



# **THE NEW IMAGE PROCESSING ALGORITHM FOR QUALITATIVE AND QUANTITATIVE STM DATA ANALYSIS**

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In Partial Fulfillment

of the Requirements for the Degree

Master of Science

in Electrical Engineering

by

Ashish Jatashankar Tripathi

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## **ABSTRACT**

Image processing can be used to extract cluster parameters from STM image. The objective observation from the obtained data can be used to understand certain processes in Material Science. One such application is to study under-potential deposition where the substrate surface is modified with a sub-monolayer of different noble metal.

This thesis aims to develop a user friendly GUI (Graphical User Interface) that helps researchers to draw an inference by quantifying parameters like layer coverage, nucleation density, cluster area, and perimeter by area from an STM image. It uses an algorithm that filters noise using a custom made filter mask and then applies the OTSU segmentation technique to fit Gaussian curve on the image histogram for detecting the presence of a layer(s) of cluster in the STM image. It creates a binary image for each layer detected in the image. Cluster parameters are obtained by processing this binary image.

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# CHAPTER 1 INTRODUCTION

With the advent of computational devices, it became easier to perform number of complicated calculations on problems in a fraction of seconds. Such problem could range from computer vision to DSP (digital signal processing) [1].

Image processing is a stream of science in DSP where the input is an image and the output is either a reformed image or a set of parameters related to the image. It requires an image to be treated as some form of signal and is synthesized in various domains in order to obtain the results. It is used in areas such as multimedia, computing, secured image data communication, biomedical imaging, texture understanding, pattern recognition and content based image retrieval [2].

Image processing is relatively new in material science however the potential of using it for research, fabrication analysis and quality control is immense. This thesis aims to use image processing to objectively observe the parameters related to cluster deposition on a surface of another element [3]. In order to understand the significance, it is imperative to understand how observation are important in an experiment.

Any observation can be classified in two categories, subjective observation and objective observation. Subjective observation cannot be seen. It can be an idea, thought or based on personal opinion. It may not be correct. Objective observation is based on mathematics. Objective observation can be tested for its veracity [4]. For example, consider the given STM image in the Figure 1.1.



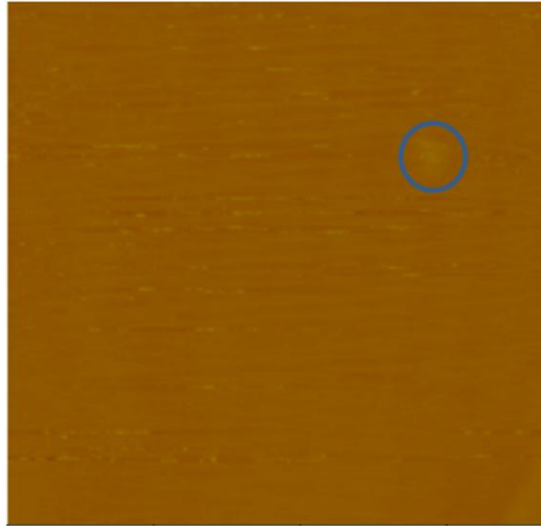


Figure 1.1 Pb UPD  $\text{Au}_{(111)}$  STM image.

In the given image it is asked to observe the number of cluster. The subjective observation would be same as objective observation. This is because the number of cluster is small however as the number of cluster increases, the subjective observation for a human is no more in conjunction with objective observation. This is evident from the image in the Figure 1.2.

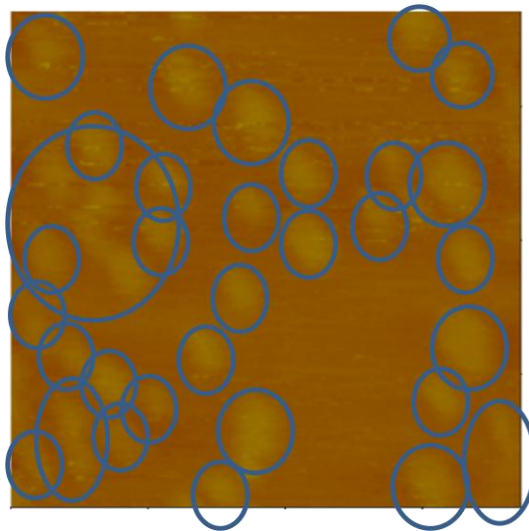


Figure 1.2 Pb UPD  $\text{Au}_{(111)}$  STM image.

Consider other parameter such as cluster density, layer coverage, in such cases subjective observation may never be as accurate. The objective of this thesis is to develop an algorithm for image processing to calculate various parameters pertaining to cluster deposition. These parameters can be used as objective observation in order to draw conclusion for research.

In image processing, it is imperative to understand the input image to be analyzed. In most cases, an algorithm is developed after studying the various properties of images. These property can be size of image, type of image, noises in the image, type of information to be retrieved from an image. The same approach is followed for developing this algorithm. Some important properties of input image is mentioned in next paragraph.

All images used as an input for this algorithm are taken from STM. STM is abbreviation for Scanning Tunneling Microscopy. This is an imaging technique used for revealing the apparent electron-density-related to the atomic structure of surfaces, using a needle-like probe near the surface under observation. It measures a tunneling current generated by altering the potential at the tip of the probe, a probable 3D representation of the sample surface is generated by scanning the tip over the surface of the object and mapping the distance for constant current level at various points. The image can be obtained through STM in an ASCII file format. It contains the information such as the scan size (in nm) to obtain the size information, scan rate (in Hz) to obtain the scan rate and the height of each point on the STM image in terms of ASCII value.

These ASCII value is a number between -32767 to 32768 with respect to an image file and could be used to find the height of a point on the image [5]. It can also be used to model the topography of the surface under consideration. One of the most notable properties of the image is the noise that should be taken in consideration. Exponential noise, Gaussian noise, Periodic noise are the major contributors of the Noise in an input image. Exponential Noise occurs due to sensors and electronic circuitry [6]. The scanning of electronic tip in an horizontal raster fashion contributes to the Gaussian Noise while the external disturbance is responsible to for the Periodic Noise. The algorithm developed, minimizes these noises before determining the required parameters.

## CHAPTER 2 IMAGE ALGORITHM PROCESS FLOW

The image processing algorithm is divided into several independent modules in order to achieve features like inheritance, polymorphism, data abstraction peculiar to object oriented programming. Object-oriented programming (OOP) is a programming paradigm used to design applications and computer programs using data structures consisting of data fields and methods [7]. The data is accessed by calling specially written functions and modules. They act as the intermediaries for retrieving or modifying the data they control. These modules when used in a particular sequence define the process flow of any algorithm. The process flow of image algorithm is given in the Figure 2.1 below.

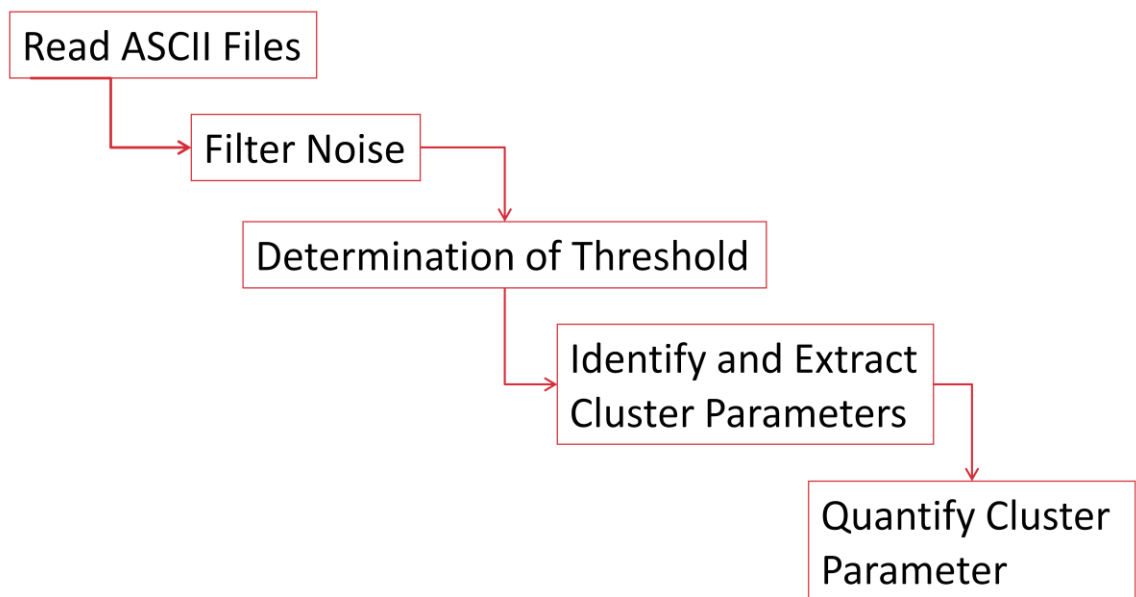


Figure 2.1 Process flow of image algorithm.

As shown in the Figure 2.1 the algorithm uses 'Read ASCII files' module to take input from user and convert it to grayscale. This matrix is used as an image file by the

algorithm. The noise present in the image is minimized using 'Filter Noise' module. 'Determination of Threshold' is used to Identify the different layers of cluster in an Image. The output from this module is a binary image of clusters in different layer. It is then processed by 'Identify and Extract Cluster Parameters' to extract parameters like cluster area and cluster perimeter by area, 'Quantify Cluster Parameters' to quantify the parameters of interest. A brief description of these modules is given below followed by a detailed explanation in later chapters.

