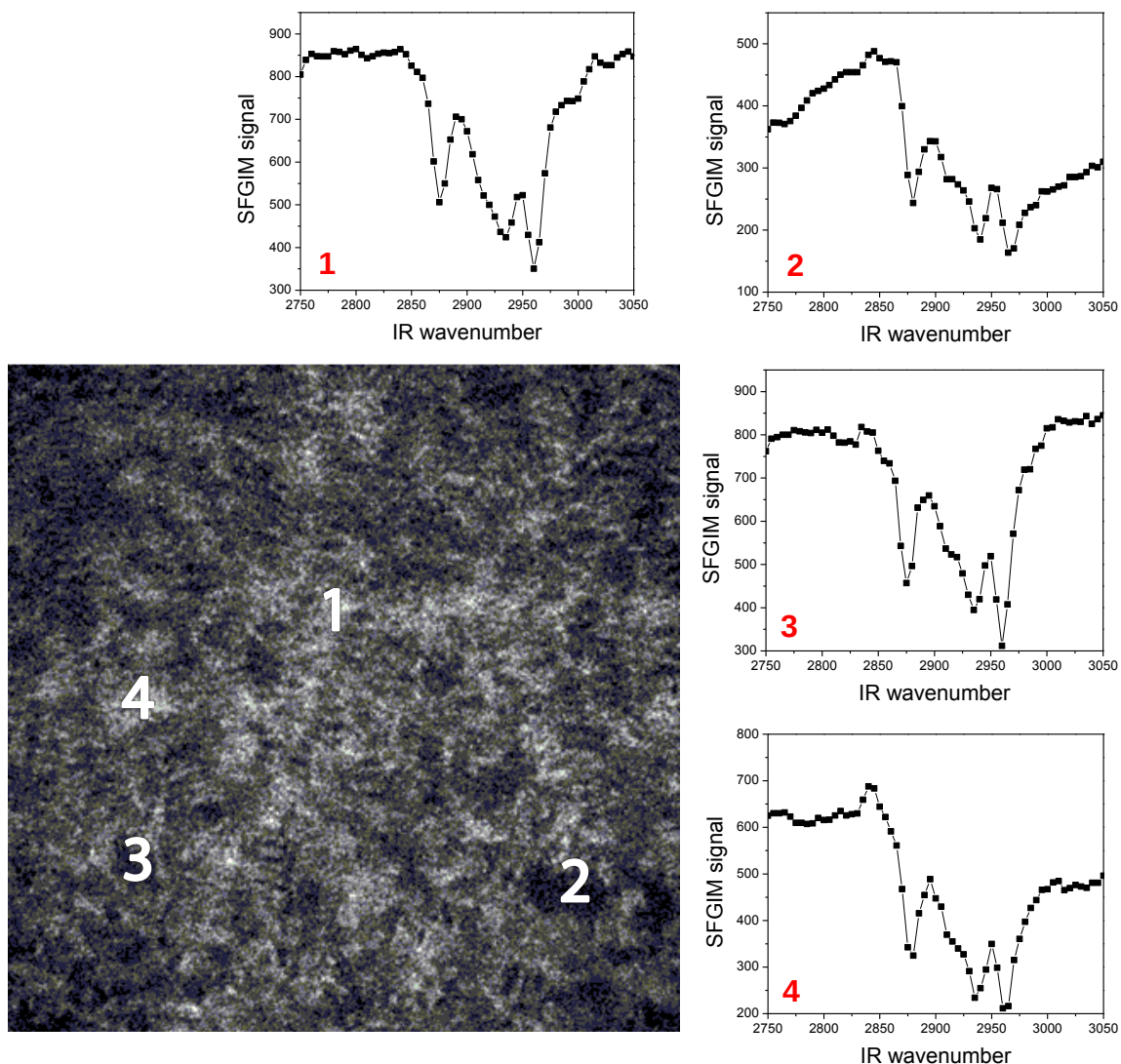


Figure 5-9. SFGIM image of the brass surface at 2875 cm^{-1} . Average SFGIM spectra of selected ROIs (10 x 10 pixel).

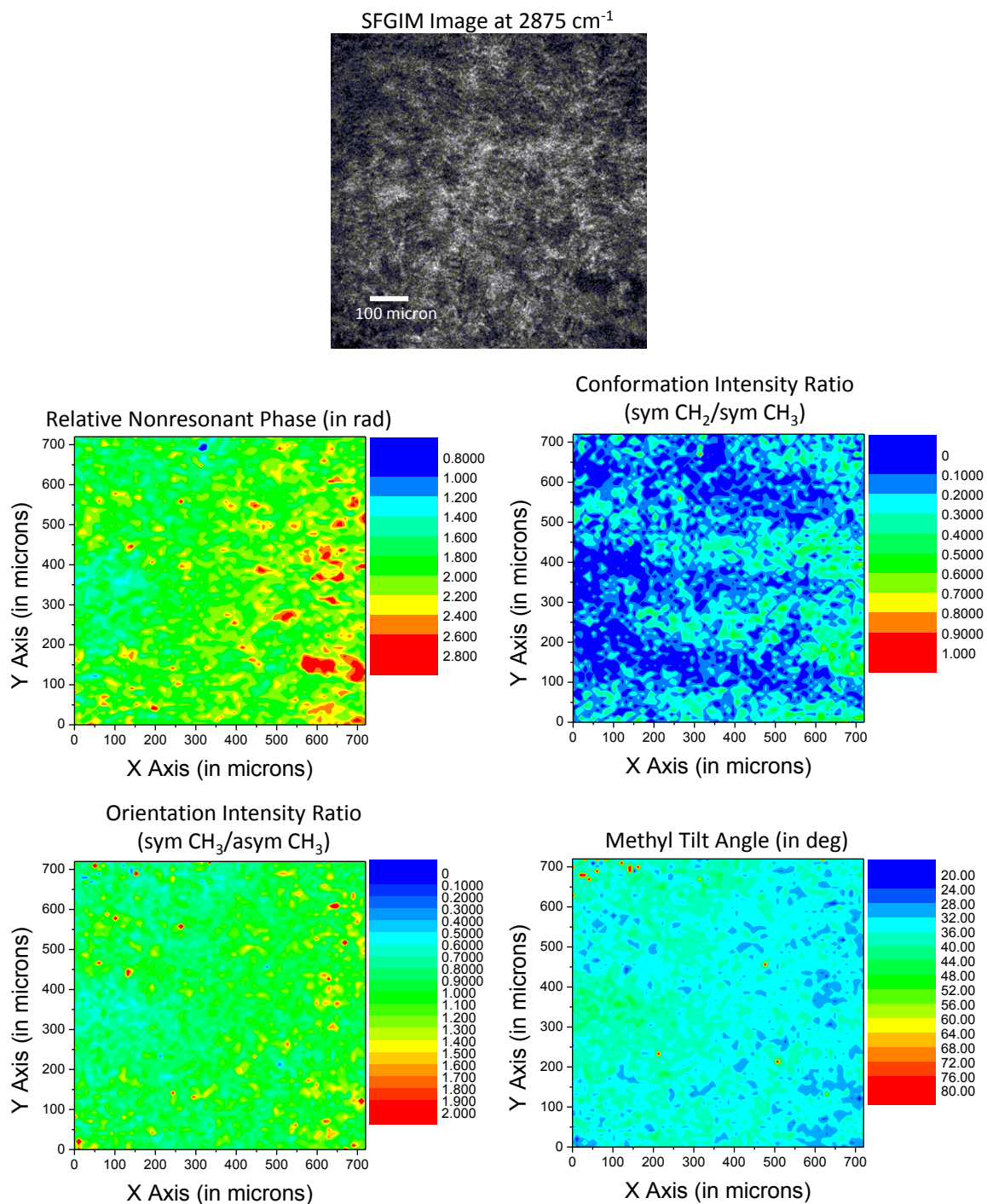


Figure 5-10. SFGIM image (at 2875 cm^{-1}) of the brass surface. Spatial maps of the nonresonant phase, conformation intensity ratio, orientation intensity ratio, and terminal methyl tilt angle. (Total surface scale: 720 x 720 pixel; ROI scale: 10 x 10 pixel)

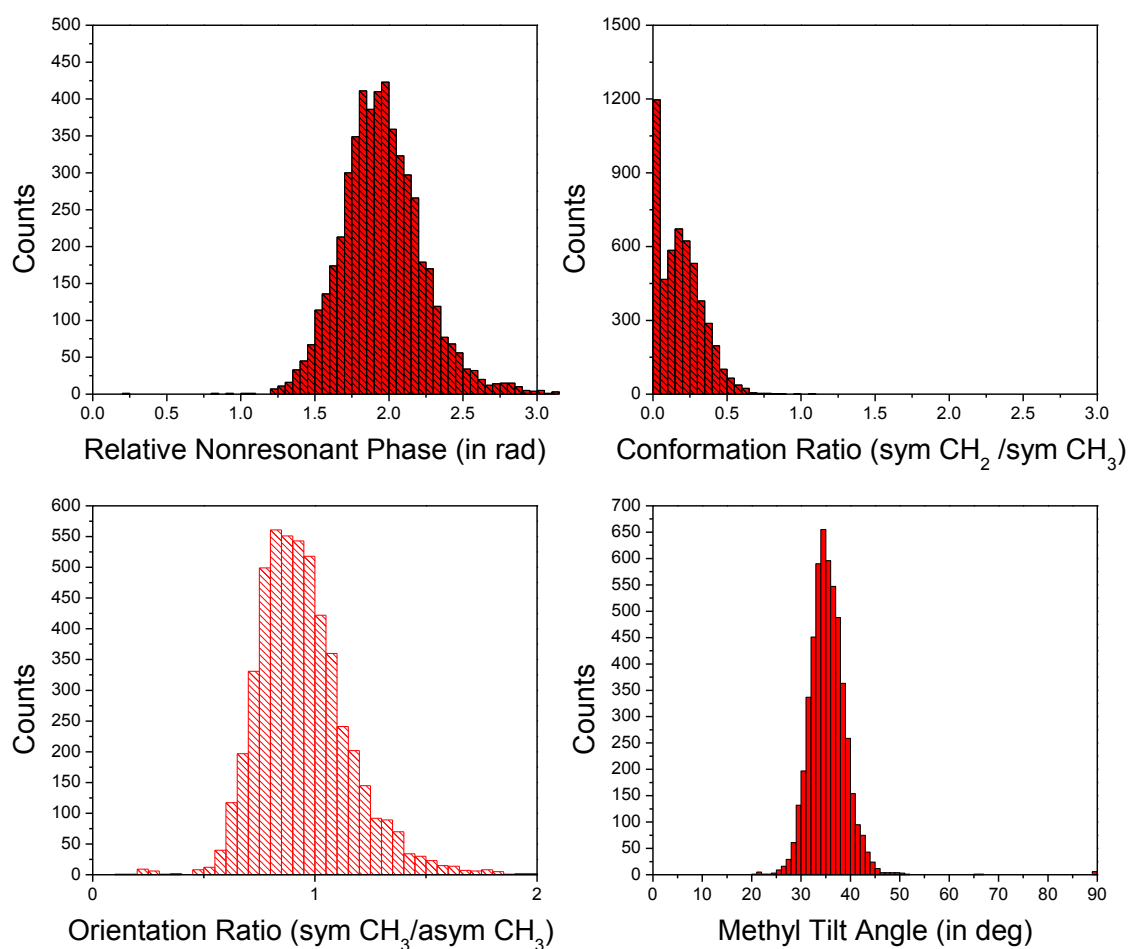


Figure 5-11. Histograms for the spatial distribution of relative nonresonant phase (in radians), conformation ratio, orientation ratio, and methyl tilt angle (in deg) for the brass surface.

5.4.3. Spatial Distribution Analysis of the Brass Sample

ODT deposited on a polished brass sample is presented in Figure 5-10 wherein there are spatial correlations in the local surface features between the SFGIM image at 2875 cm⁻¹ and the nonresonant phase map. Interestingly, the nonresonant phase of the surface is considerably heterogeneous with features showing areas with phase values

ranging from 1.0 to 3 radians which suggests the brass surface to be heterogeneous in composition (similar to the case of oxidized Cu surface).

However, it has to be noted that the brass surface has certain characteristics which make it largely different from the patterned samples of Cu-Ag and Cu-Zn. First, it is a true alloy wherein the predominant chemical component is Cu. The Cu-Zn checkerboard sample contains domains that mostly contain either Cu or Zn only. In contrast, domains on a brass sample are expected to give spectral information that is dominated by the nonresonant signal from Cu. Despite that the nonresonant signal of the brass surface is predominantly Cu in character; the presence of Zn has a considerable effect on the resulting monolayer order on brass.

Another characteristic of an alloy surface that differentiates it from patterned binary samples is the variability in surface composition and surface area of each grain domain. The dezincification process is a major factor that affects the local concentration of Zn on the brass surface.^{2, 4, 34} Brass is known to have variable surface concentration of Zn as result of the dezincification wherein zinc undergoes selective leaching from brass surface in the presence of oxygen and moisture from the atmosphere. Also, the grain sizes of the surface domains on brass vary in different length scales.

The patterned surfaces are well-defined in these two descriptions: (1) composition and (2) length scale. In the case of alloys, the composition is always in an intermediate state such that domains are not purely comprised of one element but a mixture of elements (Cu and Zn). Hence, electronic surface effects of alloys are different from those of pure metals such that this would affect the SFG nonresonant response of the substrate.

The length scales of the grain domains of the brass sample are normally polydisperse (not uniform). Hence, in order to classify the intermediate states, an estimation of length scale can be employed using the spatial distribution of nonresonant information recovered from the patterned samples.

Another particular characteristic of the Cu-Zn patterned samples is the electrochemical reactivity of the surface. Zn undergoes oxidation preferentially as it is known to have a lower standard electrode potential.³⁵ This galvanic effect will result to an electrochemically dynamic surface wherein the preferential oxidation of Zn will have direct influence on the monolayer ordering. In contrast, the brass surface is more homogeneous in terms of composition such that the electrochemical properties of the surface are a result of mixing of the surface electronic properties of the Cu and Zn components. The electrochemical activity is a possible cause for the molecular disorder on the surface of patterned Cu-Zn.

By analyzing the nonresonant phase information of the brass sample, the surface composition of the brass grains can be estimated by matching their local nonresonant phase to the signature phase information for either Zn or Cu. One qualitative procedure that can be employed is simply mapping the nonresonant signal magnitude across the surface since Zn registers a higher intensity compared to Cu.

Interestingly, from Figure 5-9, the spectral lineshapes recovered from the different ROIs from the brass surface resembles the spectral signatures of Cu and Cu₂O (see chapter for Cu undergoing oxidation, Chapter 4). Based from the fitted relative nonresonant phase values of Cu with ODT undergoing atmospheric oxidation, the phase

values range from 1.5 (reduced) to 2.25 (oxidized) radians. In Figure 5-11, the distribution for the nonresonant phase stretches from 1.5 to 2.5. This clearly suggests that the surface is a heterogeneous mixture of Cu and Cu₂O.

Local correlations are evident for spatial maps of orientation and nonresonant phase. The spatial map for the gauche defect showed no local correlation to either the nonresonant phase map or to the monolayer orientation map, which was expected since this was also the case for the Cu, Cu-Ag and Cu-Zn checkerboard samples.

5.4.4. Diffraction Effects of the Checkerboard Patterns

Interestingly, there are certain features in the Cu-Zn patterned sample that brings to attention a limitation of the SFGIM that is inherent to far-field nonlinear spectroscopic microscope setups. By observing the SFGIM image (at 2875 cm⁻¹ in Figure 5-2), interference waves as an effect of the checkerboard pattern acting as a surface diffraction grating are clearly visible on left side of the Cu-Zn sample (see Figure 5-4). Aside from the fact that Cu islands are elevated (not flat) at 100 nm with respect to the Zn substrate, the checkerboard design is widely used for diffraction gratings such that it is understandable that surface diffraction can occur on these samples. Hence, since the squares on the left are much smaller and closely-knit (as compared to the larger squares on the right), the unwanted diffraction patterns appear more strongly on the left-side of the sample. The surface diffraction affects the accuracy of the spatial analysis such that it distorts the SFG signal from the surface resulting to a mismatch of local information. For example, the ROIs of the Cu domains may contain SFG signals mixed with that of the Zn domains due to interference reinforcements (constructive and/or destructive). The

evaluation of the monolayer order of these affected areas are compromised such that (as seen from Figure 5-2) the orientation and gauche defect maps of these regions do not project local characteristics of the checkerboard pattern as it would have on the ROIs on the right side of the sample). This was not the case for the Cu-Ag sample since the domain boundaries are flat (polished surface) and the domains have larger length scales.

5.5. Conclusion

SFG imaging microscopy has been used to characterize a monolayer of ODT on brass and has demonstrated that the monolayer order on this reactive metal surface is generally distinct in distribution for both conformation and orientation as compared to patterned surfaces of Cu-Ag and Cu-Zn.

The Cu-Ag surface demonstrated a binormal spatial distribution for nonresonant phase, orientation and conformation while, on the other hand, the Cu-Zn checkerboard pattern showed significant amounts in conformational disorder and overlapping distributions for orientation and nonresonant phase. The brass surface exhibited a very narrow distribution in nonresonant phase (dominated by Cu) and monolayer orientation

In the analysis of Cu-Zn checkerboard patterns, it was emphasized that the resolution limit plays an important factor in the accuracy of spatial analysis on alloy systems. To apply the analysis to the variable length scales of grain domains of brass, the local nonresonant background information can be used to identify and isolate domains of different compositions (Cu-rich or Zn-rich).

Patterned metals such as the checkerboard Cu-Zn sample have surface characteristics that differentiate these materials from brass surfaces. These include differences in the length scales of the domains, local compositions of each domain, and local electrochemical activity of the surface. All of these surface descriptions of patterned surface are possible explanations to the heterogeneous monolayer ordering of these surfaces when compared to that of brass alloy.

References

1. Jones, D. A., *Principles and prevention of corrosion*. 2nd ed.; Prentice Hall: Upper Saddle River, NJ, 1996; p xvi, 572 p.
2. Leygraf, C., Graedel, T. , *Atmospheric Corrosion, 1st ed.* Wiley & Sons: New York: 2000.
3. Roberge, P. R., *Corrosion Engineering: Principles and Practice*. McGraw-Hill: 2008.
4. Schweitzer, P. A., *Fundamentals of Corrosion: Mechanisms, Causes and Preventive Methods*. CRC Press: Boca Raton, 2010.
5. Sinapi, F.; Forget, L.; Delhalle, J.; Mekhalif, Z. *Appl. Surf. Sci.* **2003**, 212, 464-471.
6. Sinapi, F.; Deroubaix, S.; Pirlot, C.; Delhalle, J.; Mekhalif, Z. *Electrochim. Acta* **2004**, 49, 2987-2996.
7. Fan, H.; Li, S.; Zhao, Z.; Wang, H.; Shi, Z.; Zhang, L. *Corros. Sci.*, 53, 4273-4281.