## **2.1 Read ASCII Files**

This module asks user to select the location of input file. On providing the input it reads the ASCII files and extracts the parameters such as 'scan size,' 'scan rate' from the file. At the same time it extracts the ASCII values for each point to model the image. This module works in two modes. Single image, to process a single ASCII file at a given potential and batch of Images to process a group of ASCII files at any potential.

## **2.2 Filter Noise**

As mentioned in chapter 1, the three prominent noises in an input image are Exponential noise, Gaussian noise, Periodic noise. To minimize the Gaussian noise, Gaussian low pass filter is developed [8-9], this low pass filter obstructs the frequency of more than 80 Hz. This value of 80 Hz was selected based on number of iterations and human observation. Periodic Noise is minimized with the help of notch filter. The notch filter is a band-stop filter or band-rejection filter that passes most frequencies

unaltered, but attenuates those in a specific range. The frequencies between 48 Hz to 52 Hz were attenuated. These values were selected after carefully determining the periodic noise in different image. A frequency mask is developed that contains both low pass Gaussian filter and notch filter. It is then applied to image under consideration.

### **2.3 Determination of Threshold**

This module is used for Image segmentation by determining a threshold for segmenting an image. The input image is considered to be mostly free of noise. Using a multi-Otsu segmentation module in Matlab the image is segmented in thirty two levels. To eliminate any other kind of noise curve smoothing operation is performed. The curve smoothing operation removes any sudden spikes from the histogram of number of pixels v/s Otsu level for an image under consideration. This process further diminishes the exponential noise present in the image. The peak is determined by equating the first order derivative to zero and verifying whether the second order derivative is less than zero at a particular point. These peaks are treated as mean of Gaussian curve in histogram. The threshold is selected as a point where area under the curve is sixty six percent of the total area under the Gaussian Curve. In the case where there are more than one peaks multiple values of threshold are obtained. Each value of threshold indicates a layer. So if there are two peaks, the histogram is treated as a combination of two Gaussian curve with different mean and standard deviation. In case of multiple Gaussian curves the threshold is calculated in same way as discussed earlier. Based on

the number of thresholds the module generates subsequent number of binary images. The module can efficiently detect up-to three layers in an image.

## **2.4 Identify Cluster and Extract Cluster Parameters**

This module takes binary image from 'Determine Threshold' module as an input and determines the cluster size, their shape, their location along with its area and perimeter. The output for this module is an array that contain the information about number of cluster in an image, their corresponding area, euclidian radius, perimeter and location. This module uses an inbuilt function in MATLAB to determine the mentioned parameters [10]. The minimum criteria for any spot to identify as cluster is the area of cluster should be more than  $1 \text{ nm}^2$  and the perimeter should be more than 4 nm. These parameters are converted in its equivalent SI units. A new parameter, perimeter by area is calculated for each cluster. It is useful in observing the shape of the cluster.

## **2.5 Quantify Cluster Parameter**

Quantify Cluster Parameter is used to calculate the mean, average (median) and maximum along with standard deviation of cluster area and perimeter by area ratio of the cluster. It also calculates the coverage of a layer and the density of a layer identified by the algorithm.

If input is a single image, it displays mean, average [11], maximum, standard deviation [12] of cluster area and perimeter by area ratio of cluster along with layer coverage and cluster density on the console of Matlab. In case if the input is a group of

image than it display a plot of the calculated parameters v/s the name of image file under which it was recorded.



## CHAPTER 3 READ ASCII FILES

'Read ASCII Files' is used to read the images to be processed by the algorithm. As mentioned in the previous chapter the input is an ASCII file containing the pixel information of an image along with information about the condition at which the image was recorded. It is imperative to know the condition while recording an image to understand the science behind the deposition process recorded in an image. The parameters like scan size and z-scale is important to understand the information in an image.

### 3.1 ASCII file

ASCII File is a numerical representation of recorded image and the conditions under which the image was captured by the user. This file is immediately stored in the NanoScope's capture directory as binary file. It can be divided in two subsections,

1. A header, containing various parameter settings used during the capture of the original image, a Ctrl-Z character to signal the end of the header, and padding, comprised of random data.
2. Image data, stored two bytes (216) per pixel (2's complement).

The beginning part of an ASCII file contains a header section. The header gives information about the condition under which the image was captured by SPM. The size of header depends upon the number of parameters used at the time that data is captured and the type of file saved and the version of NanoScope software. It may

contain more than 2,000 parameters. Each header is divided into separate lists (beginning with the characters\\*). Users typically, manipulate only a few of the parameters for each application. It provides crucial parameter and setting information for converting ASCII file data. The end of the header file reveals where the actual data begins [1]. The data file structure of an ASCII file is given below in the Figure 3.1.

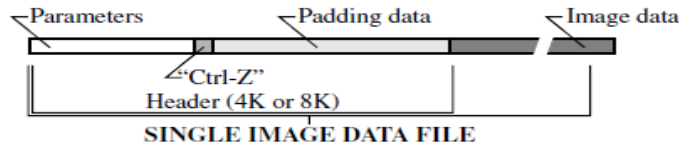


Figure 3.1 ASCII Data File Structure.

As observed in the Figure 3.1, parameters form the first part of header. It contains the numerical data pertaining to settings of device during image capture. Ctrl - Z character marks the end of parameter lists. Random padding data is added to make it to a predetermined length followed by pixel information in ASCII values [13].

The important parameters are scan size, height and width of the scan area in nanometers and z scale- factor used to convert data to calculated height in SI unit, e.g., let Z scale be 20000 then height can be calculated by using formula given below [13],

$$height(nm) = \frac{pixel\_value}{65,536} \times 20,000 . \quad (3-a)$$

### 3.2 Process Flow

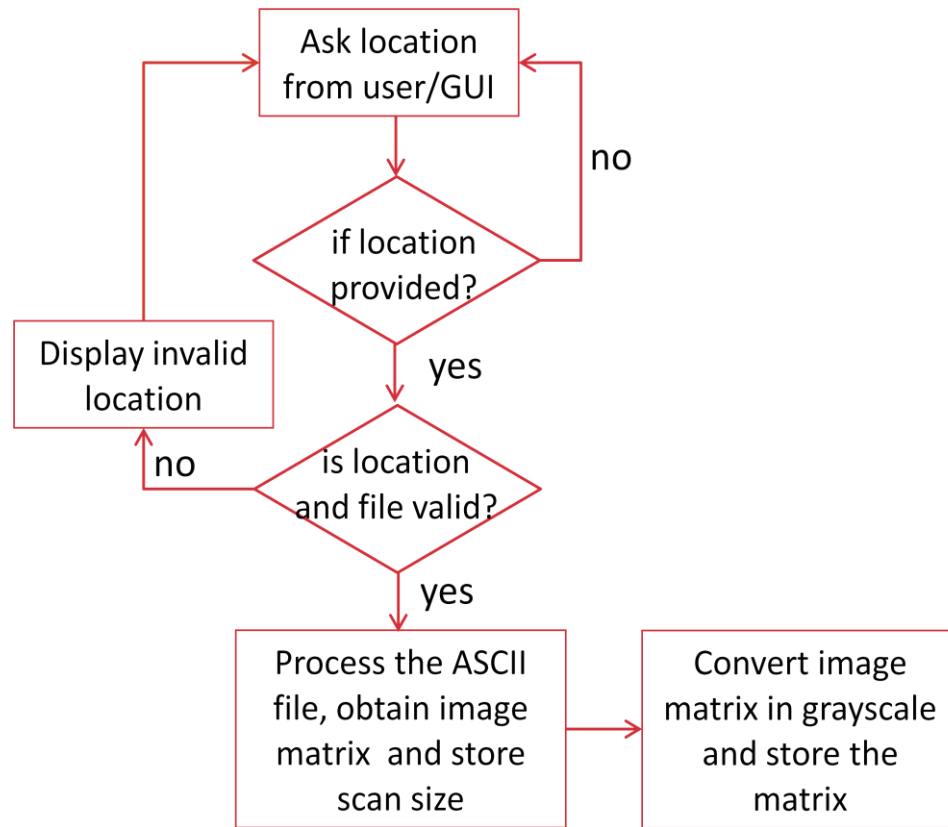


Figure 3.2 Process Flow.

As shown in the Figure 3.2 the user is asked to enter the file location. Once the file location is verified by the module, it processes the files and retrieves the z-scale ratio, scan size and the image matrix size. In some cases, a file may not contain header so a default value of 1 is assumed for both z-scale ratio and scan size. Scan size is always assumed to be in nanometers by the module. The image matrix is converted to a gray scale using an inbuilt Matlab function for further processing [14].

At the beginning of algorithm, with the help of GUI designed for the algorithm, the user is asked if a single file is to be processed or batch of image files should be

processed. Appropriate function is invoked based on the user selection by the module to read ASCII file and stores image as a matrix. This matrix is converted to grayscale before processing [10-11].

## CHAPTER 4 FILTER NOISE

Image captured through STM are noisy. A noise can be termed as any unwanted signal produced by electrical fluctuations in the sensor or the circuitry of a scanner. Image noise is random variation of brightness or color information, and is usually an aspect of electronic noise. Most algorithms for converting image sensor data to an image, whether in-camera or on a computer, involve some form of noise reduction. They use predefined mathematical procedure to determine whether the actual differences in pixel values constitute noise or real photographic detail, and average out the former while attempting to preserve the later. It should be noted that no algorithm can make this decision accurately and hence there is a tradeoff made between noise removal and preservation of fine, low-contrast detail that may have characteristics similar to noise [15].

STM images generally contains Gaussian noise, high frequency noise and periodic noise. The standard model of an amplifier noise is additive and independent at each pixel. Gaussian noise is caused by the thermal vibrations of atoms in conductors [15]. High frequency and periodic noise are due to improper calibration and undesired image capturing condition. The filter noise module uses a frequency domain filtering technique to minimize these noise. The sub-module creates a frequency mask for filtering. This frequency mask was created by studying number of noisy STM images in frequency domain.

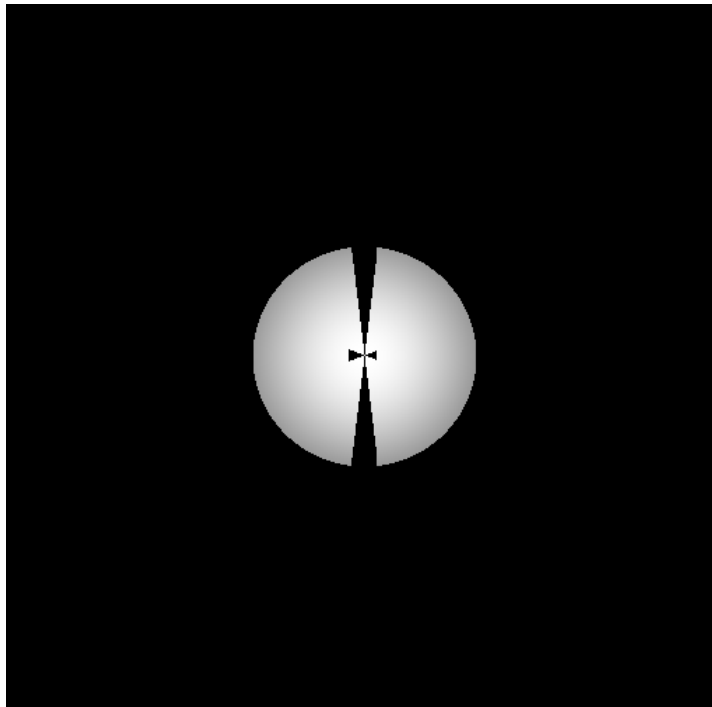


Figure 4.1 Image Mask Filter.

Figure 4.1 shows the shape of image mask filter in frequency domain. The mask filter is a modified low pass frequency filter that has a v-shape opening along the vertical axis of frequency domain to eliminate low frequency lateral periodic noises from the image. In some STM images, vertical periodic noise was observed. These periodic noise transform to a group of closely coagulated point on the horizontal axis in frequency domain. To eliminate this noise the mask has a triangular opening on either side of horizontal axis near the origin.

## 4.1 Process Flow

The image matrix is provided as an input to Filter Noise module. Using an inbuilt FFT [16] function in MATLAB, the image is transformed into frequency domain. Filter mask is then applied and the resultant frequency domain is transformed back into image. The entire process is explained in the Figure below.

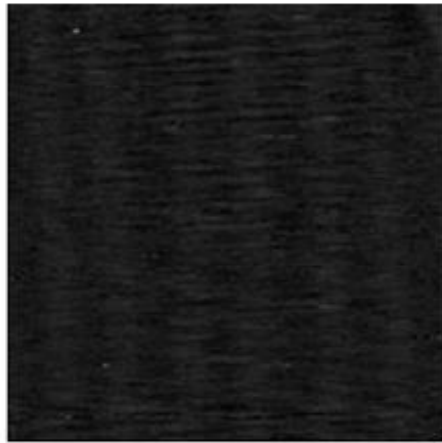


Figure 4.2.1 STM image Pb Deposition on Au(111) at 50 mV w.r.t. SCE

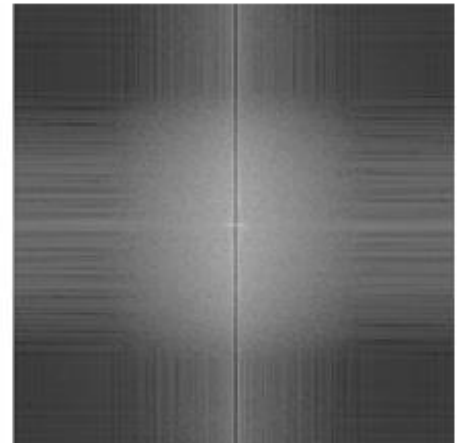


Figure 4.2.2 DFT of STM image Pb Deposition of Au(111) at 50 mV w.r.t. SCE

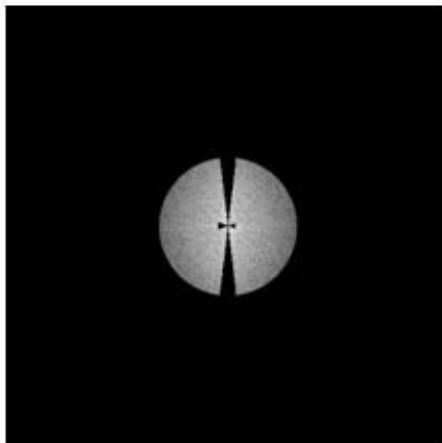


Figure 4.2.3 DFT of STM image After Applying Filter Mask for Pb Deposited on Au(111) at 50 mV w.r.t. SCE

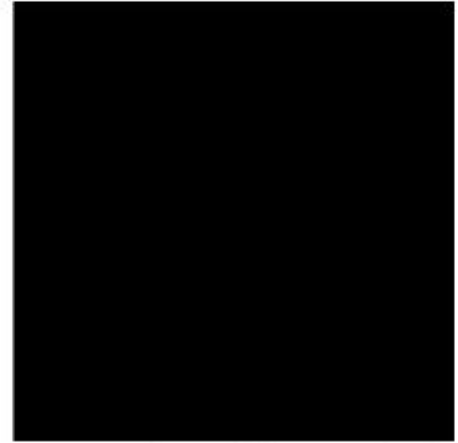


Figure 4.2.4 STM image of Pb Deposition of Au(111) at 50 mV w.r.t. SCE after applying Filter

Figure 4.2 Process flow for filtering image.

Filter Noise sub-module uses 'filter\_file\_gui' function for reducing the noise discussed in this chapter. The output of this function is grayscale image matrix.

Thus to conclude, the most prominent noise present in STM image are Gaussian noise due to electrical circuitry of STM, high frequency noise and periodic noise due to external disturbance while capturing the image. A number of STM images were studied in order to determine the approximate position of this noise. It was found that periodic noise can be observed alongside the axis in frequency domain. Based on their relative position a filter mask was developed and is used by the sub-module to minimize these noise in an Image. The output of this sub-module is an image matrix with minimum noise.



## CHAPTER 5 DETERMINATION OF THRESHOLD

Filter module is used to minimize the noise present in STM image. The output from filter module can be termed as filtered image. This filtered image is applied as an input to 'Determination of Threshold' module. 'Determination of Threshold' module is used to obtain the binary image of cluster layers.

### 5.1 Process Flow

The filtered image is a grayscale image with pixel values between 0 to 1. In most of the image, there is approximately more than one thousand distinct values between 0 to 1. For example, consider the filtered image of Pb UPD on Pt<sub>SML</sub>/Au<sub>(111)</sub> in 10<sup>-2</sup> M Pb<sup>2+</sup> and 0.1 M HClO<sub>4</sub> solution taken at -250 mV w.r.t SCE (Standard Calomel Electrode) in the Figure 5.1.

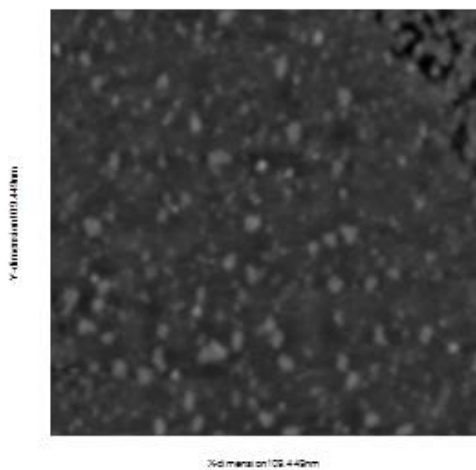


Figure 5.1 Filtered Image of STM image Pb UPD on Pt<sub>SML</sub>/Au<sub>(111)</sub> in 10<sup>-2</sup> M Pb<sup>2+</sup> and 0.1 M HClO<sub>4</sub> solution taken at -250 mV w.r.t. SCE.

As observed in the image there are two layers of cluster. This image has 262,144 distinct values of pixel varying from 0 to 1. In Matlab, if histogram is plot for this image using 'hist' function, the histogram obtained is in form of 10 equally spaced containers and returns the number of elements in each container as a row vector. Since filtered image is an m-by-n matrix, hist function will consider the columns of Y as vectors and returns a 10-by-n matrix r. Each column of r contains the results for the corresponding column of Y, number of elements of Y can be complex or integer number [17]. The histogram obtained for the image in the Figure 5.1 is given in the Figure 5.2.