8. Bain, C. D.; Troughton, E. B.; Tao, Y. T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321-35.
9. Laibinis, P. E.; Bain, C. D.; Nuzzo, R. G.; Whitesides, G. M. *J. Phys. Chem.* **1995**, *99*, 7663-7676.
10. Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y. T.; Parikh, A. N.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7152-7167.
11. Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 9022-9028.
12. Denayer, J.; Delhalle, J.; Mekhalif, Z. *J. Electroanal. Chem.* **2009**, *637*, 43-49.
13. Hutt, D. A.; Liu, C. *Appl. Surf. Sci.* **2005**, *252*, 400-411.
14. Hedberg, J.; Leygraf, C.; Cimat, K.; Baldelli, S. *J. Phys. Chem. C* **2007**, *111*, 17587-17596.
15. Leygraf, C.; Hedberg, J.; Qiu, P.; Gil, H.; Henriquez, J.; Johnson, C. M. *Corrosion (Houston, TX, U. S.)* **2007**, *63*, 715-721.
16. Hosseinpour, S.; Hedberg, J.; Baldelli, S.; Leygraf, C.; Johnson, M. *J. Phys. Chem. C* **2011**, *115*, 23871-23879.
17. Cimat, K.; Baldelli, S. *J. Phys. Chem. B* **2006**, *110*, 1807-1813.
18. Cimat, K.; Moore, H. J.; Barriet, D.; Chinwangso, P.; Lee, T. R.; Baldelli, S. *J. Phys. Chem. C* **2008**, *112*, 14529-14537.
19. Cimat, K.; Baldelli, S. *J. Phys. Chem. C* **2007**, *111*, 7137-7143.
20. Hernandez, M.; Chinwangso, P.; Cimat, K.; Srisombat, L.-O.; Lee, T. R.; Baldelli, S. *J. Phys. Chem. C* **2011**, *115*, 4688-4695.
21. Cimat, K.; Moore, H. J.; Lee, T. R.; Baldelli, S. *J. Phys. Chem. C* **2007**, *111*, 11751-11755.

22. Santos, G.; Baldelli, S. *J. Phys. Chem. C* **2012**, *116*, 25874-25887.
23. Zhuang, X.; Miranda, P. B.; Kim, D.; Shen, Y. R. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59*, 12632-12640.
24. Feller, M. B.; Chen, W.; Shen, Y. R. *Phys. Rev. A* **1991**, *43*, 6778-6792.
25. Dreesen, L.; Humbert, C.; Celebi, M.; Lemaire, J. J.; Mani, A. A.; Thiry, P. A.; Peremans, A. *Applied Physics B: Lasers & Optics* **2002**, *74*, 621.
26. Ishibashi, T.-a.; Onishi, H. *Appl. Phys. Lett.* **2002**, *81*, 1338.
27. Baldelli, S.; Eppler, A. S.; Anderson, E.; Shen, Y.-R.; Somorjai, G. A. *J. Chem. Phys.* **2000**, *113*, 5432-5438.
28. Wang, H.-F.; Gan, W.; Lu, R.; Rao, Y.; Wu, B.-H. *Int. Rev. Phys. Chem.* **2005**, *24*, 191-256.
29. Lu, R.; Gan, W.; Wu, B.-h.; Zhang, Z.; Guo, Y.; Wang, H.-f. *J. Phys. Chem. B* **2005**, *109*, 14118-14129.
30. Wang, J.; Paszti, Z.; Even, M. A.; Chen, Z. *J. Am. Chem. Soc.* **2002**, *124*, 7016-7023.
31. Hirose, C.; Akamatsu, N.; Domen, K. *Appl. Spectrosc.* **1992**, *46*, 1051-1072.
32. Hirose, C.; Akamatsu, N.; Domen, K. *J. Chem. Phys.* **1992**, *96*, 997-1004.
33. Hirose, C.; Yamamoto, H.; Akamatsu, N.; Domen, K. *J. Phys. Chem.* **1993**, *97*, 10064-9.
34. Uhlig, H. H.; Revie, R. W., *Corrosion and corrosion control : an introduction to corrosion science and engineering*. 3rd ed.; Wiley: New York, 1985; p xiv, 441 p.
35. Haynes, W. M.; Lide David, R., *CRC handbook of chemistry and physics*. CRC Press Boca Raton, FL: Vol. 91.

Chapter 6: Conclusive Remarks

The work presented in this dissertation has mostly been focused on analysis of spatial distribution of molecular order of ODT of reactive metals surfaces of Cu and brass. In what follows the main results are summarized together with an outlook on possible further studies.

The spatial distribution analysis of SFGIM was further improved to analyze not only controlled environments, but also to probe real samples since one of the motivations of this project is to be able to determine whether the sample is homogeneous or heterogeneous. It has always been assumed that a surface is homogenous based on the averaging of the acquired signal. But this was not always true, due to development of other microscopic techniques that has atomic resolution of the surface and determined that the surface was inhomogeneous. Therefore, by only considering the average signal, many local features of the surface are overlooked and thus, leading to an inaccurate understanding of the system. The ability to visualize the surface enhances our understanding of surface chemistry of reactive metal surface.¹⁻⁸

This first study focused on evaluating the sensitivity of the SFGIM technique to measure the experimental orientation distribution of Au-ODT using the δ -function distribution approximation at different length scales. Factors such as instrumental configuration and surface properties have direct effects on the calculated methyl tilt angle and distribution width. By changing the length scale of the ROIs of the SFGIM image, the relationship of the resolution limit and signal sensitivity of the instrumentation in

revealing hidden domains of monolayer defects across the surface was demonstrated. By using smaller ROI scales, buried information in averaged SFG signal as collected in conventional instrumentation can now be exploited as spatial maps to measure surface heterogeneity.

The statistical analysis made it possible to compare orientation distributions on Au and Cu. Using a composite sample, it was shown that monolayer orientation distribution on Cu are statistically broader than on Au which indicates that SFGIM can distinguish and segregate monolayer populations based on substrate properties.

The spontaneous atmospheric oxidation of Cu from was monitored as a change in the nonresonant phase response of SFG spectral lineshapes. Hence, surface reactions such as surface oxidation can be monitored as an effect of the local electronic properties of the metal using SFG spectroscopy. The spatial distributional analysis of Cu-ODT shows that there is an overall decrease in the mean tilt angle and an increase in the amount of alkyl gauche defects as a result of the oxidation of the metal surface. An overall increase in monolayer disorder as result of the surface oxidation was observed. Spatial correlations between the orientation order and the relative nonresonant phase were monitored suggesting that the formation of the oxide induces orientation disorder in the localized regions of the surface. On the other hand, the changes in the conformational order were spatially uncorrelated with respect to the local oxide formation. It was demonstrated that the local structural behavior of molecules may or may not match local changes in physical properties. Hence, shifts in the overall distribution (mean values and widths) of

monolayer order (orientation and conformation) do not always translate to spatial correlation with the local electronic properties of the surface.

It was demonstrated that SFGIM can be used to examine atmospheric corrosion processes when ODT on copper is exposed to atmosphere, to in situ monitor oxide growth with a significantly higher sensitivity to monolayer order (both orientation and conformation) than any other commonly used techniques in surface science.

SFG imaging microscopy has been used to characterize a monolayer order of ODT on brass wherein its spatial distribution for both conformation and orientation were compared to patterned surfaces of Cu-Ag and Cu-Zn. The Cu-Ag surface demonstrated a well-separated spatial distribution for nonresonant phase, orientation and conformation representing monolayer order specific to the Cu and Ag components of the surface. Localized deviations in the orientation ratio at the Cu-Ag boundary were observed that could be related to a mixing of surface electronic properties of Cu and Ag. In contrast, the Cu-Zn checkerboard pattern showed significant amounts in conformational disorder and broad distributions for orientation and nonresonant phase. The monolayer disorder could have been a result of the surface instability brought about by the galvanic effects on the surface. The brass surface exhibited a very narrow distribution in nonresonant phase (dominated by Cu) and monolayer orientation as result of the homogeneity of the surface composition.

Studying much more complex metal systems such as metal oxides and alloys are deemed possible within the scope of statistical analysis of SFGIM. The SFG technique was made to evolve from method that relies on averaged signal into a surface microscopic technique that defines the real spatial heterogeneity of the surface. Major improvements in spatial correlation of surface properties such as monolayer orientation, conformation, and phase information were achieved. The ability to visualize the relationship of the surface properties in two-dimensional space is an ultimate advantage of SFGIM that leads to a promising direction towards studying dynamic processes (such as corrosion and catalysis) on reactive surfaces.

References

1. Cimatu, K.; Baldelli, S. *J. Phys. Chem. B* **2006**, *110*, 1807-1813.
2. Cimatu, K.; Baldelli, S. *J. Phys. Chem. C* **2007**, *111*, 7137-7143.
3. Cimatu, K.; Baldelli, S. *J. Am. Chem. Soc.* **2008**, *130*, 8030-8037.
4. Cimatu, K.; Moore, H. J.; Barriet, D.; Chinwangso, P.; Lee, T. R.; Baldelli, S. *J. Phys. Chem. C* **2008**, *112*, 14529-14537.
5. Cimatu, K.; Moore, H. J.; Lee, T. R.; Baldelli, S. *J. Phys. Chem. C* **2007**, *111*, 11751-11755.
6. Hedberg, J.; Leygraf, C.; Cimatu, K.; Baldelli, S. *J. Phys. Chem. C* **2007**, *111*, 17587-17596.
7. Hosseinpour, S.; Hedberg, J.; Baldelli, S.; Leygraf, C.; Johnson, M. *J. Phys. Chem. C* **2011**, *115*, 23871-23879.
8. Santos, G.; Baldelli, S. *J. Phys. Chem. C* **2012**, *116*, 25874-25887.

Appendix A

Supporting Information

Scale Dependence of the Orientation and Conformation Distribution Analysis of a Molecular Monolayer Using Sum Frequency Generation Imaging Microscopy

As a consistency check, the methyl tilt-angle distributions (in Figure 3-2) for small ROI scales are used to predict distributions maps for large ROI data sets as seen in Figure S1. The maps for each data set were calculated from methyl peak intensity ratios fitted from 10 x 10 ROI scale dataset (averaged over larger length scales). In Figure A1 f-h, the projected orientation distributions correspond to angles ($\sim 39^\circ$) consistent to calculated gaussian mean for large ROI scales as seen in Figure 3-2. Although the distribution parameters of the large ROI dataset can be calculated from the small ROI results, the calculated parameters are averaged over larger areas on the sample resulting to θ and σ values close to the averaged (non-imaging) SFG results. By using smaller ROI scales, hidden populations of defects that are not SFG-favored are revealed in the spatial maps. However, this consistency check demonstrates the accuracy of the distribution analysis to project orientation distributions of SFG data averaged over larger length scales.

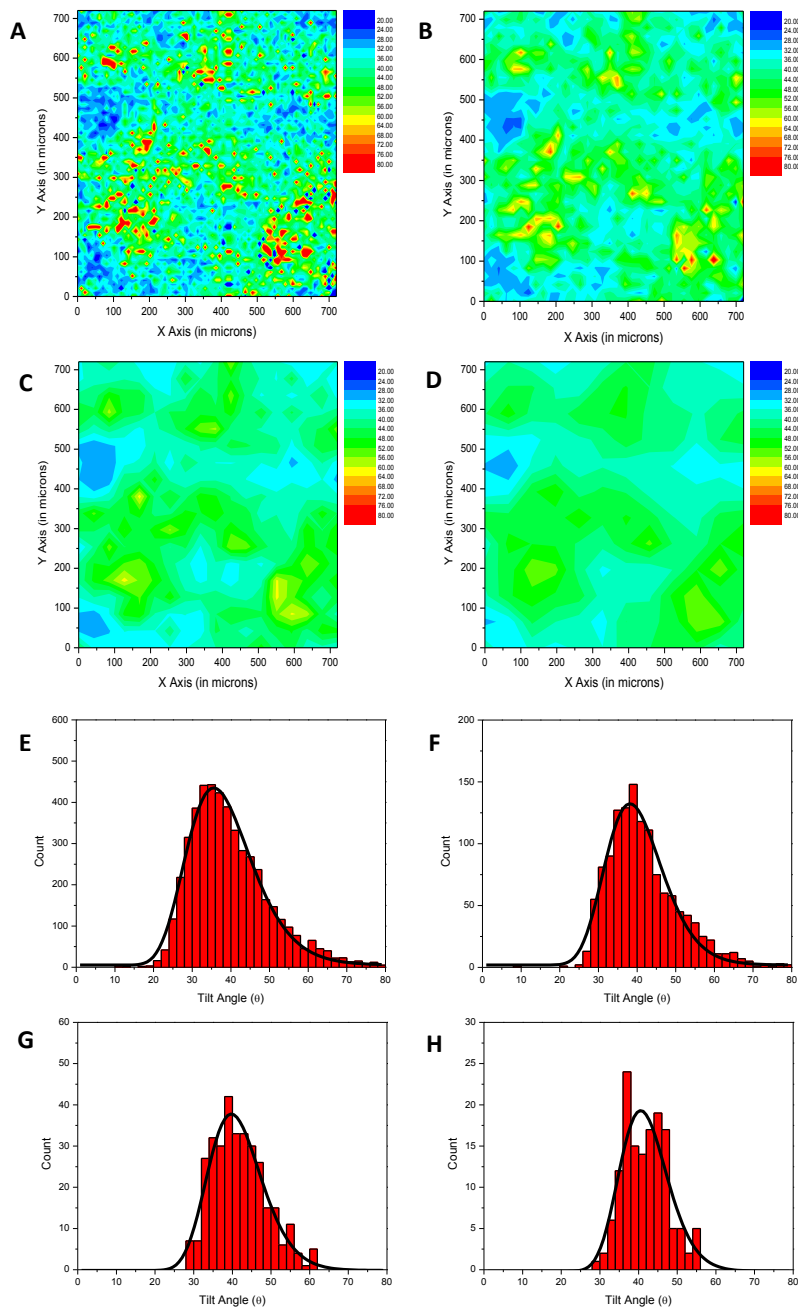


Figure A-1. (A) Spatial map and (E) histogram of methyl tilt angles calculated from fitted SFGIM data (10 x 10 pixel ROIs). Corresponding spatial map and histograms of methyl tilt angles projected from fitted SFGIM data averaged for larger ROI data sets: (B & F) 20 x 20, (C & G) 40 x 40, and (D & H) 60 x 60 pixel ROI.

Appendix B

Effect of Probe Beam Wavelength to the Nonresonant Sum Frequency Signal of Alkanethiol-covered Copper studied by Sum Frequency Generation Spectroscopy and Spectroscopic Ellipsometry

Introduction

Films of oxide are naturally formed on the surface of Cu metal under atmospheric conditions. The electronic properties of such films play a crucial role in adhesion of coatings and for its reactivity in corrosive environments, thus need to be understood for corrosion inhibition.^{1, 2} Because the thickness of these oxide films is in the range of a few nanometers and the films grow continuously with time, the understanding of the changes in structure as well as the growth kinetics of the formed oxides is of importance for assessing overall performance of the corrosion inhibitors on Cu.

The interaction of the metal with the surrounding atmosphere occurs in a complex interfacial system. Basically, four phases can be involved in the reaction: gas, liquid (in form of an absorbed water layer) and two solid phases: metal and metal oxide. The reaction kinetics varies dramatically with reaction conditions, such as relative humidity, contaminations and temperature.^{1, 3, 4} The initial steps of oxide formation include: (1) chemisorption of oxygen and water molecules, (2) oxygen dissociation and lateral growth of oxide islands and (3) growth (in thickness) of the oxide film.

At the initial onset of the study, the focus has been on investigating how changes in the nonresonant SFG signal can be used to in situ monitor the initial oxidation of

copper. It is known that the line shape observed in a SFG spectrum from a monolayer adsorbed on a metal surface is dependent upon the relative phase difference between the resonant and nonresonant contributions of the SFG signal. Thus, because the spectral features significantly are affected by alterations in the nonresonant background, it can be used to describe the oxidation process in real time.

However, due to the influence of the metal electronic properties on the sum-frequency generation spectra as a function of the probe (pump) beam wavelength, the process of comparing the reliability of using conventional SFG and SFGIM in monitoring the initial oxidation of Cu is made difficult. The sensitivity of the spectral shape to the SFG probe beam depends on several characteristics of the surface molecules: monolayer order distribution, surface concentration and average orientation on the surface. Also, variations in the spectral lineshape is strongly affected by the nonlinear optical configuration of the SFG technique that includes the angle geometry (as defined by the conservation of momentum) and the frequency range of both IR and probe beam used in the SFG emission.

Spectroscopic ellipsometry (SE) has been used to determine optical constants of bulk copper oxide as well as its crystalline films, and different models have been used to model the obtained spectra. In a previous work, the analysis of SE measurements of freshly prepared native oxide films on metallic Cu under ambient conditions were investigated.⁵ The growth kinetics of the oxide films was monitored in a controlled atmosphere and humidity. Further, the time dependence has been studied of the

absorption spectrum of the oxide layer, which reflects the electronic structure of the oxide film.

Background: Sum Frequency Generation

Because SFG is a $\chi^{(2)}$ process, a signal is only generated in a medium that lacks inversion symmetry, such as the surface. Therefore, a plot of IR wavelength vs sum frequency intensity is interpreted as the vibrational spectrum of the molecules on the surface. Due to phase matching conditions, SFG output is directional, which allows for the efficient collection of signal photons.^{6, 7} The phase-matching condition is also responsible for the lateral resolution of surface features, which is important for the imaging method. The orientation of the molecules at the surface can be determined by varying the polarization of the light fields that probe the sample. Since the sum frequency signal is coherent, the phase of the signal can be used to determine the sign of the susceptibility, which indicates whether the functional group is directed up or down at the surface.^{8, 9}

SFG Interference Model for Cu₂O oxide Film on Copper

For a single interface between 2 media, the SFG intensity is proportional to the intensities of the incident visible and IR beams and to the square of the second-order nonlinear susceptibilities ($\chi_{ijk}^{(2)}$) of the interface,

$$I_{IR}(\omega) \propto \left| \sum_{i,j,k} L_{ii}(\omega_{SFG}) L_{jj}(\omega_{vis}) L_{kk}(\omega_{IR}) \chi_{ijk}^{(2)} \right|^2 I_{vis} I_{IR} \quad (1)$$

where $(i,j,k = x, y, \text{ or } z)$ are the coordinates in the interface-fixed reference frame; I_{SFG} , I_{vis} , and I_{IR} are the power densities of the SFG, visible, and IR beams,

respectively; $\chi_{ijk}^{(2)}$ is the second-order susceptibility of the interface and comprises a third rank tensor containing 27 elements.

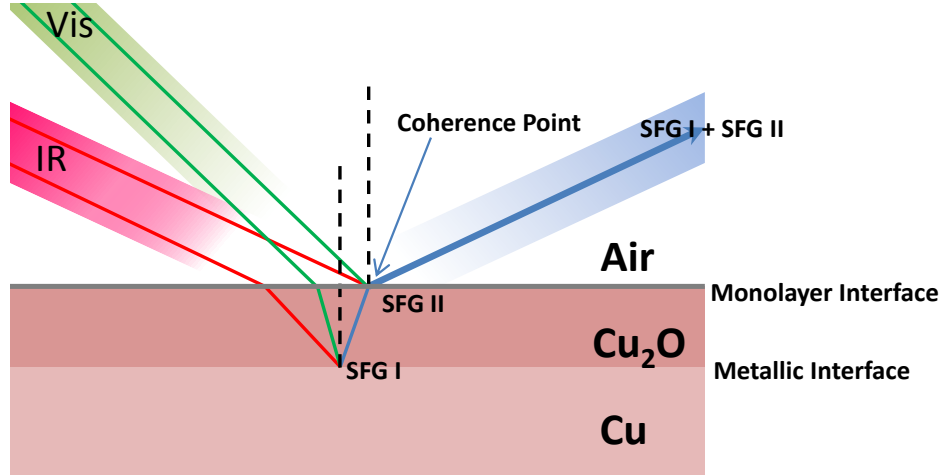


Figure B-1. A schematic diagram for the interference model of a thin-film of oxide on a Cu substrate.

L_{ii} , L_{jj} , and L_{kk} ($i, j, k = x, y, z$) in equation 1 are the Fresnel coefficients or local field factors (L factors) relating input macroscopic electric fields to the macroscopic fields at the interface.

In the scheme shown in Figure B-1, where a thin film of oxide is introduced between two media (air and bulk metal), two interfaces appear (the upper interface I between air and the oxide film, and the buried interface II between oxide and metal) and both of them will contribute to the SFG signals. Furthermore, when the thickness of the film is comparable to the wavelength of the pumped or emitted beams, the thickness

induced interference effect will also occur.¹⁰⁻¹² In order to include these effects, the expressions for the SFG signals can be rewritten as

$$I_{IR}(\omega) \propto \left| \frac{\sum_{i,j,k} L_{ii}^I(\omega_{SFG}) L_{jj}^I(\omega_{vis}) L_{kk}^I(\omega_{IR}) \chi_{ijk}^{(2),I} + \sum_{i,j,k} L_{ii}^{II}(\omega_{SFG}) L_{jj}^{II}(\omega_{vis}) L_{kk}^{II}(\omega_{IR}) \chi_{ijk}^{(2),II}}{\sum_{i,j,k} L_{ii}^I(\omega_{SFG}) L_{jj}^I(\omega_{vis}) L_{kk}^I(\omega_{IR}) \chi_{ijk}^{(2),I} + \sum_{i,j,k} L_{ii}^{II}(\omega_{SFG}) L_{jj}^{II}(\omega_{vis}) L_{kk}^{II}(\omega_{IR}) \chi_{ijk}^{(2),II}} \right|^2 I_{vis} I_{IR} \quad (2)$$

where superscripts I and II denote the two interfaces in Figure B-1. L factors for incident and output electric fields at the upper interface I can be obtained by introducing multiple reflection and transmission terms. The L factors in equation 2 are functions of parameters such as film thickness, refractive indices, and incident beam angles and can be calculated with the optical geometry of the SFG instrumentation. On the other hand, the susceptibility parameters only depend on the structures of the species at the interface. The relationships of the optical properties (specifically the refractive indices) to the SFG spectral behavior are governed by this interference model.

Spectroscopic Ellipsometry

The general objective of spectroscopic ellipsometry is to measure the ellipsometric ratio,

$$\rho = \frac{r_p}{r_s} = \tan(\Psi) e^{i\Delta} \quad (3)$$

where $i = \sqrt{-1}$, Ψ is the amplitude component, Δ is the phase difference, r_p denotes the amplitude reflection coefficient in p-polarisation and r_s the amplitude reflection coefficient in s-polarization.¹³ Here, all layers on the surface are of thickness <10 nm, which means it is in a region where the first order perturbation theory around the step profile is valid. For non-absorbing layers, this implies a coupling between information about refractive index change and thickness change in the perturbation parameter.¹⁴ The presence of non-absorbing layers on a metallic substrate shifts the Δ to lower values

compared to the substrate, and Ψ shifts to a lesser extent. Absorption reduces the magnitude of the respective amplitude reflection coefficient. Therefore, on a metallic substrate as investigated here, in good approximation only r_p is affected by the absorption from the thin film. As $\rho = \frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta}$, absorption will decrease $\tan(\Psi)$, hence Ψ , compared to the case without absorption.

Experimental Section

Sample Preparation and Exposure. Polycrystalline coupons (Goodfellow, 99.99%) of copper were used as sample material. The samples were rectangular with an area of 2cm^2 and thickness of 1mm. The samples were polished down to $0.25\ \mu\text{m}$ using diamond compound, sonicated with ethanol for 5 min between each step. The standard reagent of alkanethiol was used as received to prepare the SAMs on the metals. (ODT, $\text{CH}_3(\text{CH}_2)_{17}\text{SH}$, 98%; anhydrous, 99% minimum; Ethanol, absolute-200 Proof, Aaper). Before the copper coupon was dipped for two hours in ODT-ethanol solution for SAMs deposition, the coupon was first chemically etched to remove native oxide using amidosulfonic acid (ASA, 99.5%, EMD) solution for 30 seconds and then rinsed with ethanol. After the SAMs deposition, the metal sample is then washed with ethanol and dried with nitrogen gas stream before it was inserted into the sample cell.

The sample cell is high vacuum glass fitting equipped with CaF_2 window that permits transmission of the input (1064 nm and IR) beams. A thinner quartz window was installed on the side of output beam of the SFG ($\sim 815\text{ nm}$) due to space constraints on the detection side of the SFG microscope. The freshly polished sample is placed inside and

the cell is evacuated down to pressures of 1×10^{-5} torr to avoid surface artifacts. The cell is then backfilled with inert gas before the SFGIM measurement. Oxidation of the copper sample was performed by opening the sample cell to the atmosphere followed by the image acquisition.

SFG Imaging Microscopy. A picosecond pulsed Nd:YAG laser (EKSPLA) with a 20 Hz repetition rate was used for the following experiments. The Nd:YAG laser pumps the optical parametric generator/amplifier (OPG/OPA) to generate the IR beam, which is tunable from 2000 to 4000 cm^{-1} . The incoming beams (1064 nm and IR) were used to probe the surface. The polarization combination of the two incoming beams was pp where p-polarized light corresponds to light polarized parallel to the plane of incidence. The SFG microscope was set with a reflection configuration collecting the intermediate image from the grating by use of a 10x objective for magnification and tube lens for collimation. A Roper CCD camera with 1024×1024 pixel array was used for detection. By continuously scanning at fixed rates within the IR range of $2750\text{--}3050 \text{ cm}^{-1}$, one image is produced every 5 cm^{-1} . This IR frequency range captures the C-H vibrational frequencies for methyl and methylene groups in alkyl chains of ODT. The images were stacked using ImageJ and extraction through the stack generates the SFG spectrum. By picking out regions-of-interest (ROIs) from the image, spatial distribution of SFG spectra is demonstrated. With a field of view of 1 mm^2 , the lateral resolution is 2 microns.

Results and Discussion

Nonresonant Response of SAMs-Metal Systems

There are few studies that demonstrated the behavior of the spectral lineshape of SAMs-metal samples as a function of the nonresonant SFG signal as an effect of the surface electronic properties of the substrate of the interfacial system.¹⁵⁻¹⁷ In order to understand the mechanisms that control the electron energetic levels of organic/metal interfaces, the determination of the energy barriers between the Fermi level of the metal and the HOMO and LUMO levels of organic materials across the interfaces is essential for surface and interface studies of organic thin films. For understanding the occupied states, ultraviolet photoelectron spectroscopy (UPS) is one of the powerful techniques for studying the valence electronic structure of material. The electron injection barrier at the metal/organic interface is significantly altered by the interfacial dipole layer, by which the vacuum level at the organic layer is shifted relative to that at the metal layer. The dipole layer has been studied for organic/metal interfaces by using photoelectron spectroscopic technique. Ishii *et al.* proposed various origins of the dipole layer at the organic/metal interface: (1) charge transfer, (2) mirror force, (3) pushback effect due to the surface rearrangement, (4) chemical interaction, (5) interface state, and (6) permanent dipole of the adsorbate.¹⁸

As presented in previous studies in SFG measurements of metal surfaces, factors that affect the nonresonant response include the experimental geometric configuration of the SFG setup,^{19, 20} the pump beam wavelength,^{17, 21} and the metal electronic structure.^{7, 22} Difficulty of SFG analysis on metals had led to studies that try to minimization of the

nonresonant background using experimental (broadband temporal delay) and theoretical (MEMs analysis) methods.²³⁻²⁸ However, large amount of spectral information is lost through these methods that prevent accurate SFG analysis that generate a reliable description of the molecular order. Hence, the orientation and conformation analysis using SFG spectral data are carried out using fitting analysis that include change in nonresonant behavior as an effect of metal properties and pump beam wavelength.

The change in the electronic properties of the Cu surface being oxidized to Cu(I) have a direct effect on the nonlinear response of NR component of the $\chi_{\text{eff}}^{(2)}$. Similar studies that investigated the effect of the electronic properties of metal to NR response suggest that noble metals (Cu, Ag, Au) has higher polarization dependence compared to some transitions metals particularly Fe, Co and Ni.^{29, 30} Studies that investigate change in electronic structure as gauged by the absorption spectrum at photon energies near the bandgap of the metal substrate are used to monitor formation of the native oxide layers on metals surfaces such as copper and zinc.^{5, 31} Dreesen *et al.* monitored the nonresonant signal of three different metal substrates (Au, Ag and Pt) using a two-colour SFG setup in a counter-propagating configuration. Comparing the SFG spectra of dodecanethiol on these metals, the study showed that nonresonant phase of Au drastically evolves across the visible wavelength range (450-650 nm). By using a different pump probe wavelength of 1064 nm for the SFGIM measurements instead of the conventional 532 nm for averaged SFG setups used by Hosseinpour *et al.*,¹⁵ the nonlinear response of SFGIM for the oxide growth as a function of nonresonant phase is observed as intrinsically different due to effects of electronic structure of Cu oxidation.

Effect of Pump Beam Wavelength: Exposure of Cu/ODT

The effects on molecular structure of the oxide formation can be detected closely by using the SFGIM technique to generate maps of orientational and conformational parameters gathered from fitted spectra of the monolayer extracted from SFGIM hyperspectral stacks. By actual comparison between the change in CH₃ tilt angle and amount of CH₂ alkyl chain defects of prior and after images of the surface, the expected growth of the copper oxide film can be assessed effectively in the two-dimensional space of the substrate surface.

The advantage of using SFGIM to reveal hidden domains of monolayer defects has been demonstrated previously using different length scales in surface dimensions.³² The systematic bias of conventional averaged SFG techniques towards monolayers with signal-favored orientation distributions is avoided in SFGIM which allows the localized detection of defect sites. As an instant method for identification of the anodic sites on surface, the areas that register a change in nonresonant phase can be isolated to have undergone atmospheric oxidation.

Figure B-2 shows the SFG spectral response of ODT with the oxidation of the Cu substrate. Based on averaged spectral SFG results using a 532 nm pump beam, the nonresonant phase shift is demonstrated by the spectral lineshape prior and after air exposure. The formation of thin oxide film beneath the ODT SAMs had been observed in previous studies using SFG spectroscopy complemented with techniques such as

reflection-absorption infrared spectroscopy (RAIRS), cathodic reduction and X-ray photoelectron spectroscopy (XPS).^{33, 34}

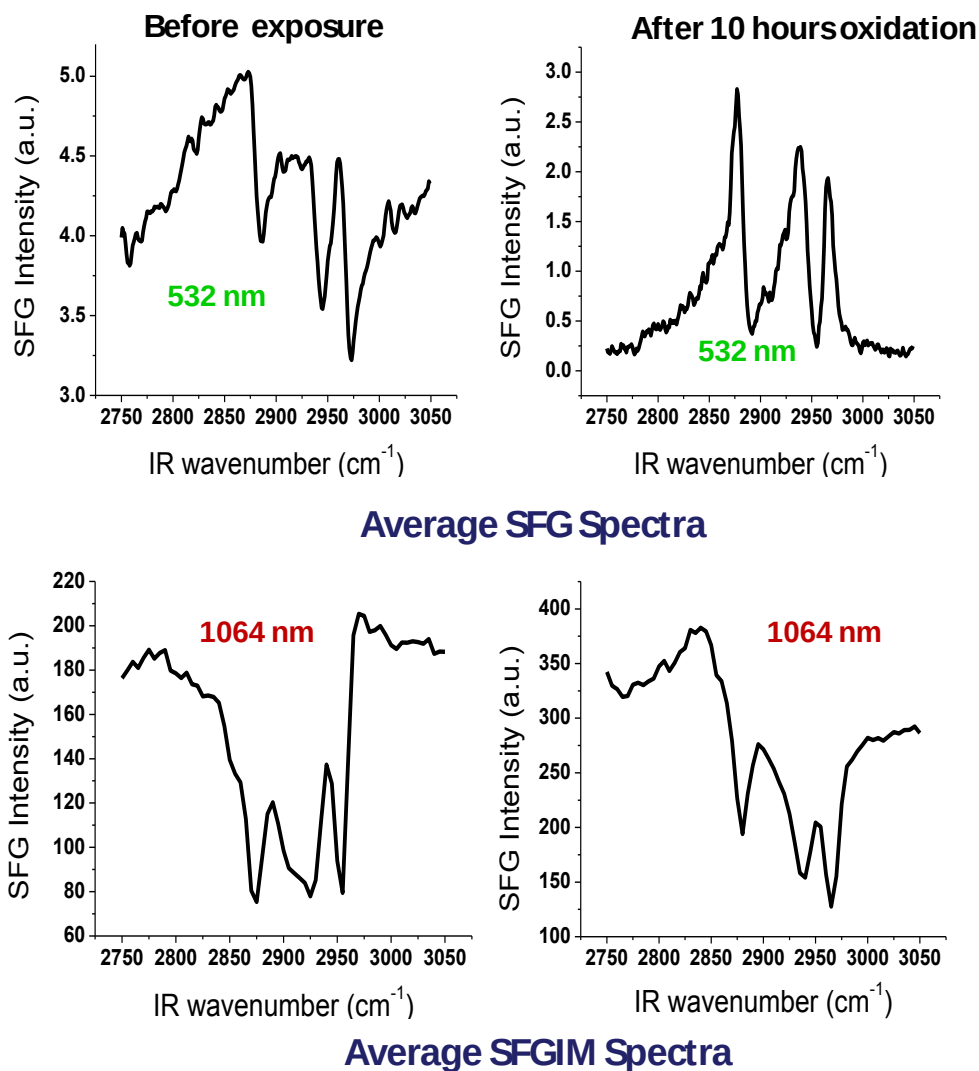


Figure B-2. Spectral comparison of SFG lineshapes of the oxidation of Cu using pump beam wavelengths (532 and 1064 nm)

Hosseinpour *et al.* previously investigated the effect of oxide formation to the nonresonant SFG phase of the Cu/ODT spectra.¹⁵ The sensitivity of SFG to detect change in substrate composition was efficiently employed to a metal surface that is susceptible to atmospheric corrosion. In addition to the advantage of using SFG, the change in monolayer order in terms of orientation was also observed based on the methyl stretch amplitudes recovered from fitted spectra.

However, by using a different pump probe wavelength of 1064 nm instead of the conventional 532 nm, the nonlinear response to the oxide growth as a function of nonresonant phase is less obvious. It is observed in the SFG spectra of Cu/ODT that for each pump beam source (532 and 1064 nm), the nonresonant background has a signature phase response corresponding to the set of molecular vibrational modes present. The difference in geometric configuration (co-propagating) between the averaged SFG and SFGIM setups are minimal such that it would have considerable effects to the nonresonant response.

The change in the nonresonant phase due to surface oxidation is larger for the 532 nm spectra compared to that of 1064 nm. The change in the electronic property of Cu being oxidized to Cu(I) have a direct relationship to the nonlinear response of NR component of the $\chi_{\text{eff}}^{(2)}$. Dreesen *et al.* monitored the nonresonant signal of three different metal substrates (Au, Ag and Pt) using a two-colour SFG setup in a counter-propagating configuration. Comparing the SFG spectra of dodecanethiol on these metals, the study showed that the nonresonant phase of Au drastically evolves across the visible

wavelength range (450-650 nm). Similar studies that investigated the effect of the electronic properties of metal to NR response suggest that noble metals (Cu, Ag, Au) has higher polarization dependence compared to some transition metals particularly Fe, Co and Ni.^{29, 30} These studies further emphasize that the metal SFG contribution is directly correlated to the metal density of states and its band structures. Understanding the difference in the electronic structure between elemental Cu and Cu₂O will also explain the pump wavelength dependence of the SFG lineshapes. Studies that investigate change in electronic structure as gauged by the absorption spectrum at photon energies near the bandgap of the metal substrate are used to monitor formation of the native oxide layers on metals surfaces such as copper and zinc.^{5, 31}

Spectroscopic Ellipsometry

Aside from the oxide thickness measurements, SE is capable of estimating growth kinetic mechanisms of the oxide films in different atmospheric conditions based on absorption spectra largely influenced by the differences between metal electronic structures of the pure element to its oxide.

In analyzing SE measurements from thin films on surfaces, it is therefore useful to consider light absorption of the film is negligible at photon energies below the band gap energy of the metal surface. As the absorption is governed by the band structure of the surface, a fast response in terms of the Δ and Ψ are expected with change in the electronic structure during the initial stage of oxide formation.

Conclusions

Self-assembled monolayers of ODT absorbed on copper surfaces can act as inhibiting organic coatings, protecting the copper from atmospheric corrosion. However, the penetration of oxygen through ODT is still possible but to a much lower extent, and thus a copper oxide layer with the thickness of a few nanometers can form at the copper interface. Formation of this oxide layer changes the phase between the resonant and nonresonant SFG contributions, as well as the amplitude of the nonresonant portion of the sum frequency signal. As a result, the SFG line shape will change. This alteration in spectral shape can be detected only if the ODT is deposited on an oxide-free copper surface, and correlates with the formation of a thin copper oxide film on the copper surface, which will induce changes in the electronic properties of the substrate and consequently influence the nonresonant SFG signal and thus the spectrum of ODT on copper.

By comparing the spectral features of alkanethiol on metals with well-known experimentally established SFG phase information²¹ (i.e. gold, silver) to copper that is commonly used as an alloy component, this study demonstrates the ability of SFGIM to map out the spatial chemical definition for complex metal substrates that could, later on, be used to locate corrosion-prone domains in more industrial metallic substrates with 2 or more elemental components (alloy substrates such as dezincified intergranular sites on brass surfaces). This demonstrate advantages of using SFG to examine atmospheric corrosion processes when ODT on copper, to in situ monitor oxide growth qualitatively with a significantly higher sensitivity than other commonly used techniques in corrosion science.