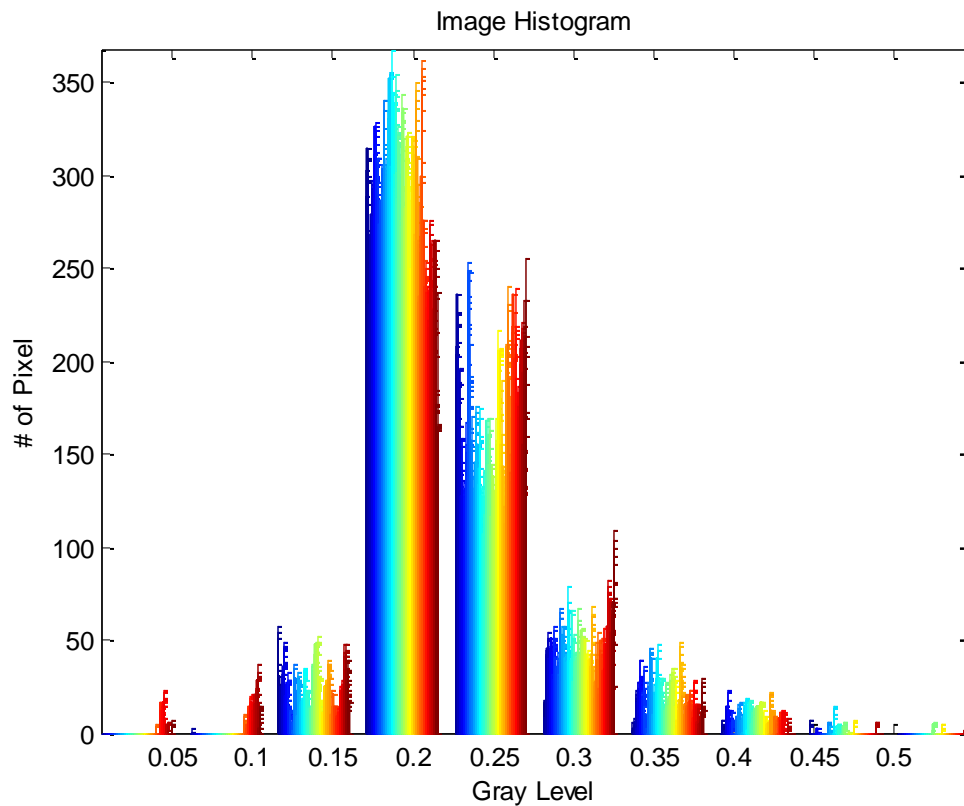


Figure 5.2 Image Histogram using 'hist' function in Matlab.

The objective of this module is to obtain binary image with 'layer of cluster' as 'Object' (in white) while 'other features' are treated as 'Background' (black) from the

filtered image. This should be done based on the image histogram segmentation. In case if there is more than one layer of cluster, the module gives more than one binary image. To divide the image in the Object and the Background, it becomes imperative to perform an Otsu segmentation on the filtered image. Otsu method performs histogram based image segmentation by assuming that image consists of two class, background and object. This method calculates the optimum threshold separating those two classes such that their combined intra class variance is minimal [18]. Similarly multilevel Otsu is used to find the optimal threshold between more than two classes based on their intra class variance. Since the filtered image may contain more than one layer of cluster, multilevel Otsu method should be used. Multilevel Otsu method is not used directly to classify the cluster layer because this method assumes the histogram is multi-modal and equally spaced however it may not be true [18]. Hence it could be used to divide the image histogram in thirty two different classes. This helps in obtaining smooth and continuous histogram of image as shown in the Figure 5.3.

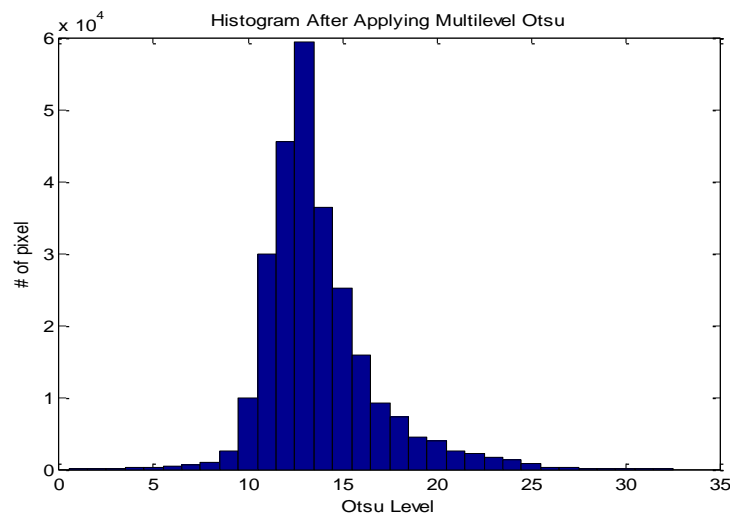


Figure 5.3 Histogram after applying multilevel Otsu.

If the Figure 5.2 and the Figure 5.3 are compared, it could be observed that histogram in the Figure 5.3 is smooth as compared to the Figure in 5.2. This is because the histogram in the Figure 5.3 is classified in thirty two different classes which is very less when compared to 261,144 distinct values in the Figure 5.2. The cluster in the image can be separated by determining the threshold in the histogram. This threshold is determined by fitting a Gaussian curve in the histogram based on approximate position of Gaussian peak. The Gaussian peak is identified using a differentiation and double differentiation method.

The histogram of filtered image may still contain spikes which is sometimes observed due to ringing effect in filtered image. Ringing effect is observed due to sharp cutoff frequencies used in the filter mask. It causes an overshoot of feature in an image [19-20]. It should be noted that 'filter module' minimizes the noise in an image but may not be able to eliminate it completely. Hence, these noise can be observed as spikes in the histogram. It can be eliminated using curve smoothing technique. According to this technique  $y$  can be a noise if,

$$\text{for } y=f(x) \text{ where } y = \# \text{ of pixel and } x = \text{corresponding weight}, \quad (5-a)$$

$$y' > y_{-1}', \text{ where } y' = f'(x), y_{-1}' = f'(x-1), \quad (5-b)$$

$$y' > y_{+1}', \text{ where } y' = f'(x), y_{+1}' = f'(x+1), \quad (5-c)$$

$$y_{-1}' > y_{-2}' \text{ where } y_{-1}' = f'(x-1), y_{+1}' = f'(x+1), \quad (5-d)$$

$$y_{+1}' > y_{+2}' \text{ where } y_{-2}' = f'(x-2), y_{+2}' = f'(x+2). \quad (5-e)$$

If all the above condition is satisfied the noise is removed by averaging,

$$y=(f(x-1)+f(x+1))/2. \quad (5-f)$$

The curve smoothing is performed for twenty iteration in-order to ensure that histogram curve is free of spikes. Next step is to fit the Gaussian curve on the histogram, this is done by obtaining the peaks of the histogram curve. The number of peaks determine the number of Gaussian curve that could be fitted on histogram curve. Peak value and peak position can be found using the following two condition [21],

$$y'>0, y_{+1}'\leq 0 \text{ where } y'=f'(x) \text{ and } y_{+1}'=f'(x+1), \quad (5-g)$$

$$y''\leq 0 \text{ where } y''=f''(x). \quad (5-h)$$

This formula is used to find maximum of histogram curve [21].

Once the peak position and peak value is obtained, it could be treated as mean value of the Gaussian curve. In order to obtain the standard deviation of Gaussian curve, the histogram is traced towards zero on horizontal axis until [22],

$$x_{mean+standard\_deviation} = 0.6065 * peak\_value. \quad (5-i)$$

$$\text{Thus standard deviation, } \sigma = |x_{mean} - x_{mean+standard\_deviation}|. \quad (5-k)$$

Once mean and variance is obtained, Gaussian curve can be plotted on histogram based on the Formula (5-l) given on next page,

$$y_{Gaussian} = y_{mean} \times e^{-0.5\left(\frac{x-\mu}{\sigma}\right)^2}, \quad (5-l)$$

where  $\mu$  = Peak Position [21-24].

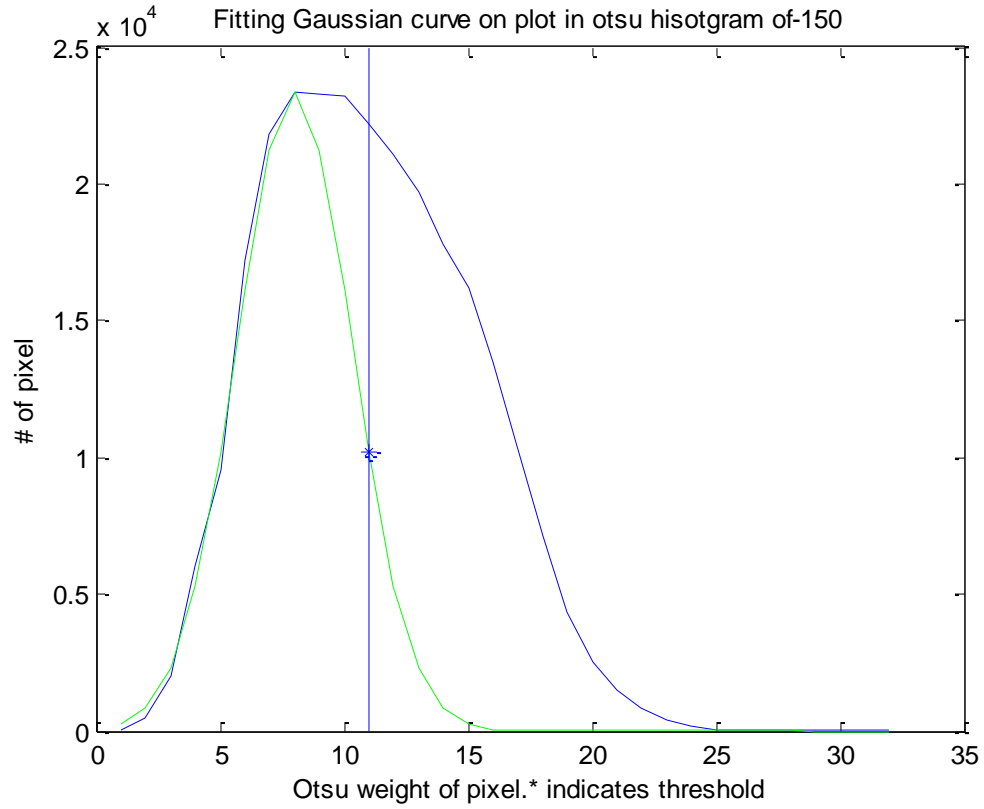


Figure 5.4 Gaussian Curve fitted on histogram obtained after multilevel Otsu method.