REFERENCES

1. Leygraf, C., Graedel, T. , *Atmospheric Corrosion*, 1st ed. Wiley & Sons: New York: 2000.
2. Roberge, P. R., *Corrosion Engineering: Principles and Practice*. McGraw-Hill: 2008.
3. Jones, D. A., *Principles and prevention of corrosion*. 2nd ed.; Prentice Hall: Upper Saddle River, NJ, 1996; p xvi, 572 p.
4. Schweitzer, P. A., *Fundamentals of Corrosion: Mechanisms, Causes and Preventive Methods*. CRC Press: Boca Raton, 2010.
5. Platzman, I.; Brener, R.; Haick, H.; Tannenbaum, R. *J. Phys. Chem. C* **2008**, *112*, 1101-1108.
6. Guyot-Sionnest, P.; Hunt, J. H.; Shen, Y. R. *Phys. Rev. Lett.* **1987**, *59*, 1597-600.
7. Superfine, R.; Guyot-Sionnest, P.; Hunt, J. H.; Kao, C. T.; Shen, Y. R. *Surf. Sci.* **1988**, *200*, L445-L450.
8. Superfine, R.; Huang, J. Y.; Shen, Y. R. *Phys. Rev. Lett.* **1991**, *66*, 1066.
9. Baldelli, S.; Mailhot, G.; Ross, P.; Shen, Y.-R.; Somorjai, G. A. *J. Phys. Chem. B* **2001**, *105*, 654-662.
10. Backus, E. H. G.; Garcia-Araez, N.; Bonn, M.; Bakker, H. J. *J. Phys. Chem. C*, *116*, 23351-23361.
11. Tong, Y.; Zhao, Y.; Li, N.; Osawa, M.; Davies, P. B.; Ye, S. *The Journal of Chemical Physics*, *133*, 034704-13.
12. Tong, Y.; Zhao, Y.; Li, N.; Ma, Y.; Osawa, M.; Davies, P. B.; Ye, S. *The Journal of Chemical Physics*, *133*, 034705-9.

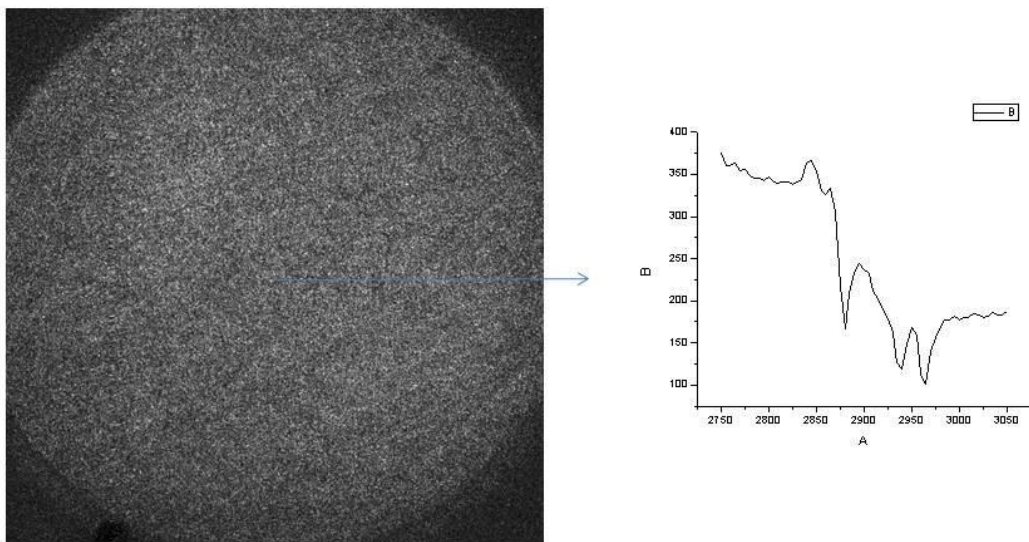
13. Tompkins, H.; Irene, E. A., *Handbook of ellipsometry*. William Andrew: 2005.
14. Lekner, J., *Theory of Reflection: Of Electromagnetic and Particle Waves*. Kluwer Academic Print on Demand: 1987; Vol. 3.
15. Hosseinpour, S.; Hedberg, J.; Baldelli, S.; Leygraf, C.; Johnson, M. *J. Phys. Chem. C* **2011**, *115*, 23871-23879.
16. Humbert, C.; Dreesen, L.; Mani, A. A.; Caudano, Y.; Lemaire, J. J.; Thiry, P. A.; Peremans, A. *Surf. Sci.* **2002**, *502-503*, 203-207.
17. Dreesen, L.; Humbert, C.; Celebi, M.; Lemaire, J. J.; Mani, A. A.; Thiry, P. A.; Peremans, A. *Applied Physics B: Lasers & Optics* **2002**, *74*, 621.
18. Ishii, H.; Sugiyama, K.; Ito, E.; Seki, K. *Adv. Mater. (Weinheim, Ger.)* **1999**, *11*, 605-625.
19. Holman, J.; Davies, P. B.; Nishida, T.; Ye, S.; Neivandt, D. J. *J. Phys. Chem. B* **2005**, *109*, 18723-18732.
20. Tanaka, Y.; Lin, S.; Aono, M.; Suzuki, T. *Applied Physics B* **1999**, *68*, 713-718.
21. Braun, R.; Casson, B. D.; Bain, C. D.; van der Ham, E. W. M.; Vreken, Q. H. F.; Eliel, E. R.; Briggs, A. M.; Davies, P. B. *J. Chem. Phys.* **1999**, *110*, 4634-4640.
22. Harris, A. L.; Chidsey, C. E. D.; Levinos, N. J.; Loiacono, D. N. *Chem. Phys. Lett.* **1987**, *141*, 350-6.
23. Lagutchev, A.; Hambir, S. A.; Dlott, D. D. *J. Phys. Chem. C* **2007**, *111*, 13645-13647.
24. Shalhout, F. Y.; Malyk, S.; Benderskii, A. V. *The Journal of Physical Chemistry Letters* **2012**, 3493-3497.

25. Stiopkin, I. V.; Jayathilake, H. D.; Weeraman, C.; Benderskii, A. V. *The Journal of Chemical Physics* **2010**, *132*, 234503-9.
26. Sovago, M.; Vartiainen, E.; Bonn, M. *J. Phys. Chem. C* **2009**, *113*, 6100-6106.
27. Busson, B.; Tadjeddine, A. *J. Phys. Chem. C* **2009**, *113*, 21895-21902.
28. Curtis, A. D.; Reynolds, S. B.; Calchera, A. R.; Patterson, J. E. *The Journal of Physical Chemistry Letters*, *1*, 2435-2439.
29. Hubner, W.; Bennemann, K. H.; Bohmer, K. *Physical Review B* **1994**, *50*, 17597-17605.
30. Hubner, W.; Bennemann, K. H. *Physical Review B* **1995**, *52*, 13411-13418.
31. Chen, Y.; Schneider, P.; Erbe, A. *physica status solidi (a)* **2012**, *209*, 846-853.
32. Santos, G.; Baldelli, S. *J. Phys. Chem. C* **2012**, *116*, 25874-25887.
33. Itoh, J.; Sasaki, T.; Ohtsuka, T. *Corros. Sci.* **2000**, *42*, 1539-1551.
34. Hosseinpour, S.; Hedberg, J.; Baldelli, S.; Leygraf, C.; Johnson, M. *J. Phys. Chem. C*.

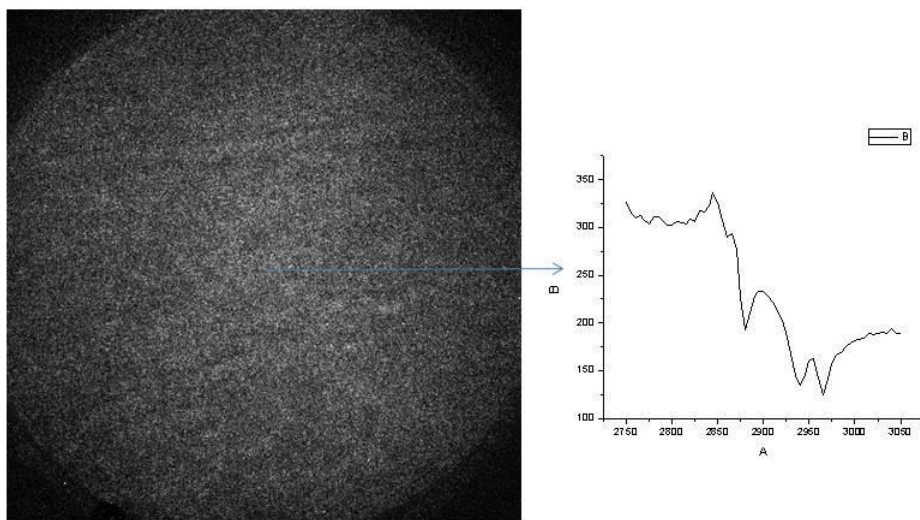
Appendix C

SFGIM Experiments on polished Cu samples

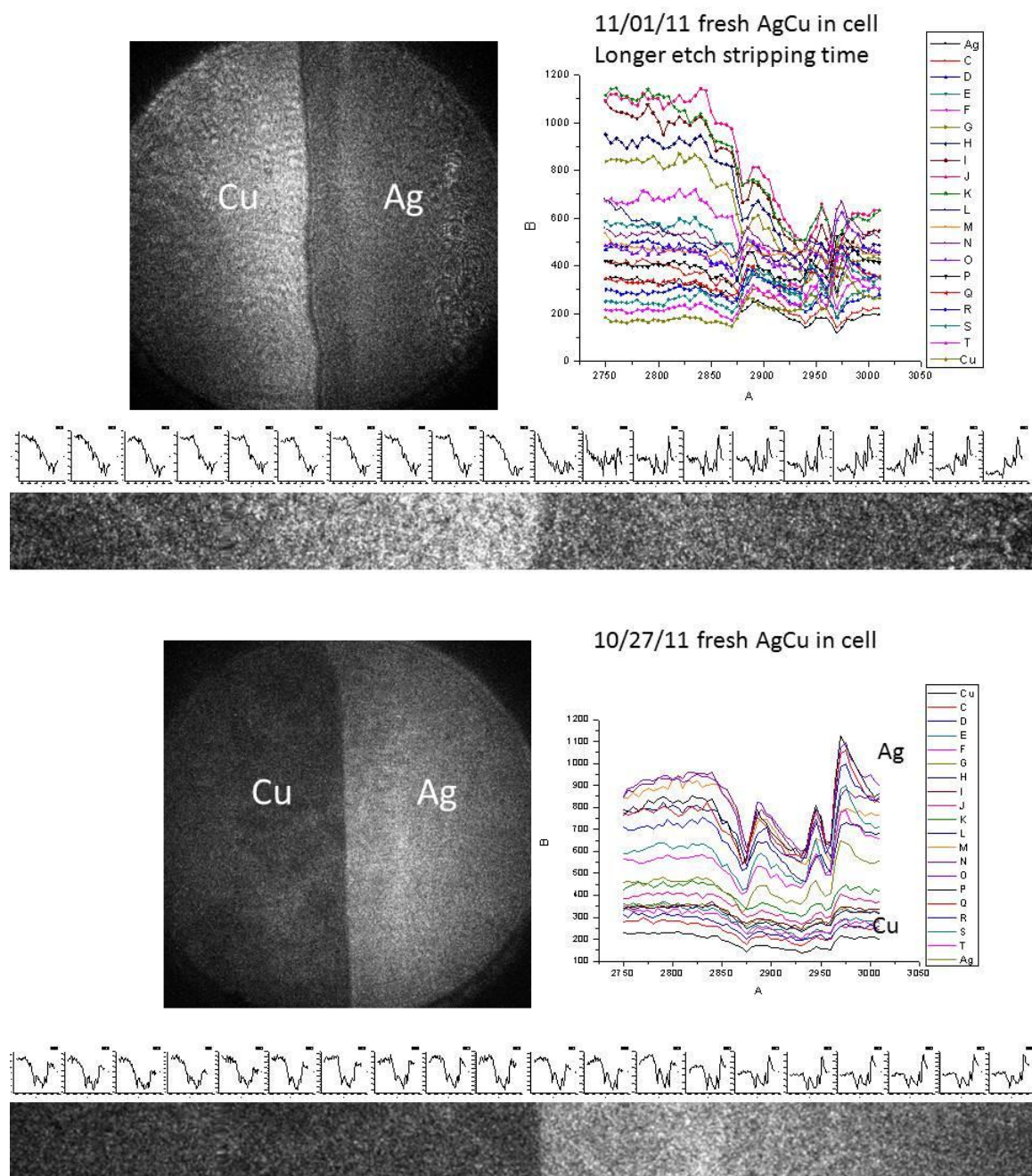
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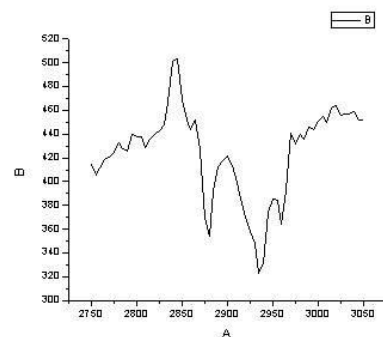
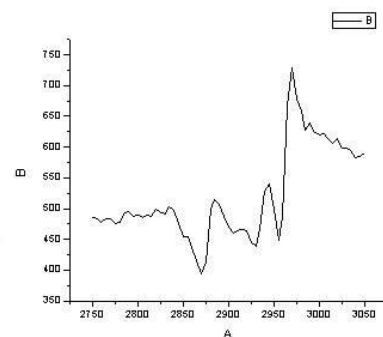
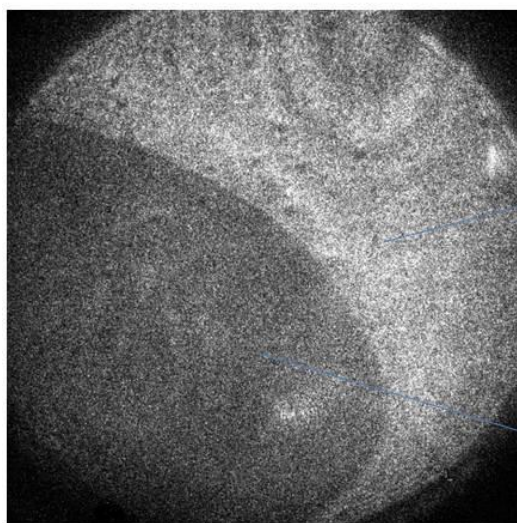
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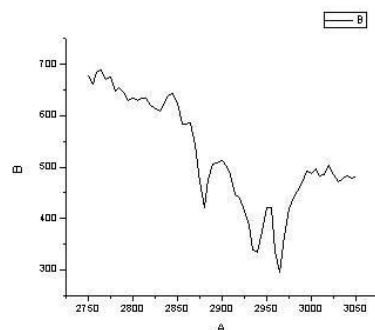
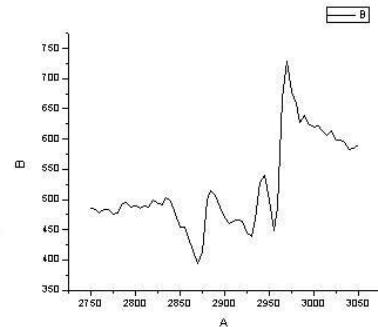
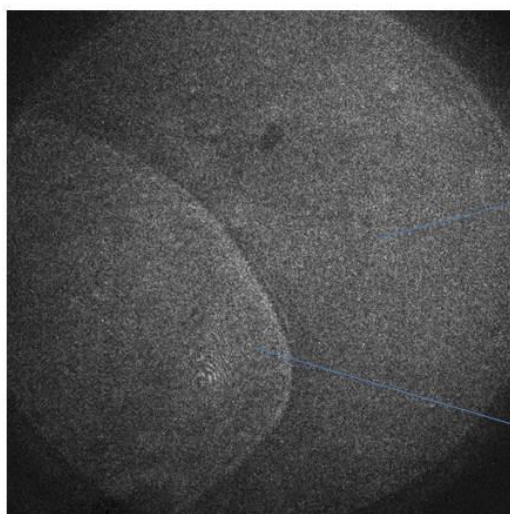
SFGIM Experiments on Cu and Ag binary alloy samples



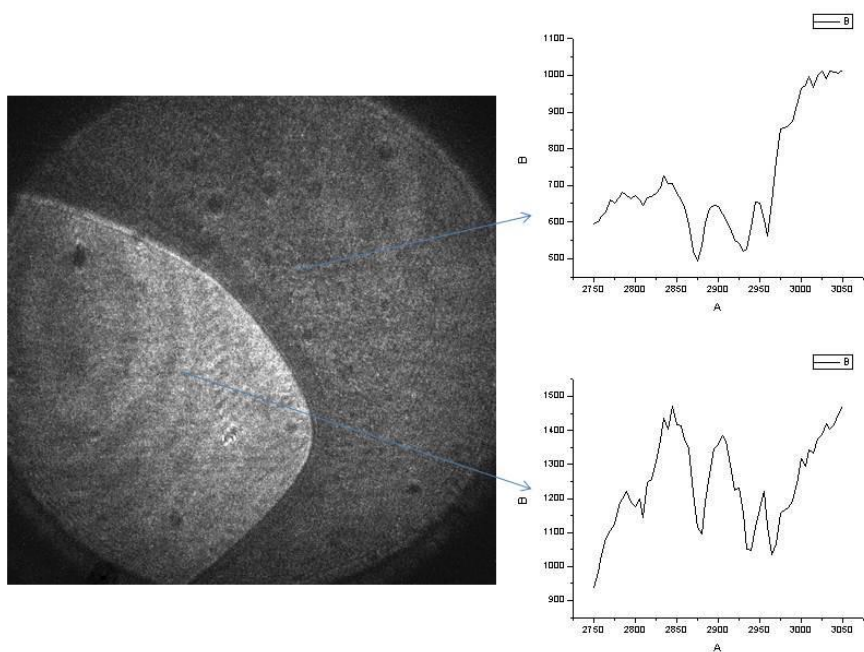
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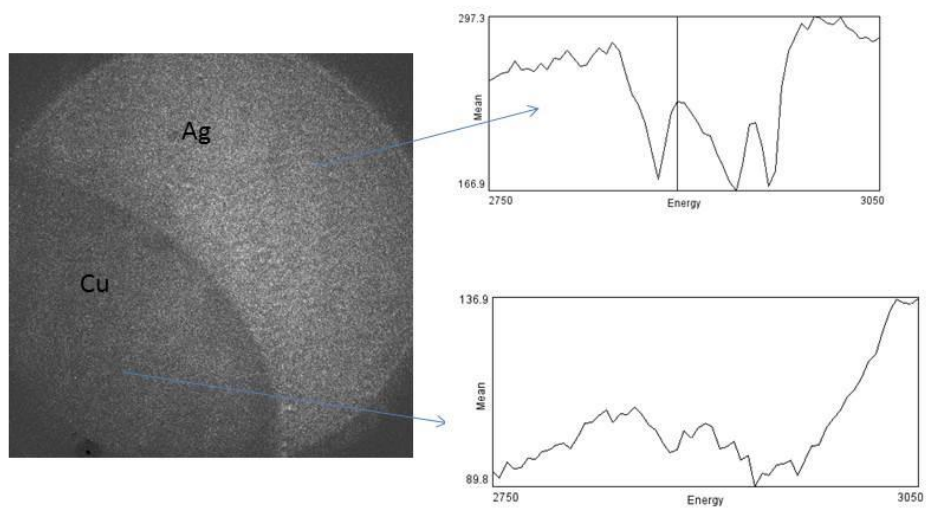
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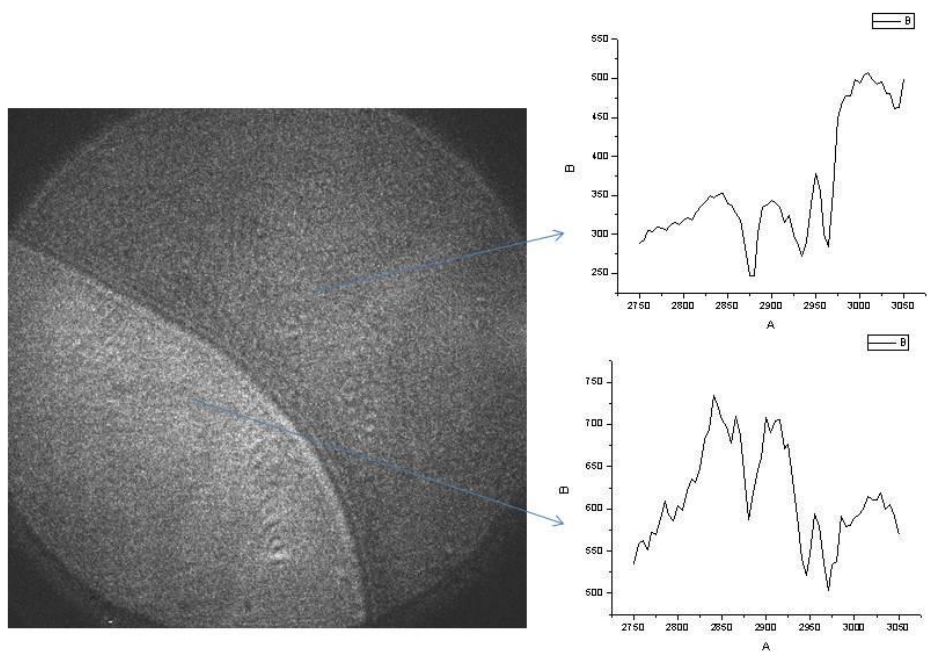
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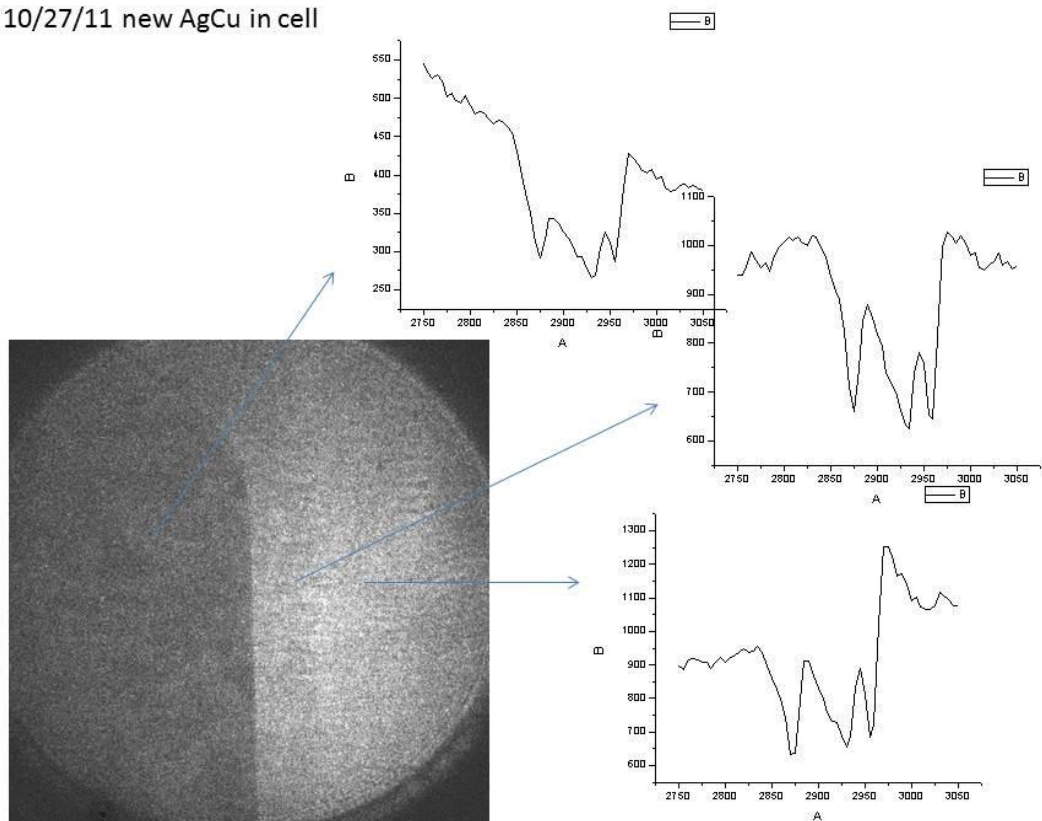
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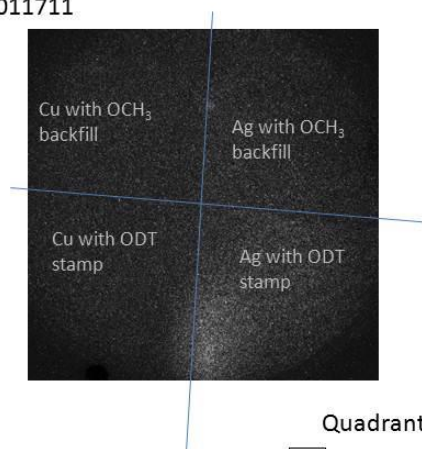
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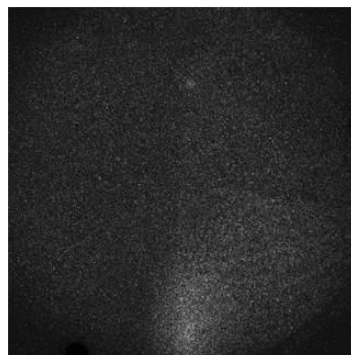
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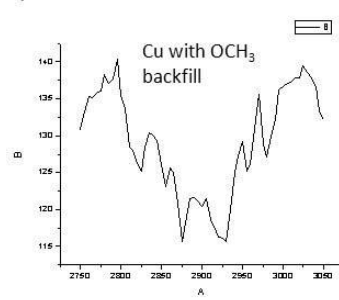
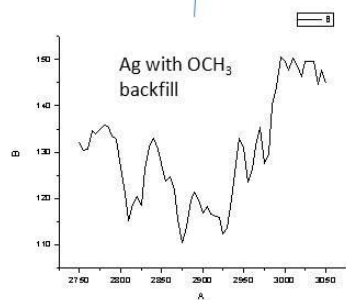
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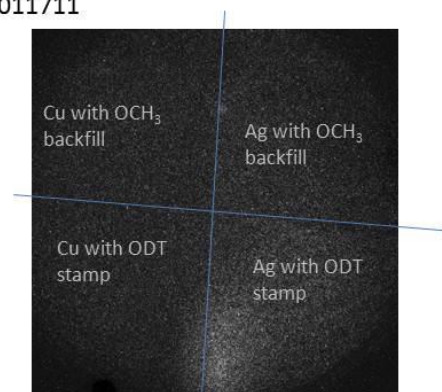
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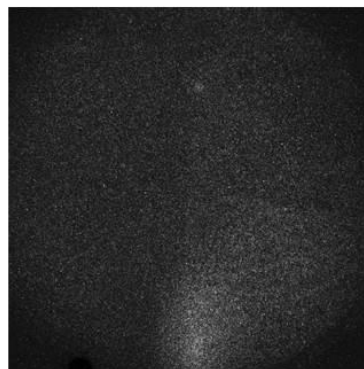
Quadrant experiment



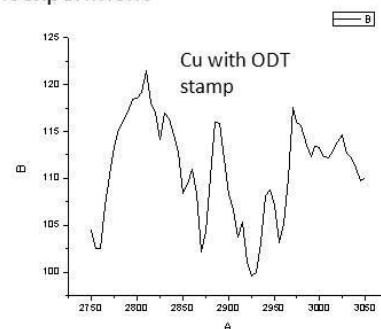
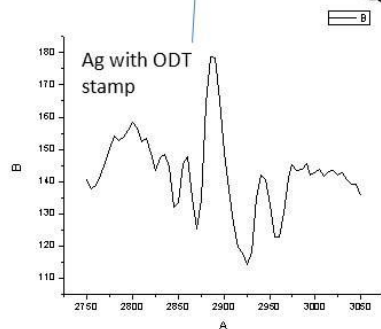
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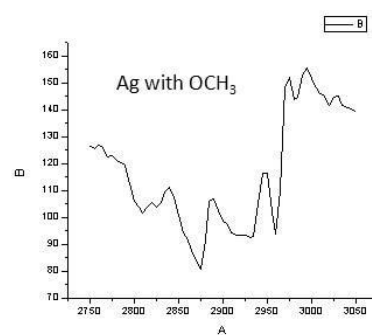
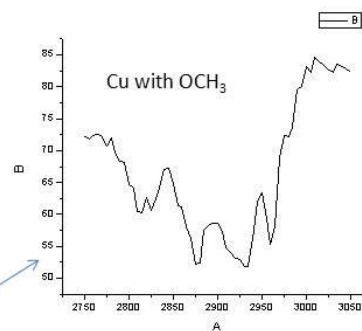
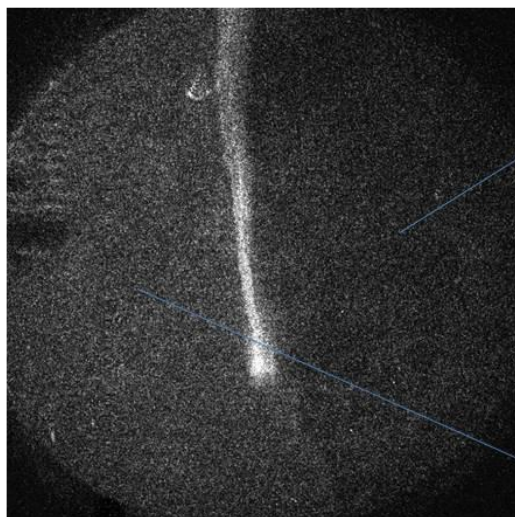


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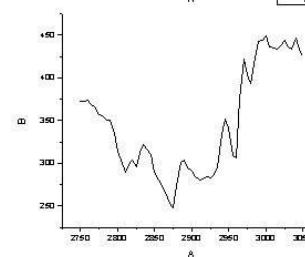
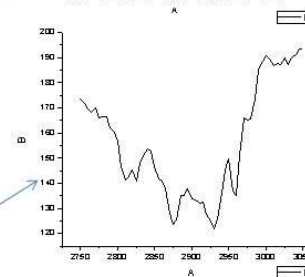
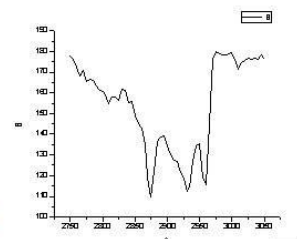
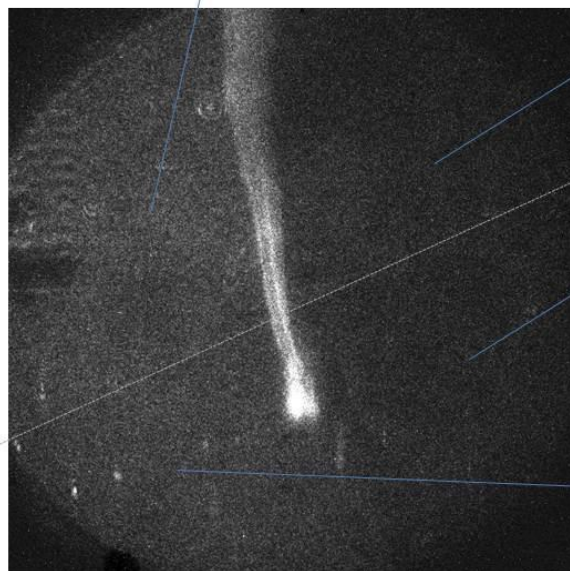
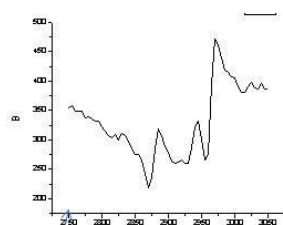


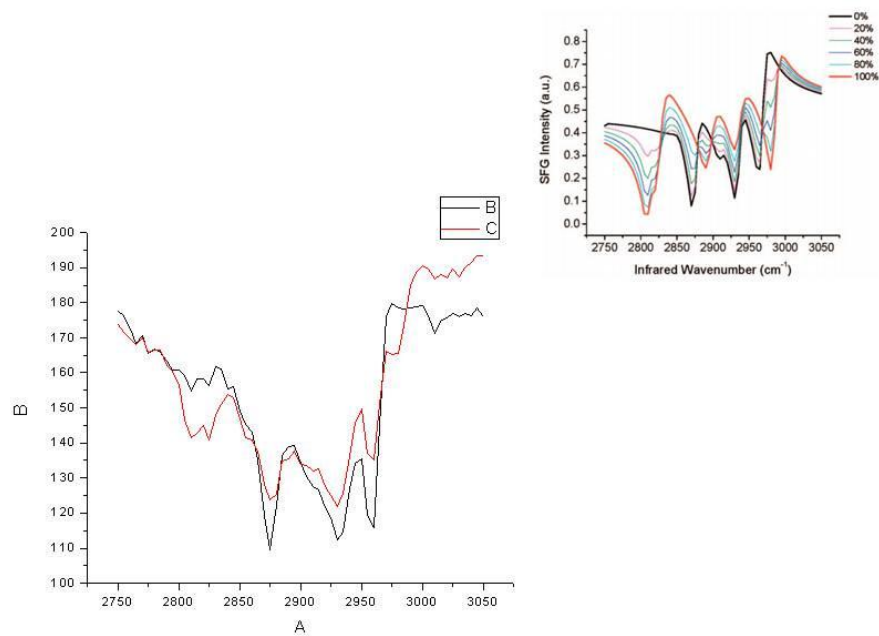
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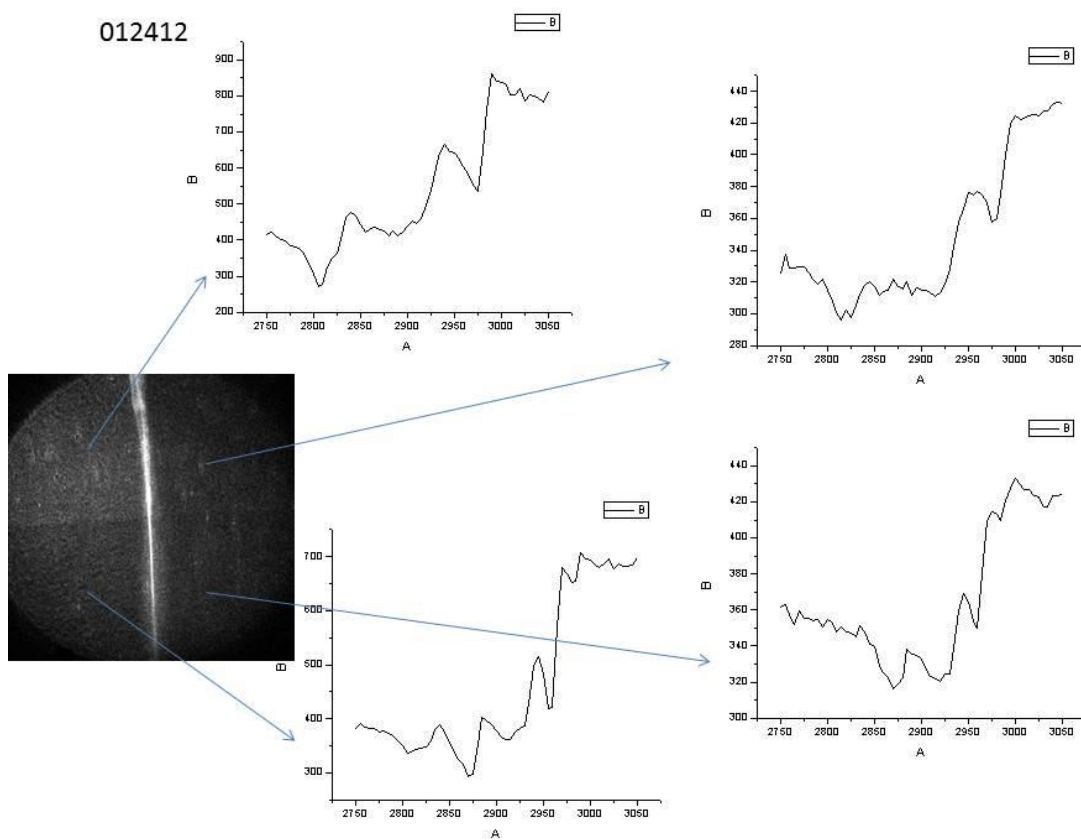


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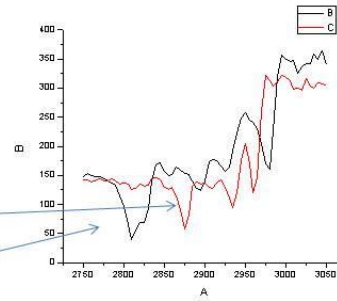
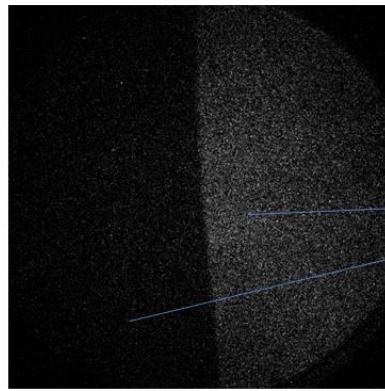