In the Figure 5.5.ii, two Gaussian curve in green and in red is fitted on the histogram obtained after performing multilevel Otsu method on the image. The '\*' signs on the plot represent the threshold level. The threshold level is selected as,

$$0.66 \times total\_area\_under\_gaussian\_curve = \int_0^{threshold\_level} f(x)dx. \quad (5-m)$$

In the Figure 5.5.ii, the '\*' sign on extreme left is always treated as the threshold level for the first layer of cluster and while the '\*' sign on the right side of graph is treated as the threshold level for the second layer of cluster [24]. The binary image for layer is obtained by treating pixel values above threshold level as '1' while pixel's with a value equal to or below the threshold level is treated as '0'. Based on the Figure 5.4, the algorithm creates two binary image as shown in the Figure 5.5.

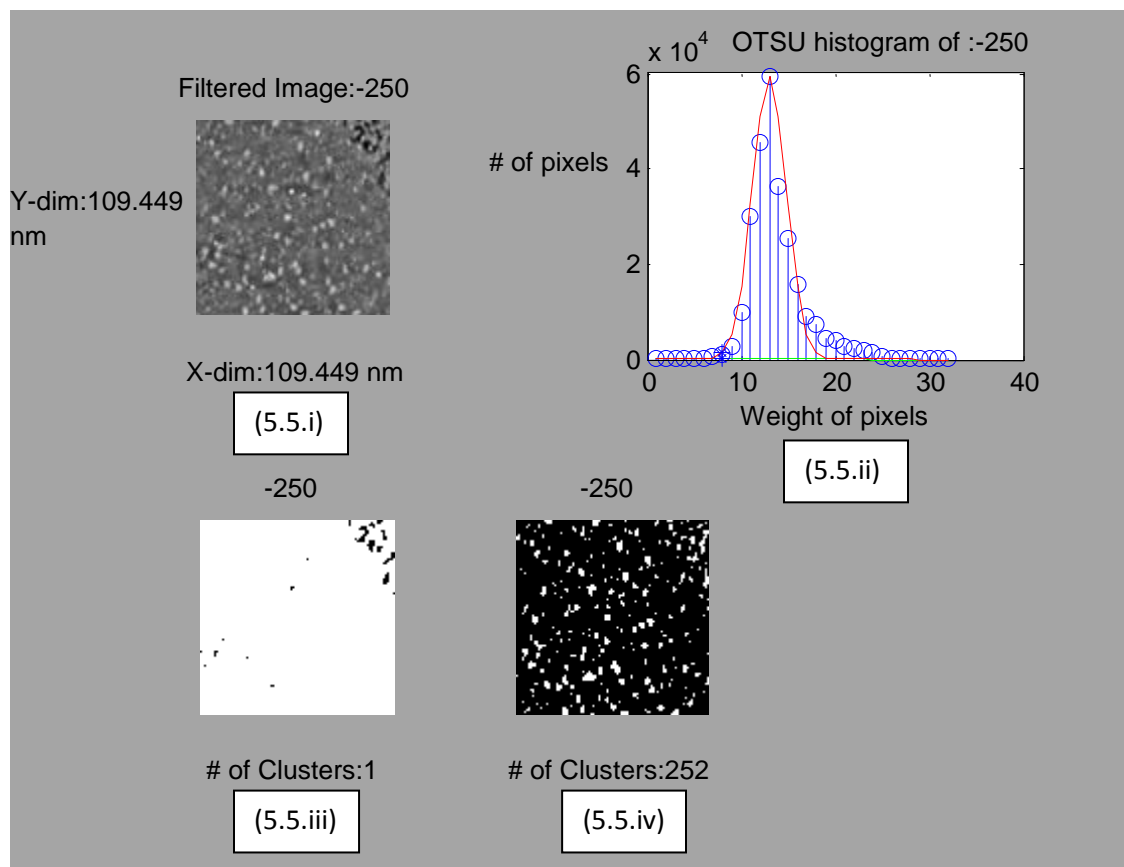


Figure 5.5.i. Filtered Image. ii. Otsu histogram with Gaussian Curve. iii. Binary image of first layer of cluster. iv. Binary image of second layer of cluster.

Thus to conclude, determine threshold module is used to identify and create binary image depending on number of cluster layers present in the filtered image. To create these binary image, the module performs multilevel Otsu on filtered image. The

Otsu histogram obtained after performing multilevel Otsu is then subjected to curve smoothing. After twenty iteration of Otsu histogram, peak position on the Otsu histogram curve is identified. This peak position is treated as mean for Gaussian curve, for subsequent Gaussian mean, standard deviation is calculated. With the help of Gaussian mean and standard deviation, a Gaussian curve is fitted on OTSU histogram.

The threshold value is selected as,

$$0.66 \times total\_area\_under\_gaussian\_curve = \int_0^{threshold\_level} f(x)dx . \quad (5-n)$$

To obtain the binary image, pixel weight of filtered image above threshold level is treated as '1' and if the pixel weight is less than or equal to threshold level than it is set to '0.' In the binary image the pixel with weight '1' represents 'Object' and that with weight '0' is represented as 'background.'



## **CHAPTER 6 IDENTIFY CLUSTER AND EXTRACT CLUSTER**

### **PARAMETERS**

In the process of extracting the parameters from STM image, image processing algorithm accepts ASCII file as an input, extract parameters like scan size, scan rate and pixel values from it. It generates an image based on the input ASCII file. This image is treated using a filter mask in filter module and is applied as input to 'Determination of Threshold' module for generating binary image of cluster layer in an image. The binary image created by 'Determination of Threshold' module is taken as an input by 'Identify Cluster and Extract Cluster Parameters' to extract the cluster parameters such as layer coverage, layer density and perimeter by area for cluster layer along with cluster area.

#### **6.1 Identify Cluster**

Binary image generated from 'Determination of Threshold' module consists of object with pixel value '1' and the background is feature with pixel value '0.' In the Figure 6.1.ii, first layer of cluster is the 'Object' which is represented by white in color while the 'Background' is in black color. Similarly in the Figure 6.2.ii, second layer of cluster is 'Object,' represented by white in color and the background is in black color.

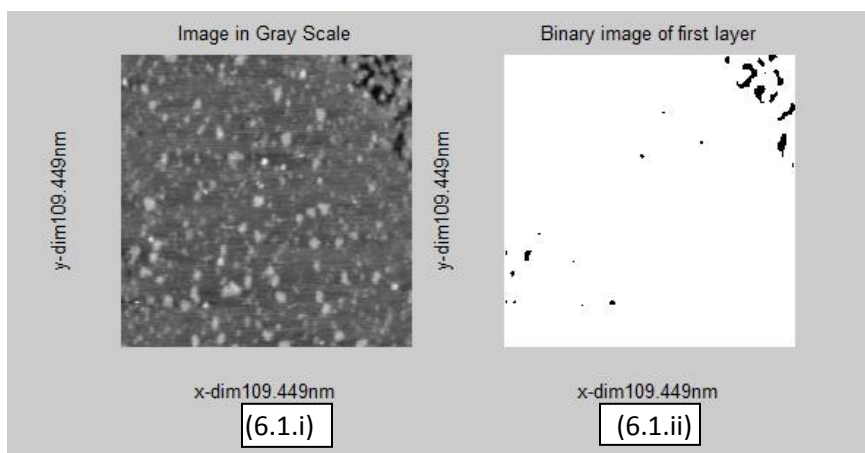


Figure 6.1.i. Pb UPD on Pt<sub>SML</sub>/Au<sub>(111)</sub> in 10<sup>-2</sup> M Pb<sup>2+</sup> and 0.1 M HClO<sub>4</sub> solution taken at -250 mV w.r.t. SCE (Standard Calomel Electrode). ii. The corresponding binary image of 'first layer of cluster' generated by 'Determination of Threshold.'

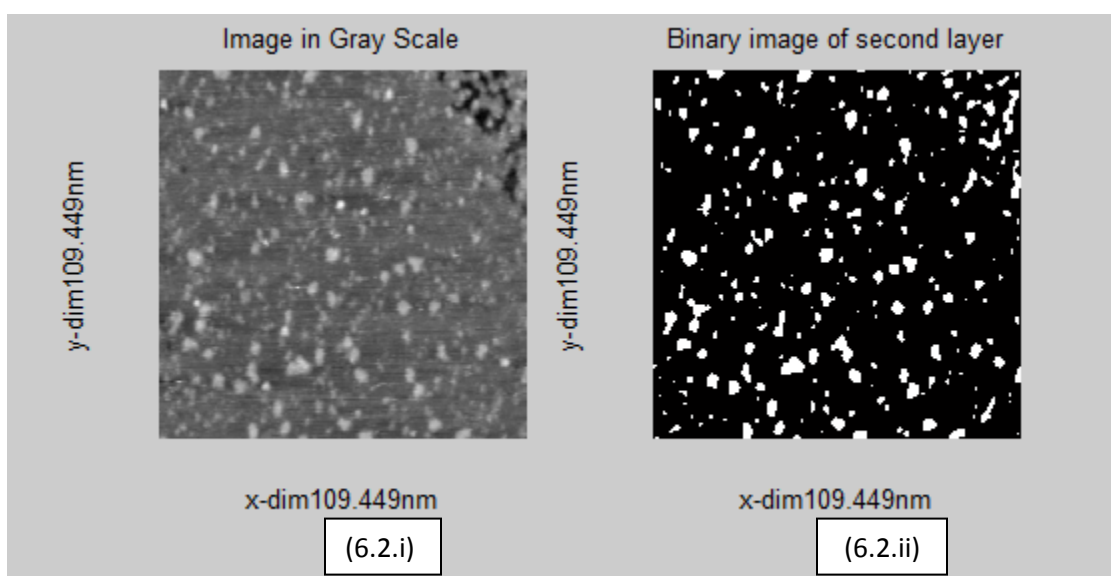


Figure 6.2.i. Pb UPD on Pt<sub>SML</sub>/Au<sub>(111)</sub> in 10<sup>-2</sup> M Pb<sup>2+</sup> and 0.1 M HClO<sub>4</sub> solution taken at -250 mV w.r.t. SCE (Standard Calomel Electrode) ii. The corresponding binary image of 'second layer of cluster' generated by 'Determine Threshold Module.'

In order to identify clusters in the binary image, 'bwlabel' is used. It is an inbuilt function in 'Matlab R2010b' that generates a matrix 'imagebw.' The size of 'imagebw' is same as the binary image containing labels of connected objects in binary image. 'bwlabel' has two input arguments binary image and a variable 'n.' The variable 'n' can

have value '4' and '8' that specifies either '4' connected objects or '8' connected objects. This function gives out two output variable 'imagebw' and 'num.' The variable 'num' gives the total count of connected objects found in 'imagebw' [25]. In the Figure 6.3.ii, the output 'imagebw' for second layer is shown.

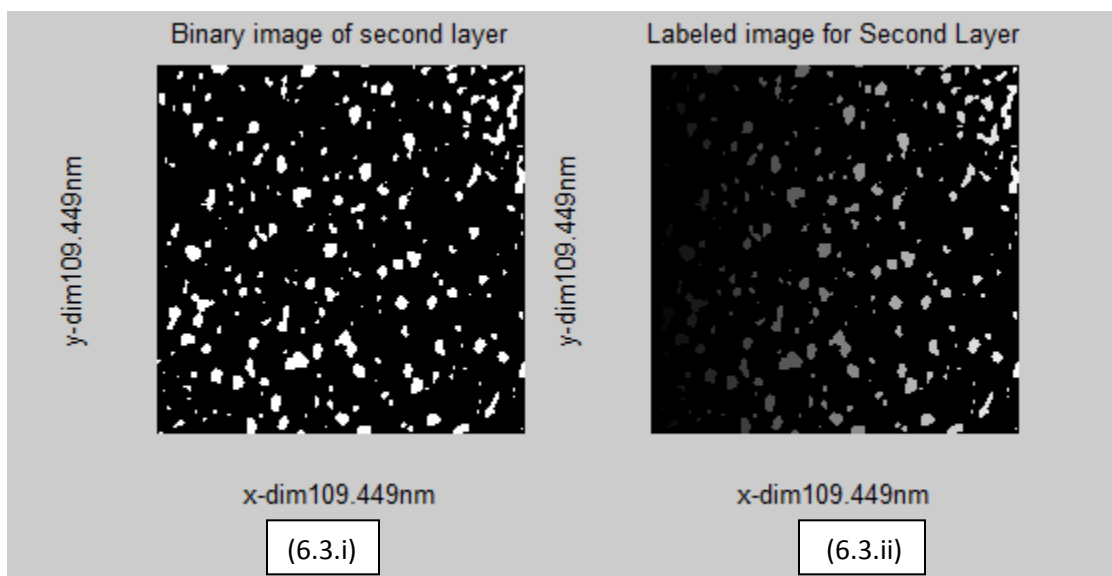


Figure 6.3.i. Binary image of 'second layer of cluster' for Pb UPD on  $\text{Pt}_{\text{SML}}/\text{Au}_{(111)}$  in  $10^{-2}$  M  $\text{Pb}^{2+}$  and 0.1 M  $\text{HClO}_4$  solution taken at -250 mV w.r.t. SCE (Standard Calomel Electrode). ii. The corresponding 'imagebw' generated by 'bwlabel' function in Matlab.

Since there is just one cluster in binary image for first layer, the difference between the output 'imagebw' generated by the 'bwlabel' function in Matlab cannot be noticed pictorially. Hence it is not shown in the Figure 6.3. The color variation for layers of cluster in the Figure 6.3.ii is observed in cluster from left to right. This is due to the labeling of cluster object from '1' to order of increase in the cluster object number. Hence the cluster object represented by '1' is less white in color and the whiteness increases with increase in the index number of cluster object.

After labeling the cluster in the layer of cluster. 'Regionprops' function in Matlab is used. This function accept 'imagebw' as an input and string array to indicate the parameters of labeled cluster that needs to be extracted from the cluster layer in 'imagebw' matrix. The output of this function is a structure array with length equal to the number of cluster in 'imagebw.' The algorithm extracts cluster parameter like 'Area,' 'BoundingBox,' 'Centroid,' 'ConvexHull,' 'ConvexImage,' 'Eccentricity,' 'EquivDiameter,' 'EulerNumber,' 'Extent,' 'Extrema,' 'FilledArea,' 'FilledImage,' 'Image,' 'MajorAxisLength,' 'MaxIntensity,' 'MeanIntensity,' 'MinIntensity,' 'MinorAxisLength,' 'Orientation,' 'Perimeter,' 'PixelIdxList,' 'PixelList,' 'PixelValues,' 'Solidity,' 'SubarrayIdx,' 'WeightedCentroid' [26]. Of these mentioned parameters only 'Area' and 'Perimeter' parameter is used. The remaining parameters are reserved for future use. If scan size for an image is provided in input ASCII file then the binary image is modified such that cluster area in a layer is more than '1 nm<sup>2</sup>' and perimeter is greater than '4 nm.' It should be noted that cluster is assumed to be square in shape and contains more than one atom. If there is no scan size mentioned in the input ASCII files no such condition is applied to binary image. The condition of cluster area and cluster perimeter will be called as cluster condition henceforth. The number of cluster before applying the cluster condition is '258' as shown in the Figure 6.4.i and it reduces to '252' after applying cluster condition.

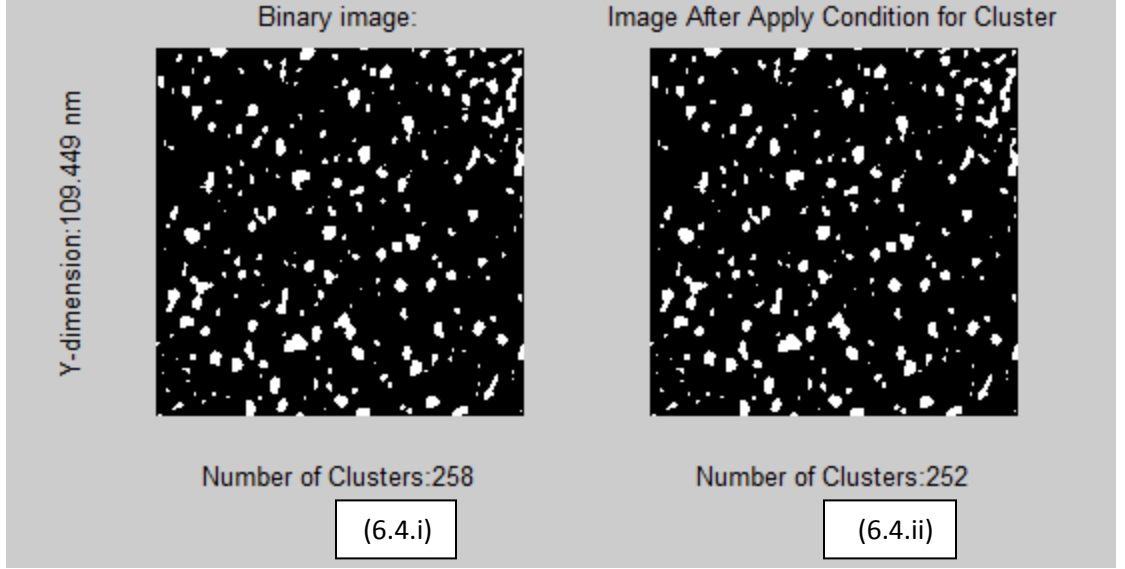


Figure 6.4.i. Binary image of 'second layer of cluster' for Pb UPD on Pt<sub>SML</sub>/Au<sub>(111)</sub> in 10<sup>-2</sup> M Pb<sup>2+</sup> and 0.1 M HClO<sub>4</sub> solution taken at -250 mV w.r.t. SCE (Standard Calomel Electrode). ii. The corresponding binary image after applying the cluster condition.

Since the matrix is in pixels hence the cluster condition should be converted into pixel from nanometers. Following mathematical formulae is used to convert cluster condition in pixels,

$$(Cluster\_Condition)_{Area\_in\_pixel} = \frac{(Number\_of\_scan\_lines)^2 \times 1.00}{(scan\_size)_{nm}^2}, \quad (6-a)$$

$$(Cluster\_Condition)_{Perimeter\_in\_pixel} = \frac{Number\_of\_scan\_lines \times 4.00}{(scan\_size)_{nm}}, \quad (6-b)$$

in case if the scan size is not available these formulas are not used.

'Regionprops' is again used on binary image generated after applying cluster condition to extract all the cluster parameters mentioned on the previous page. These parameters are provided as an output along with the binary image on which cluster condition is applied.

## 6.2 Extract Cluster Parameters

The area and perimeter parameters made available is still in pixels and needs to be converted into nanometers. This is done using the following formula,

$$(Cluster\_Area)_{nm^2} = \frac{(scan\_size_{nm})^2 \times Cluster\_Area_{pixel^2}}{number\_of\_row \times number\_of\_columns}, \quad (6-c)$$

$$(Cluster\_Perimeter)_{nm} = \frac{(scan\_size)_{nm} \times Cluster\_Perimeter_{pixel}}{number\_of\_row}. \quad (6-d)$$

In case if scan size is not available these formulas are not used.