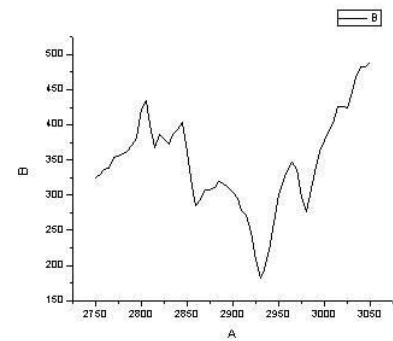
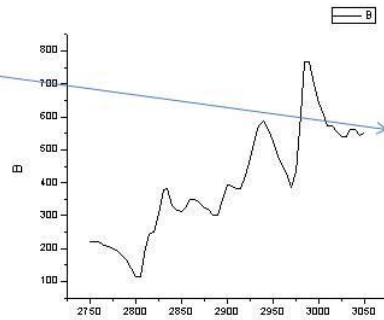
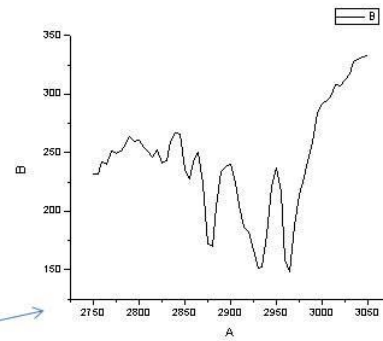
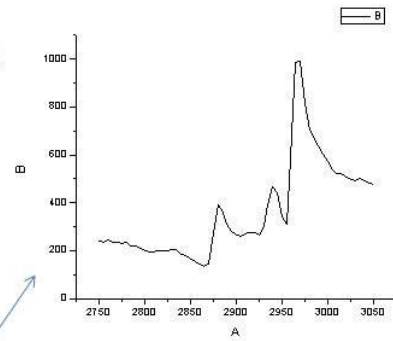
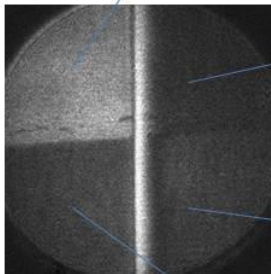
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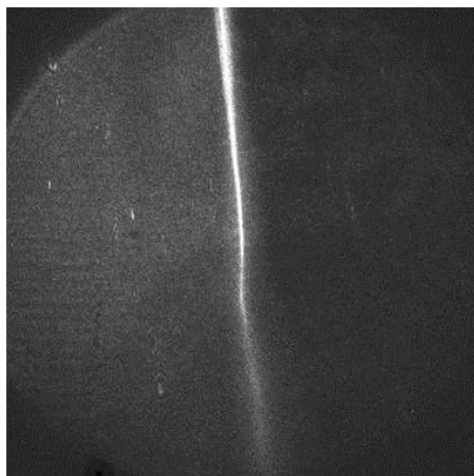


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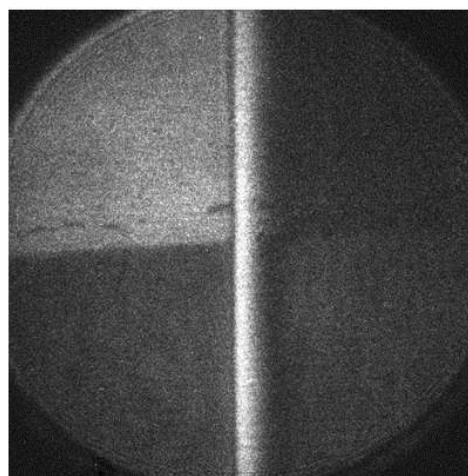


013112

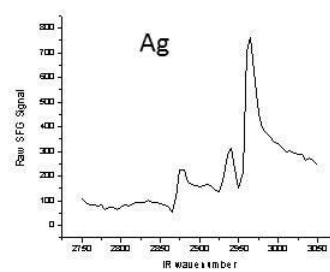
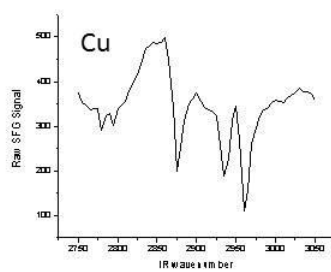
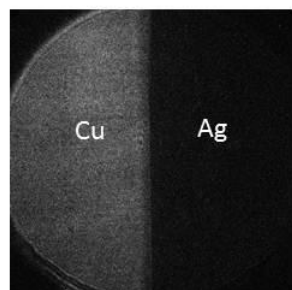
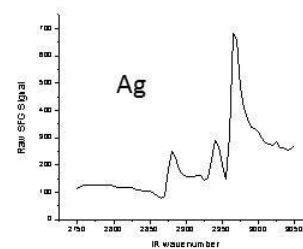
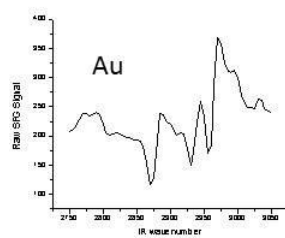
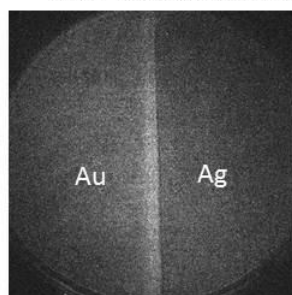
Alloy Sample - Must be repeated



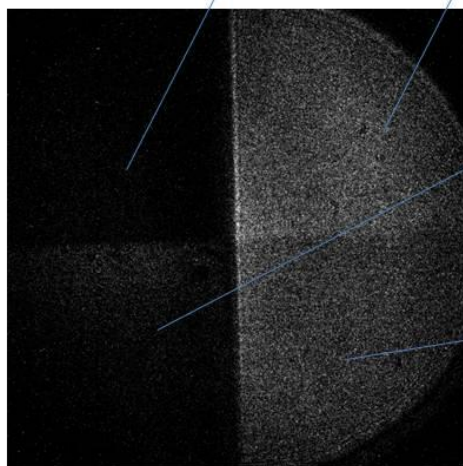
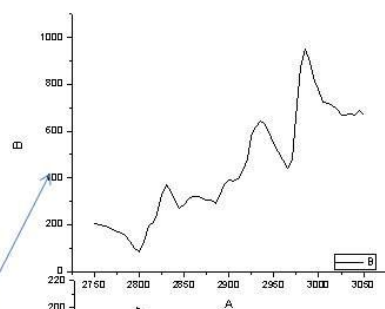
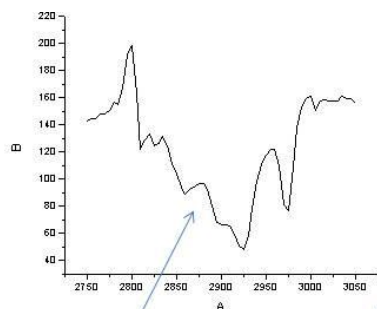
Evaporated Sample - TARGET Image



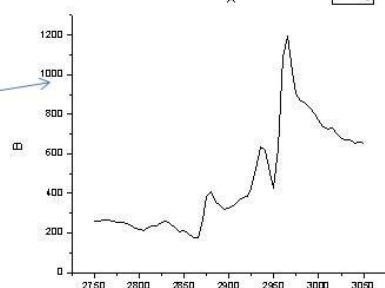
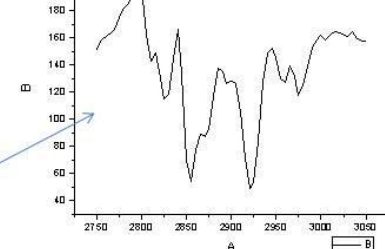
1064 nm Raw Average SFG Spectra



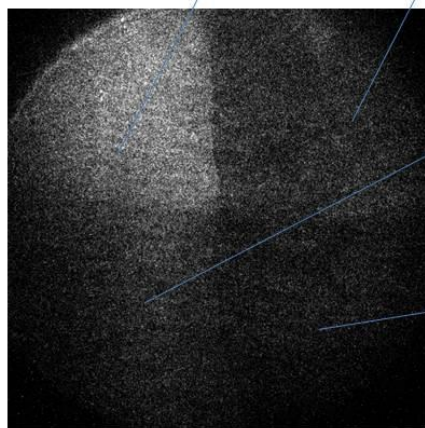
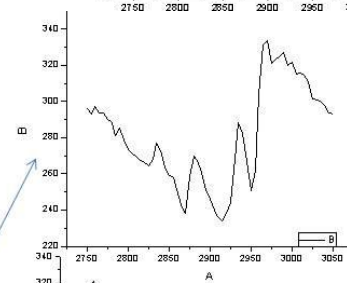
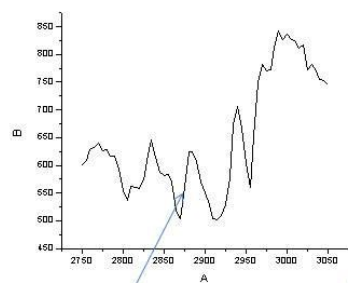
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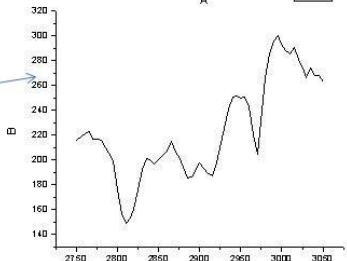
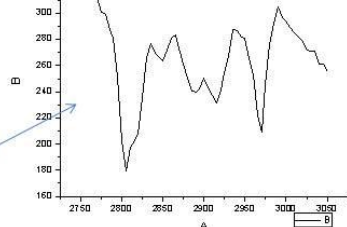
Evaporated Sample



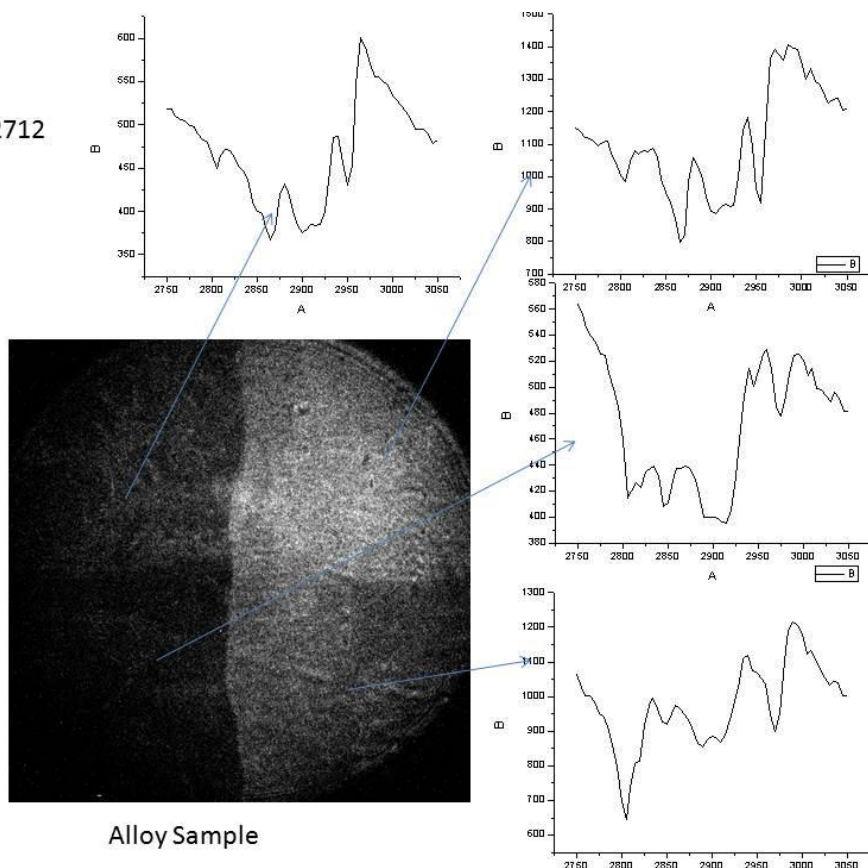
021712



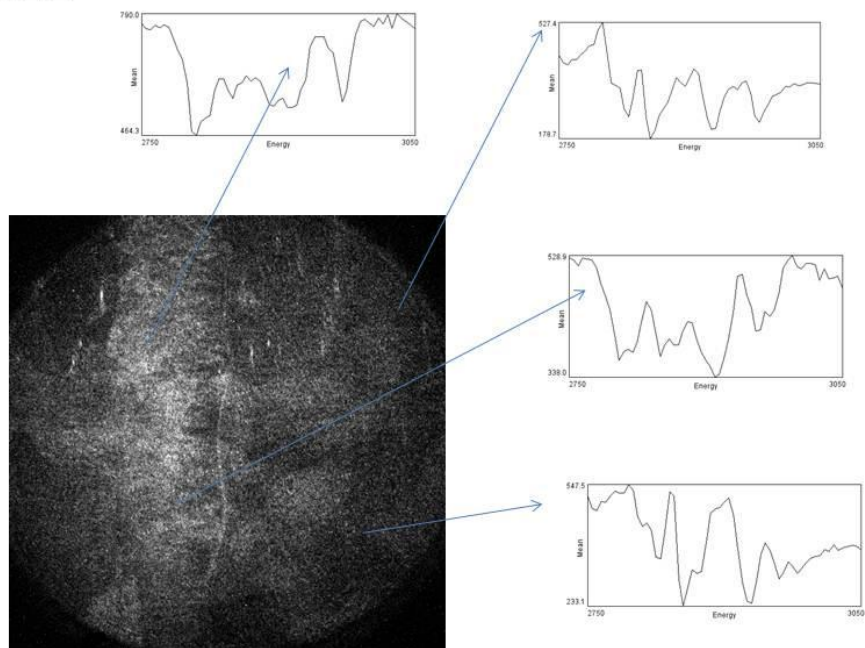
Alloy Sample



022712

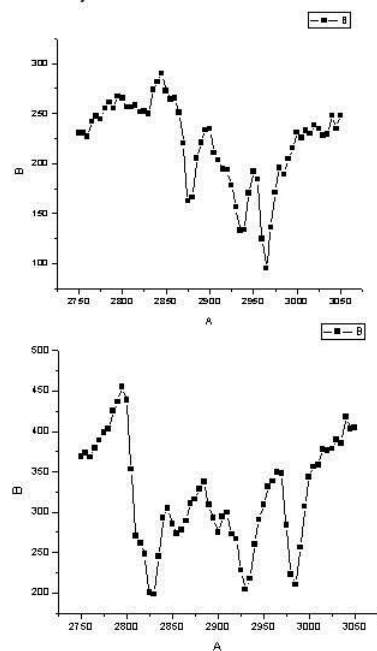
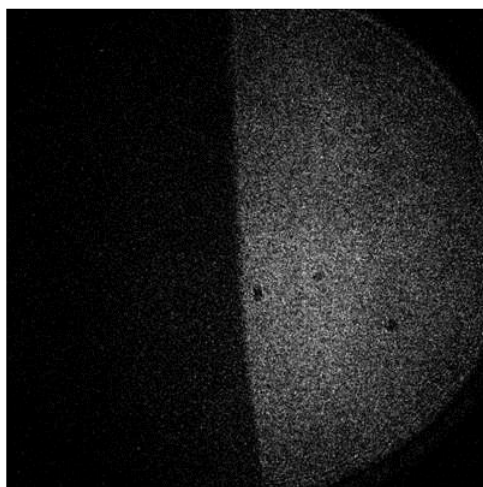


032212



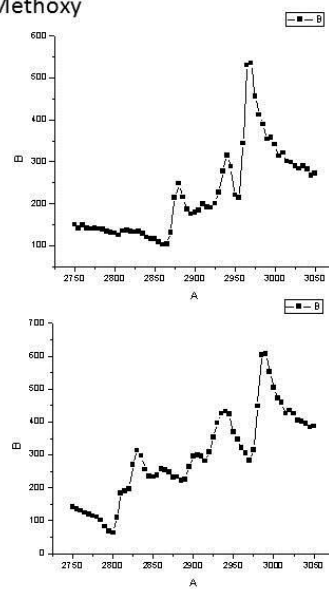
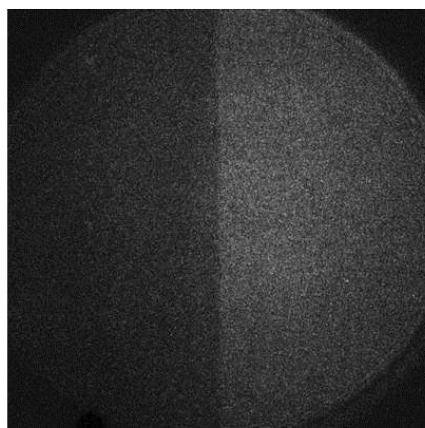
032912

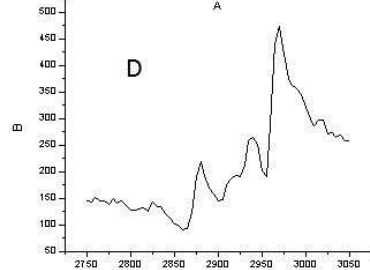
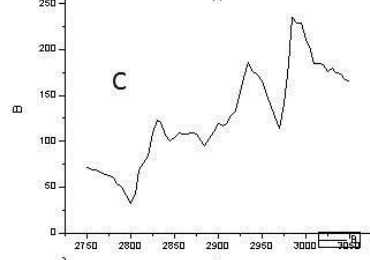
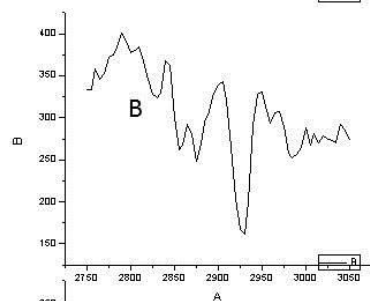
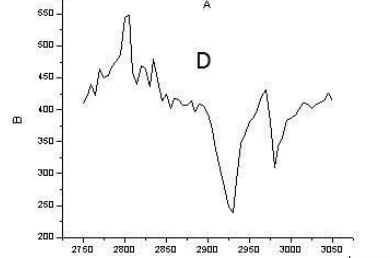
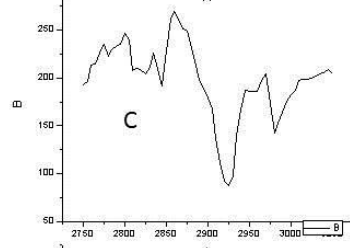
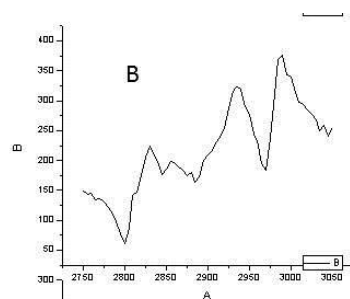
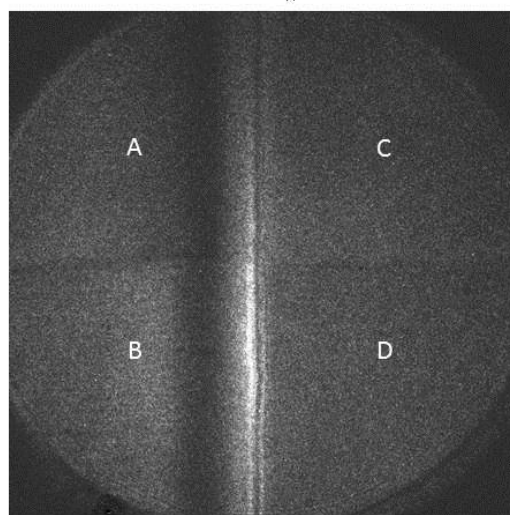
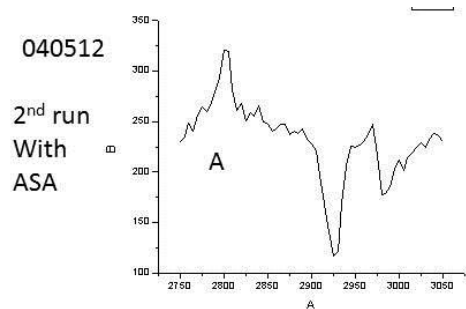
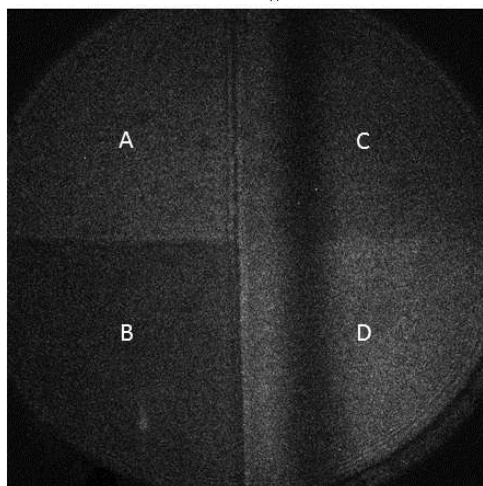
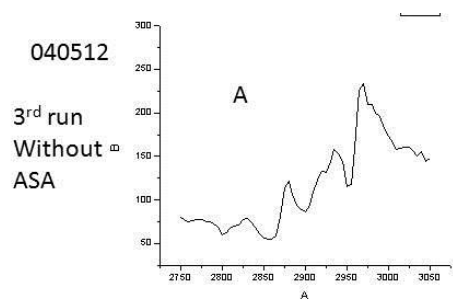
Cu cell with ODT and Methoxy