Once cluster area and cluster perimeter is obtained, perimeter by area is calculated using the following mathematical formula,

$$Cluster\_Perimeter\_by\_Area_{nm^{-1}} = \frac{Cluster\_Perimeter_{nm}}{Cluster\_Area_{nm^2}}. \quad (6-e)$$

In case if scan size is not available, then the following formula is used,

$$Cluster\_Perimeter\_by\_Area_{pixel^{-1}} = \frac{Cluster\_Perimeter_{pixel}}{Cluster\_Area_{pixel^2}}. \quad (6-f)$$

A plot of # of cluster v/s cluster area and # of cluster v/s cluster perimeter by area could be obtained based on user's requirement.

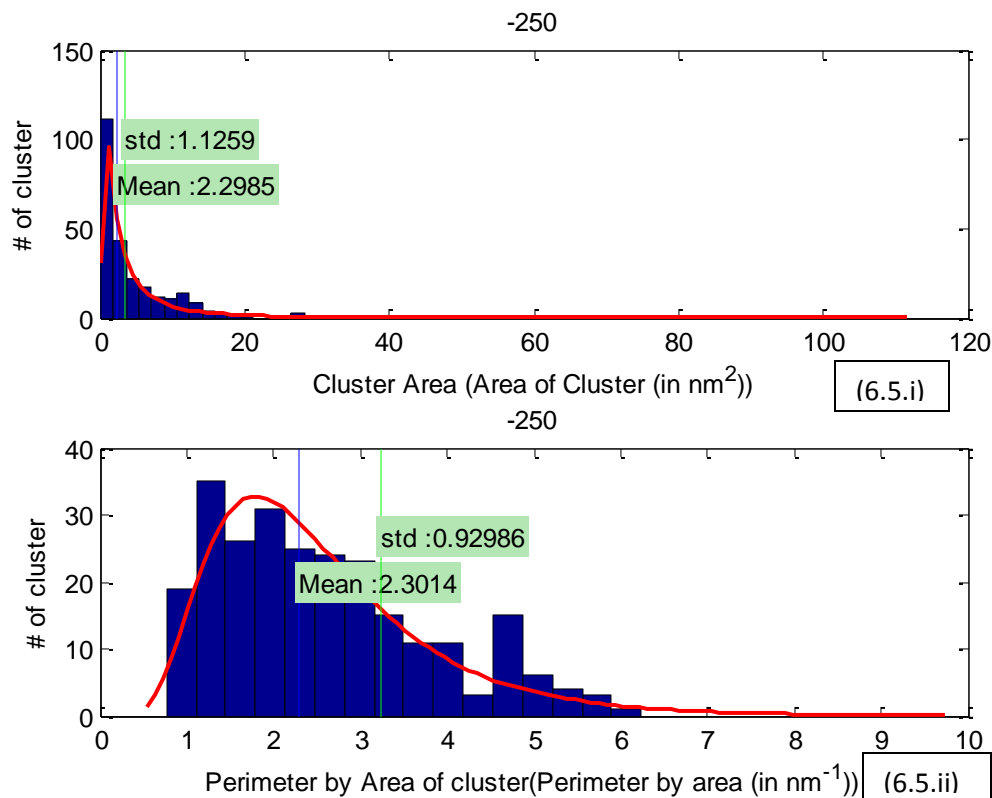


Figure 6.5.i. Plot of Cluster Area v/s Number of cluster ii. Plot of Perimeter by Area of cluster v/s Number of cluster of 'second layer of cluster' for Pb UPD on Pt<sub>SML</sub>/Au<sub>(111)</sub> in 10<sup>-2</sup> M Pb<sup>2+</sup> and 0.1 M HClO<sub>4</sub> solution taken at -250 mV w.r.t. SCE

'Identify Cluster and Extract Cluster Parameters' module plays a pivotal role in extracting the parameters of cluster from the binary image provided by 'Determination of Threshold' module. In the process of extracting the parameters it applies cluster condition to clusters identified in binary image. Parameters like 'area' and 'perimeter' is recorded after converting it in SI units, if scan size is available, for further use. 'perimeter by area' is also calculated. The output of this module are parameters such 'area,' 'perimeter,' 'perimeter by area,' and 'binary image' after applying cluster condition.

## CHAPTER 7 QUANTIFY CLUSTER PARAMETERS

The Cluster Parameters obtained from 'Identify Cluster and Extract Cluster Parameters' module is used to calculate few more important parameters pertaining to layer of Cluster. These parameters will be discussed in the later part of this chapter.

### 7.1 Process Flow

'Quantify Cluster Parameters' module accepts 'cluster area,' 'cluster perimeter,' and 'Perimeter by area' as an input. Using an inbuilt function in Matlab, it calculates the mean, mode and standard deviation of 'cluster area,' 'cluster perimeter,' and 'perimeter by area' [27-28][12]. These functions are mean (to calculate mean of a parameter), mode (to calculate maximum of a parameter) and std (to calculate standard deviation of a parameter). Apart from these parameters, the average is calculated for each of these parameters using following mathematical formula,

$$0.5 \times total\_area\_of\_cluster = \int_0^{average} f(x)dx. \quad (7-a)$$

Layer coverage is another parameter, it is defined as the ratio of area of sum of the cluster area by the total area of image. It is mostly stated in terms of percentage,

$$Layer\_coverage_{\%} = \frac{\sum cluster\_area}{scan\_size_{nm}^2} \times 100. \quad (7-b)$$



In case if scan size is not available it uses the following mathematical formula,

$$Layer\_coverage_{\%} = \frac{\sum_{no\_of\_cluster} cluster\_area}{no\_of\_rows \times no\_of\_columns} \times 100. \quad (7-c)$$

Once Layer coverage is calculated, the module calculates layer density. Layer density is defined as sum of clusters in layer over an area under consideration. The unit used to represent layer density is  $10^{14} \text{ cm}^{-2}$ ,

$$layer\_density_{\times 10^{14} \text{ cm}^{-2}} = \frac{\sum_{i=1}^{number\_of\_cluster} 1}{scan\_size_{nm}^2}. \quad (7-d)$$

In case if scan size is not available it uses the following mathematical formula,

$$layer\_density_{pixel^{-2}} = \frac{\sum_{i=1}^{number\_of\_cluster} 1}{no\_of\_rows \times no\_of\_columns}. \quad (7-e)$$

If a single file is processed the 'Quantify Cluster Parameters' module displays the value of mean, mode, standard deviation, and average value of each of the input parameter. In case, if the analysis is done on batch of files, it provides these parameters for plotting a graph based on the potential at which the image was recorded.

## CHAPTER 8 GUI(GRAPHICAL USER INTERFACE)

The algorithm developed for qualitative and quantitative STM Data Analysis is used to obtain quantitative information about various cluster parameter for a single image, batch of images, and a group of batch of images. Thus it could be beneficial for user with knowledge of UPD deposition to draw inference based on such quantitative data. However, user might not require all cluster parameter for his study. There could be possibility that user needs a data in specific format. Obtaining these output using command line is possible but tedious. Hence, a GUI (Graphical User Interface) has been developed to ease user's effort and time.

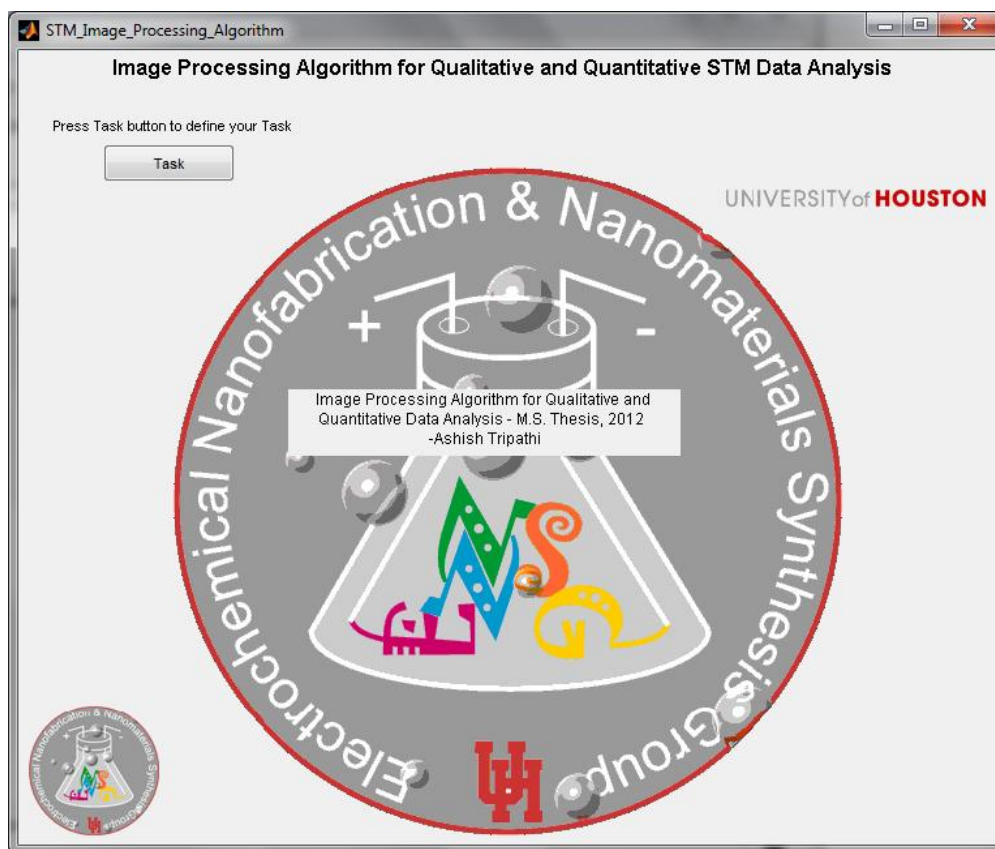


Figure 8.1 Home screen of the GUI of Image Processing Algorithm for Qualitative and Quantitative STM data Analysis.