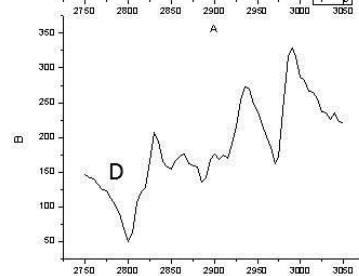
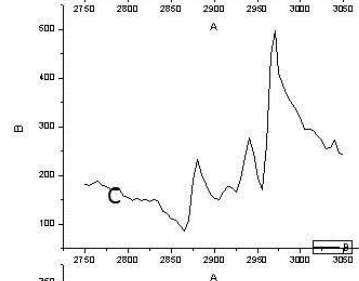
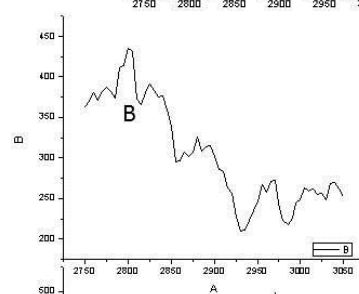
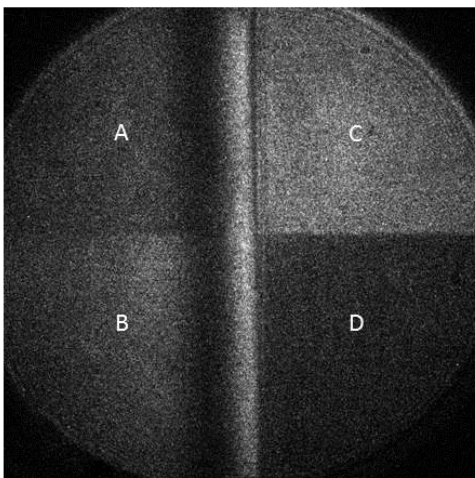
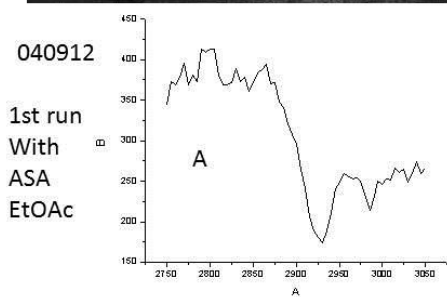
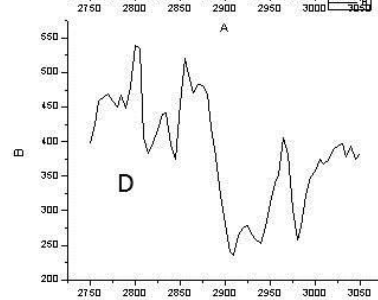
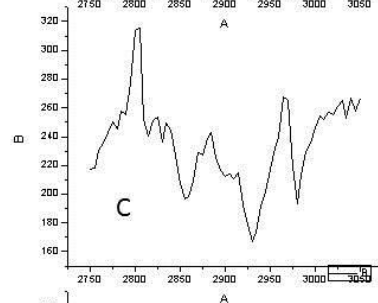
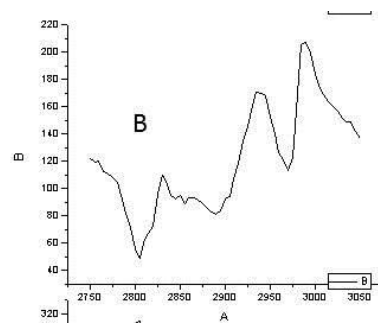
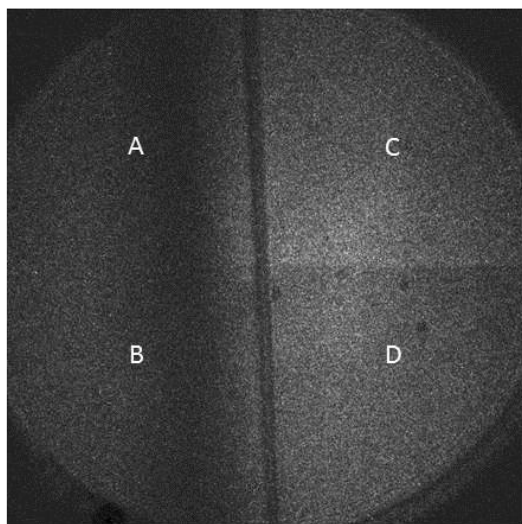
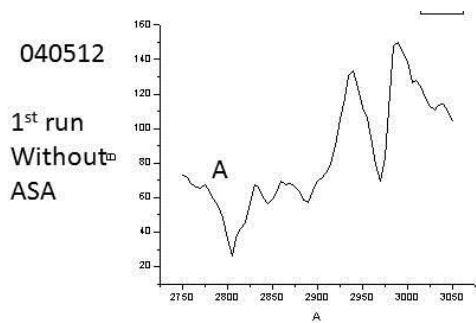


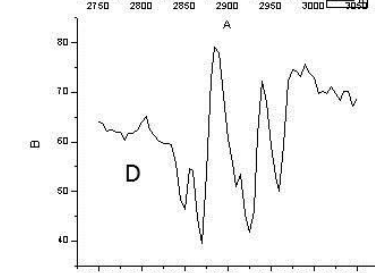
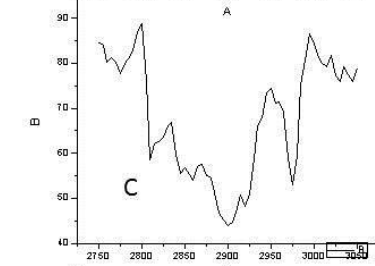
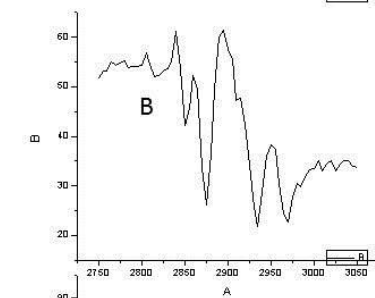
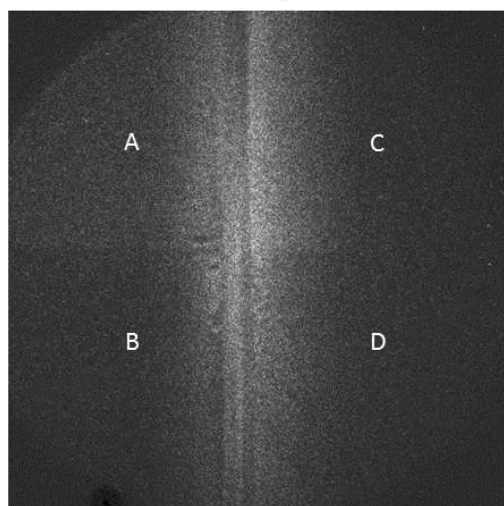
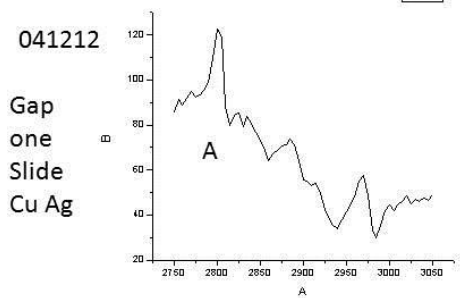
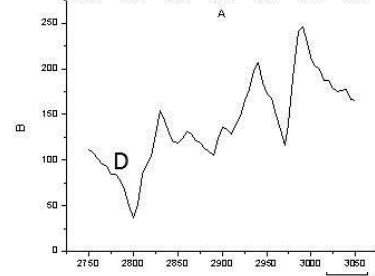
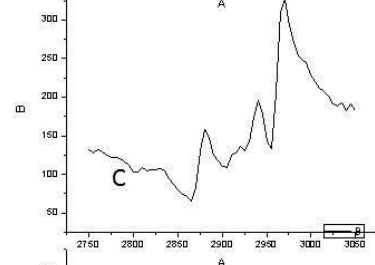
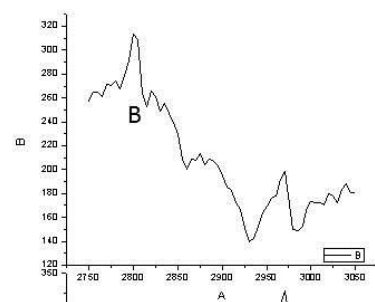
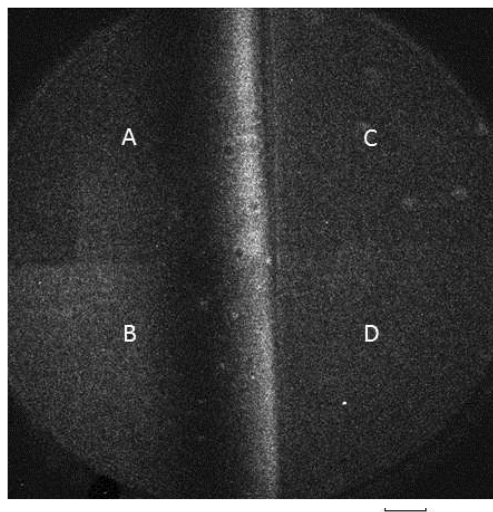
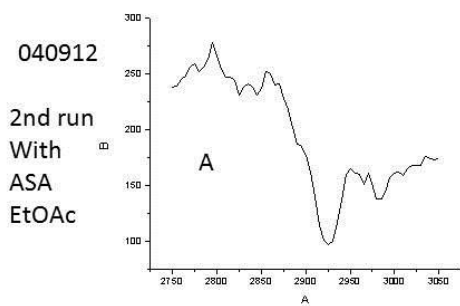
032912

Ag cell with ODT and Methoxy



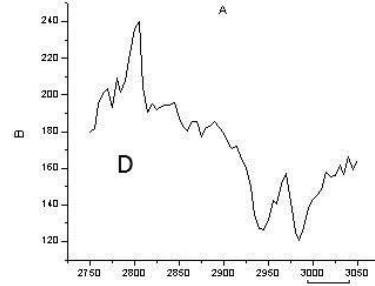
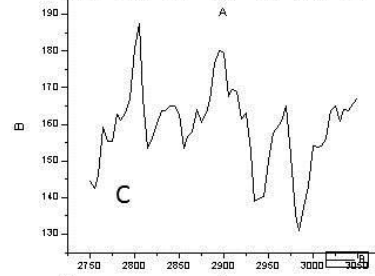
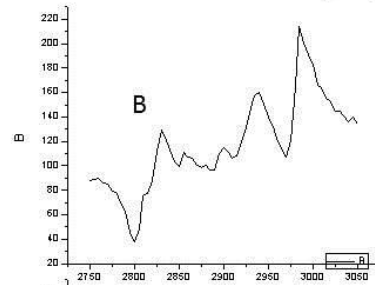
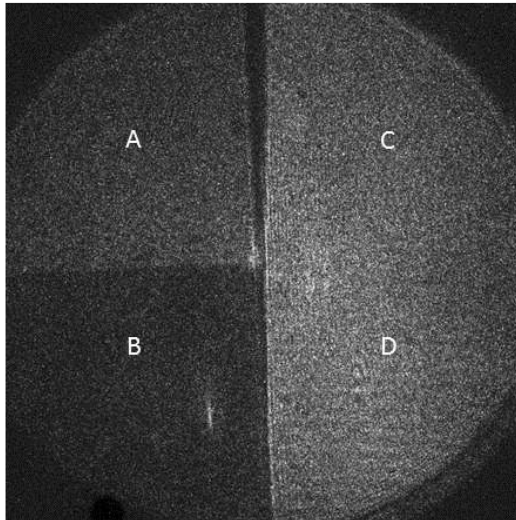
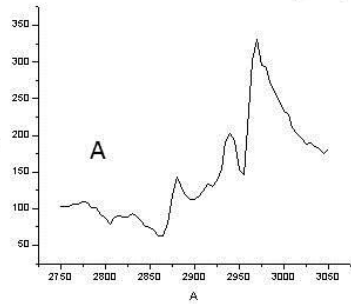






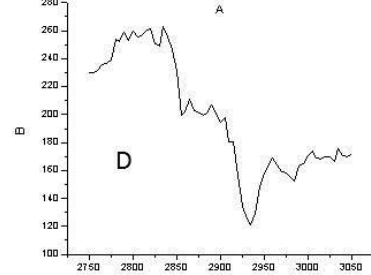
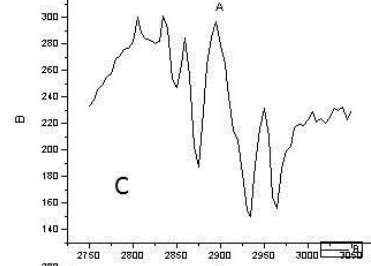
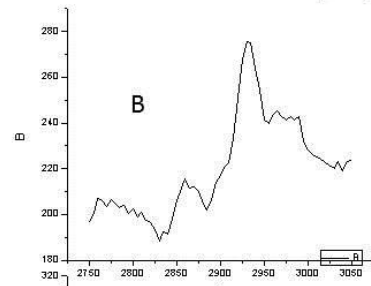
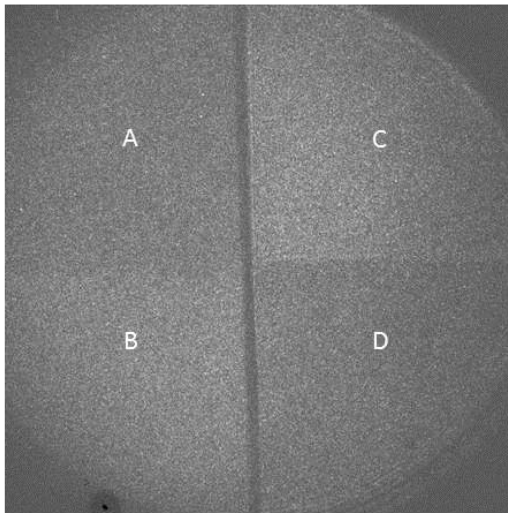
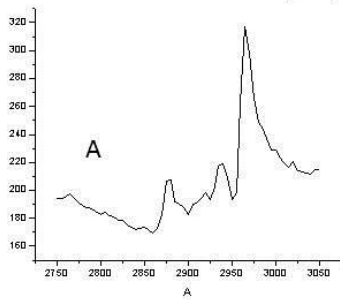
041512

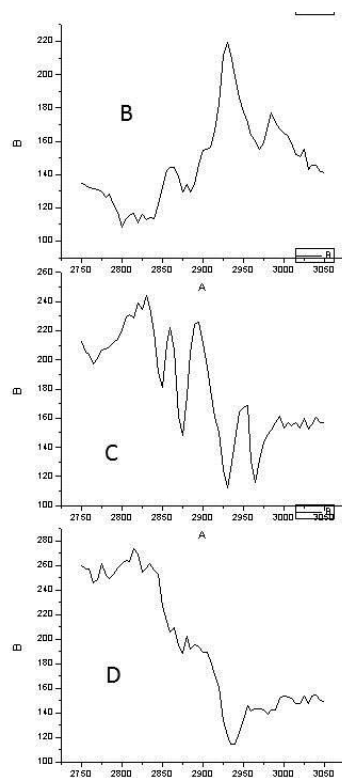
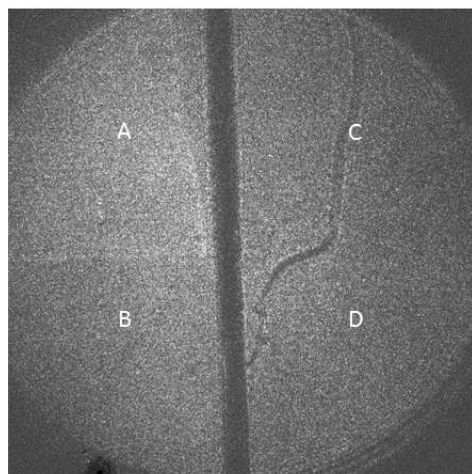
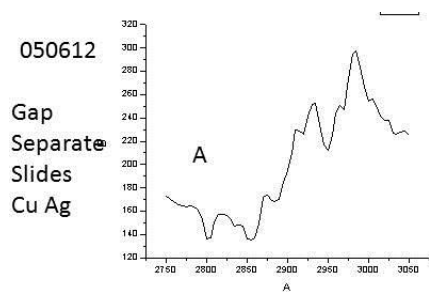
Gap
Separate
Slides
Cu Ag



050412

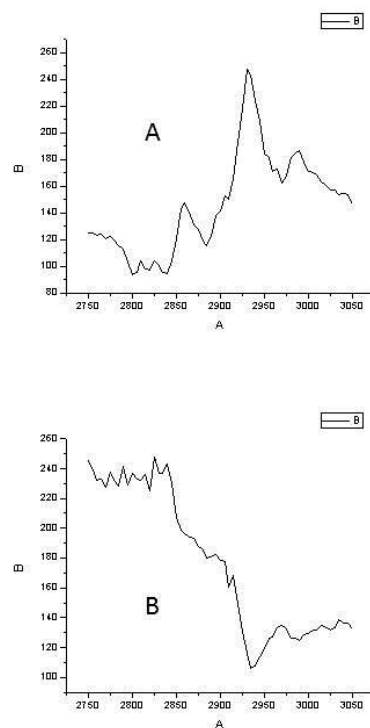
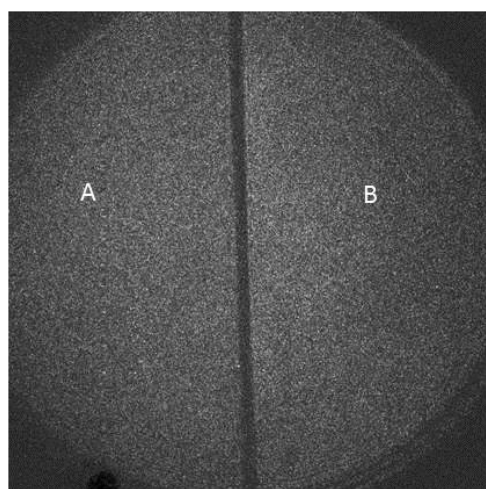
Gap
Separate
Slides
Cu Ag





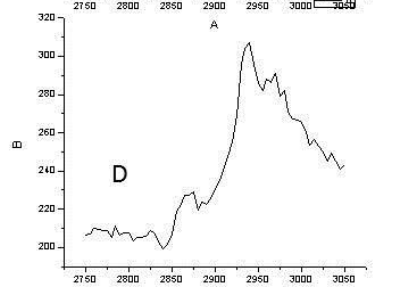
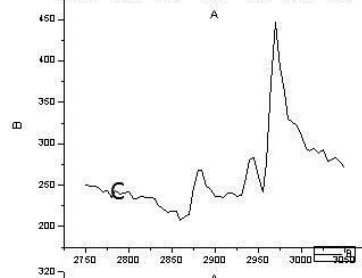
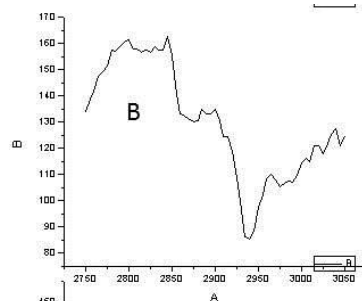
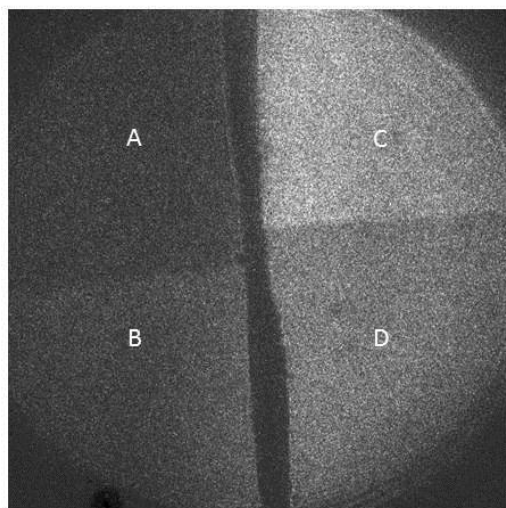
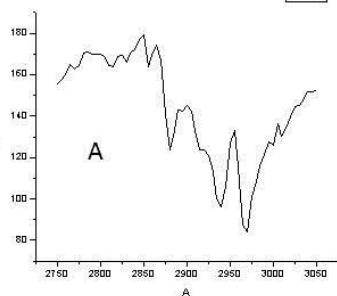
050612

Methoxy ODT



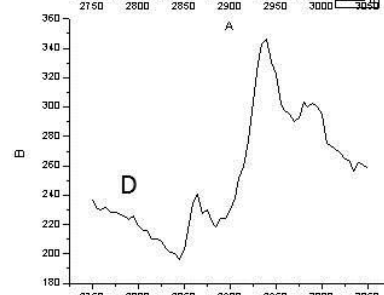
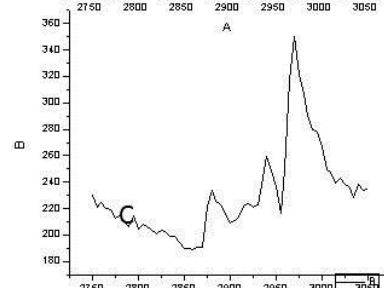
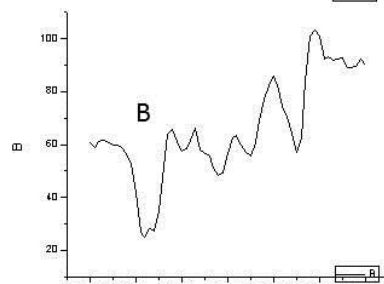
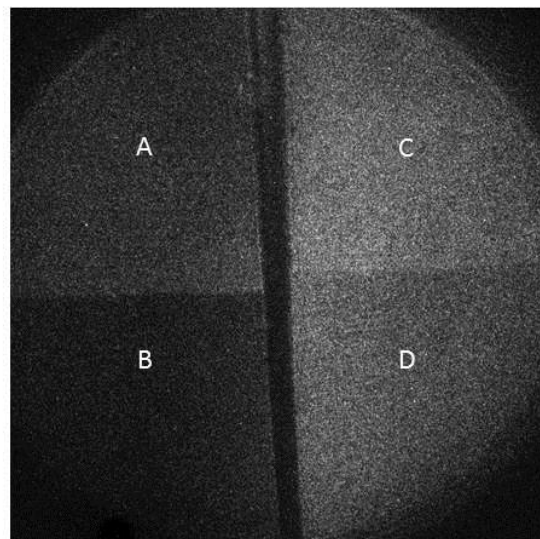
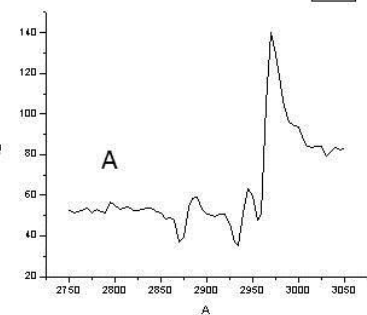
052012

Gap
Separate
Slides
Cu Ag

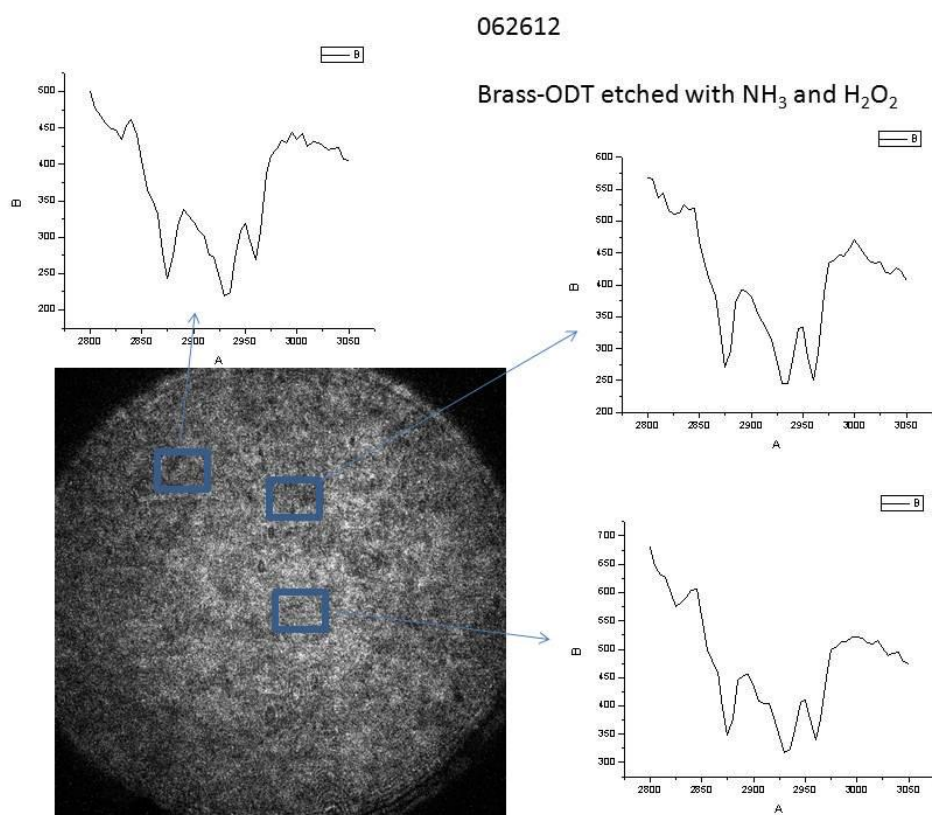
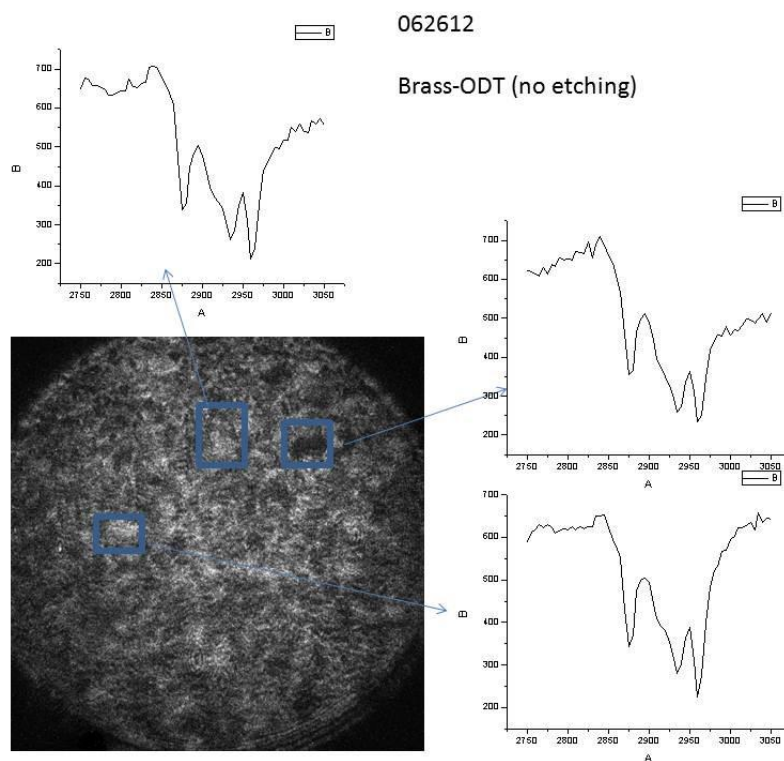


052012

Gap
Separate
Slides
Au Ag

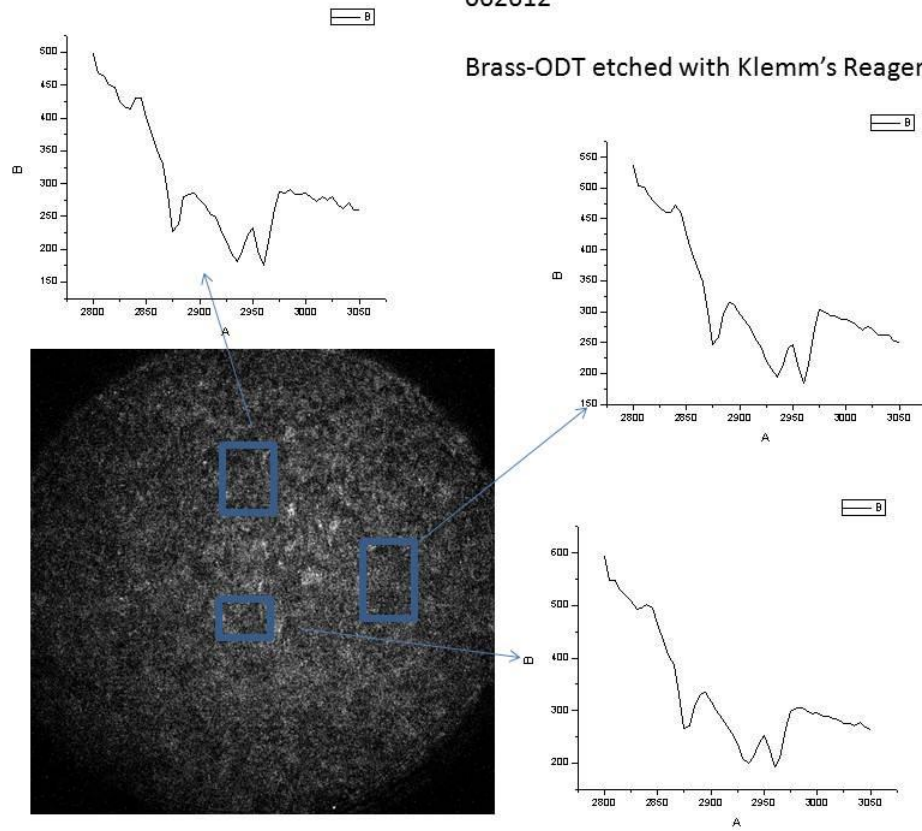


SFGIM Experiments on brass alloy samples

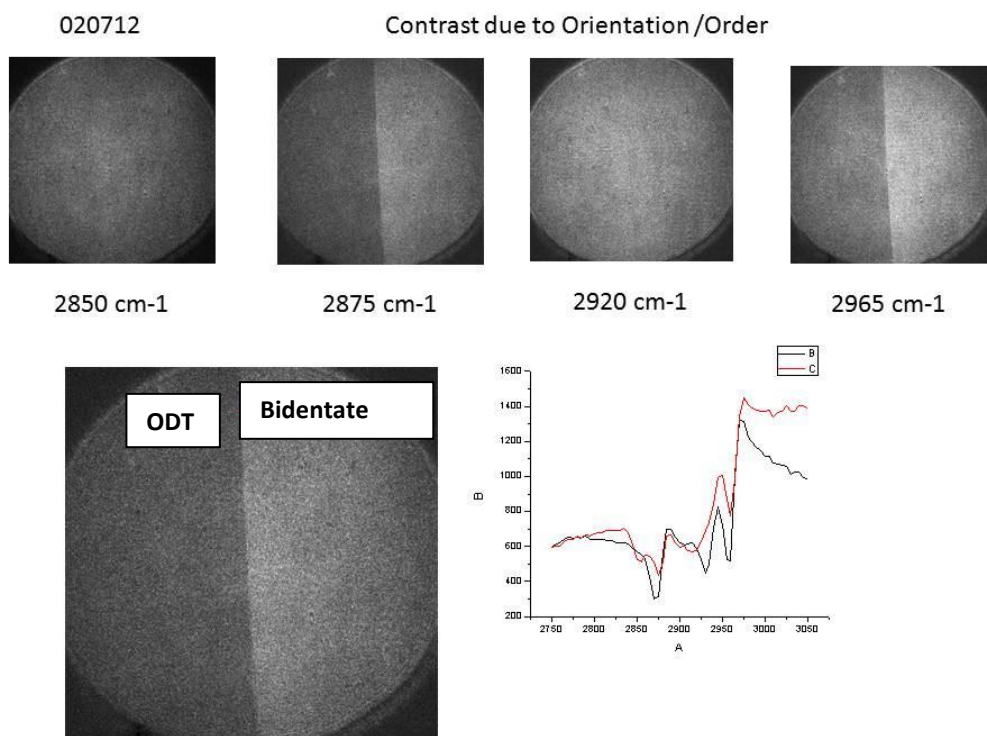
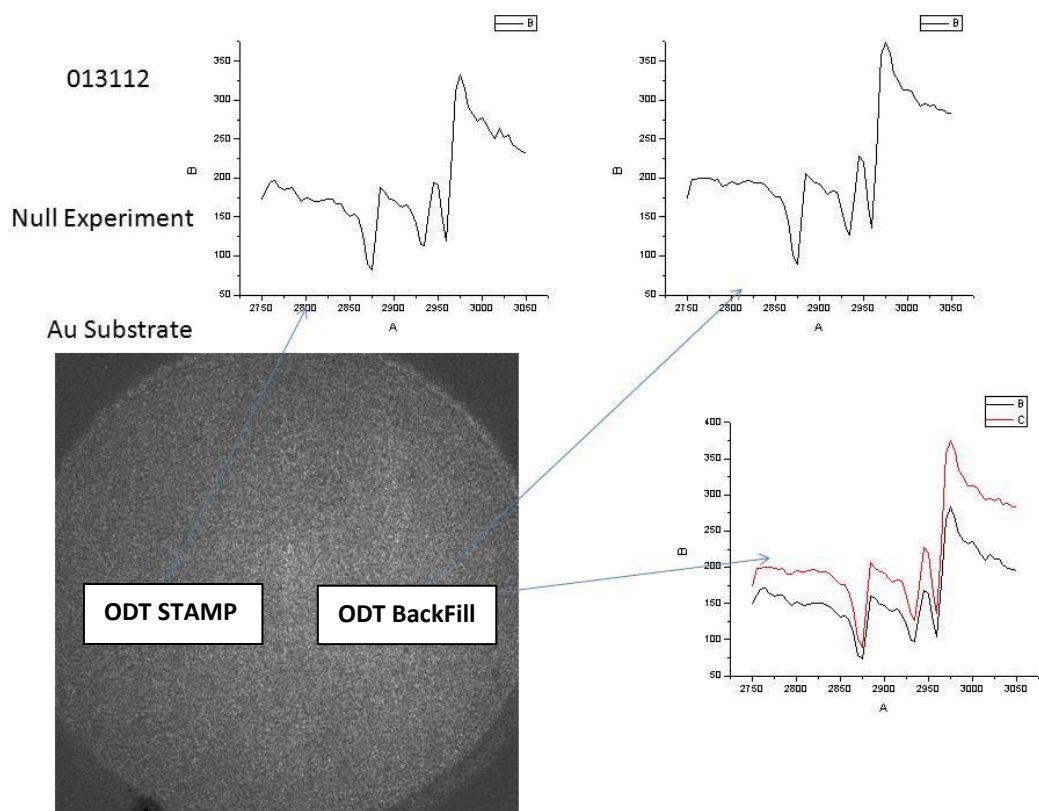


062612

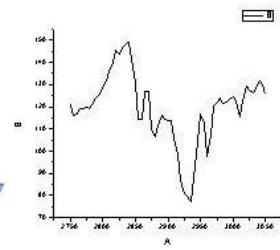
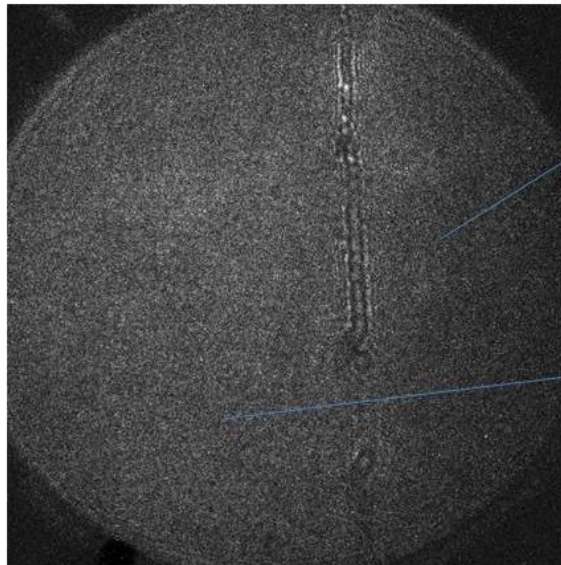
Brass-ODT etched with Klemm's Reagent



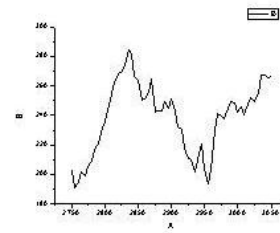
Other SFGIM Experiments (microcontact printing and graphene-deposited copper)



010511



Bare Cu with ODT



Graphene-covered Cu with ODT