Figure 8.1 shows the home screen of the GUI. This GUI has been built using structure oriented programming approach in order to include any changes pertaining to the mechanism and functioning of the GUI. Structure oriented programming is a form of procedural programming which enforces a logical structure on the program written for making it more legible to understand and modify. It employs a top down design approach and helps user to define a function or set of function in form of modules [29]. The feature, function, and activation of the GUI is discussed in later part of this chapter.

To activate the GUI, the user needs to make sure that all the Matlab files pertaining to algorithm and the GUI is in the working directory of Matlab as shown in the Figure 8.2.

Figure 8.2 Matlab home screen highlighting the algorithm and the GUI related files in current working folder of the GUI.

Type 'guide' in command window and press enter. This command is used to initiate the GUI design environment(GUIDE) for creating and editing GUIs in Matlab [30]. 'GUIDE quick start' window appears. In 'Open Existing GUI' tab select 'STM\_Image\_Processing\_Algorithm.fig' and press 'Open' button. This process is shown in the Figure 8.3.

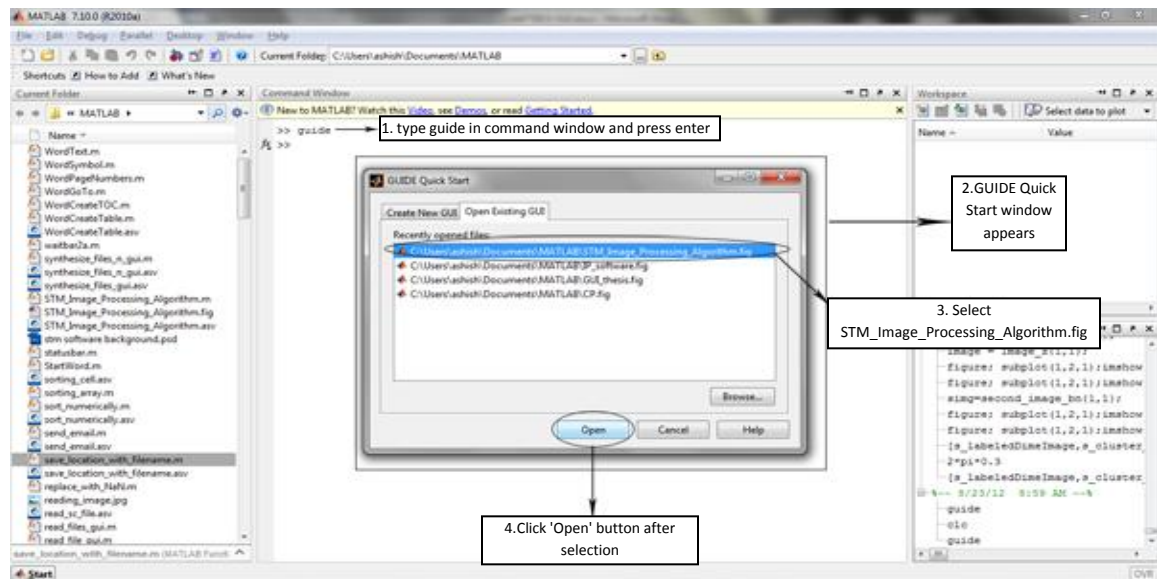


Figure 8.3 Matlab home screen highlighting the process to follow in-order to activate the GUI.

Once the process mentioned in previous paragraph is followed in an order, editable version of the GUI appears. Press 'Run Figure' button on the action bar below menu tab to activate the GUI as shown in the Figure 8.4.

The home screen of the GUI, as shown in the Figure 8.1 appears. 'Assist tag' is provided with every command button in the GUI to better assist the user. They are highlighted in the Figure 8.5.

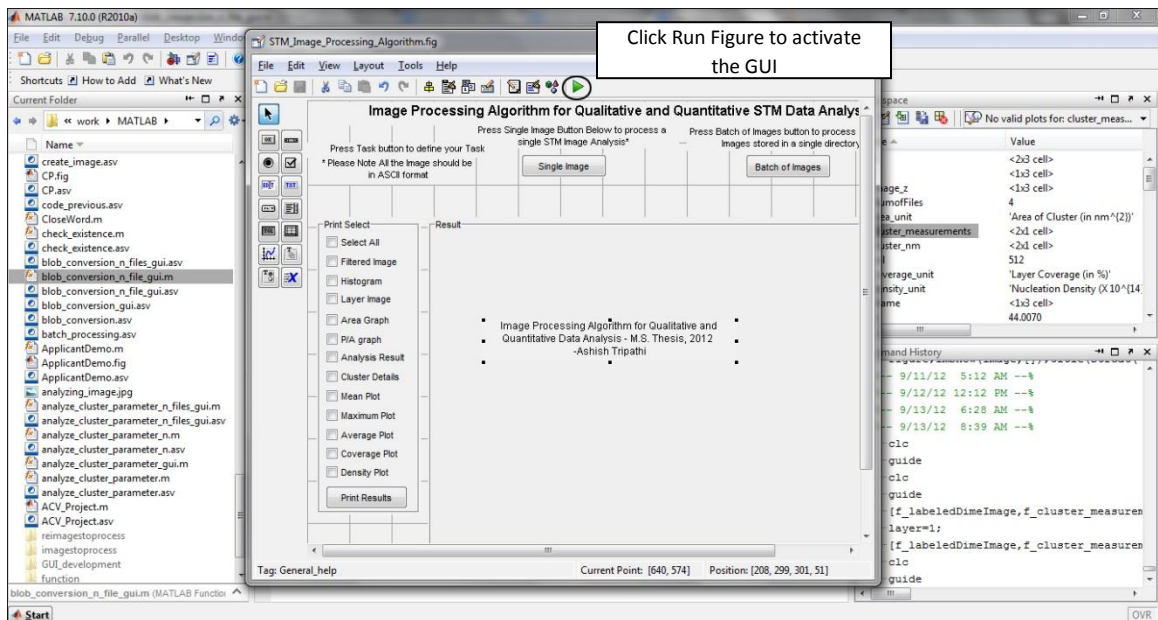


Figure 8.4 Matlab home screen highlighting the process to activate the GUI.

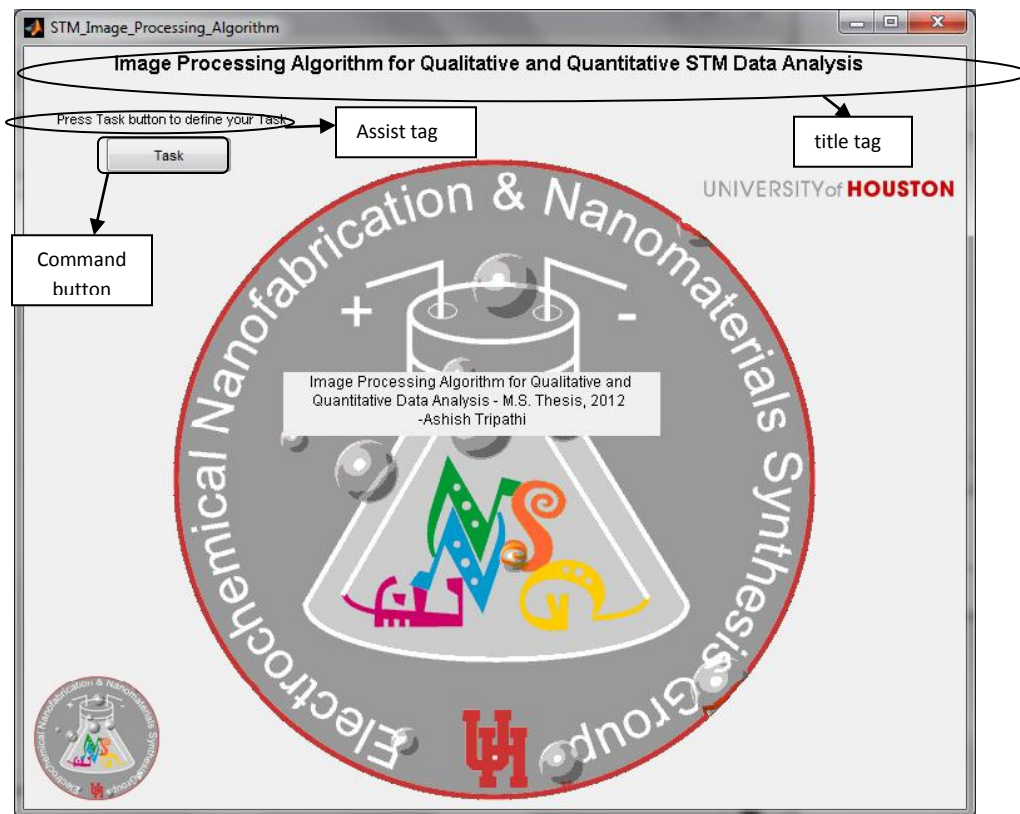


Figure 8.5 Home screen of the GUI of Image Processing Algorithm for Qualitative and Quantitative STM data Analysis highlighting 'assist tag,' 'command button,' and 'title tag.'

As shown in the Figure 8.5, 'Assist tag' is a static label text in Matlab and is used to provide information about the function performed on clicking the command button given below [30]. 'Title tag' depicts the title of the GUI.

## 8.2 Function of the GUI

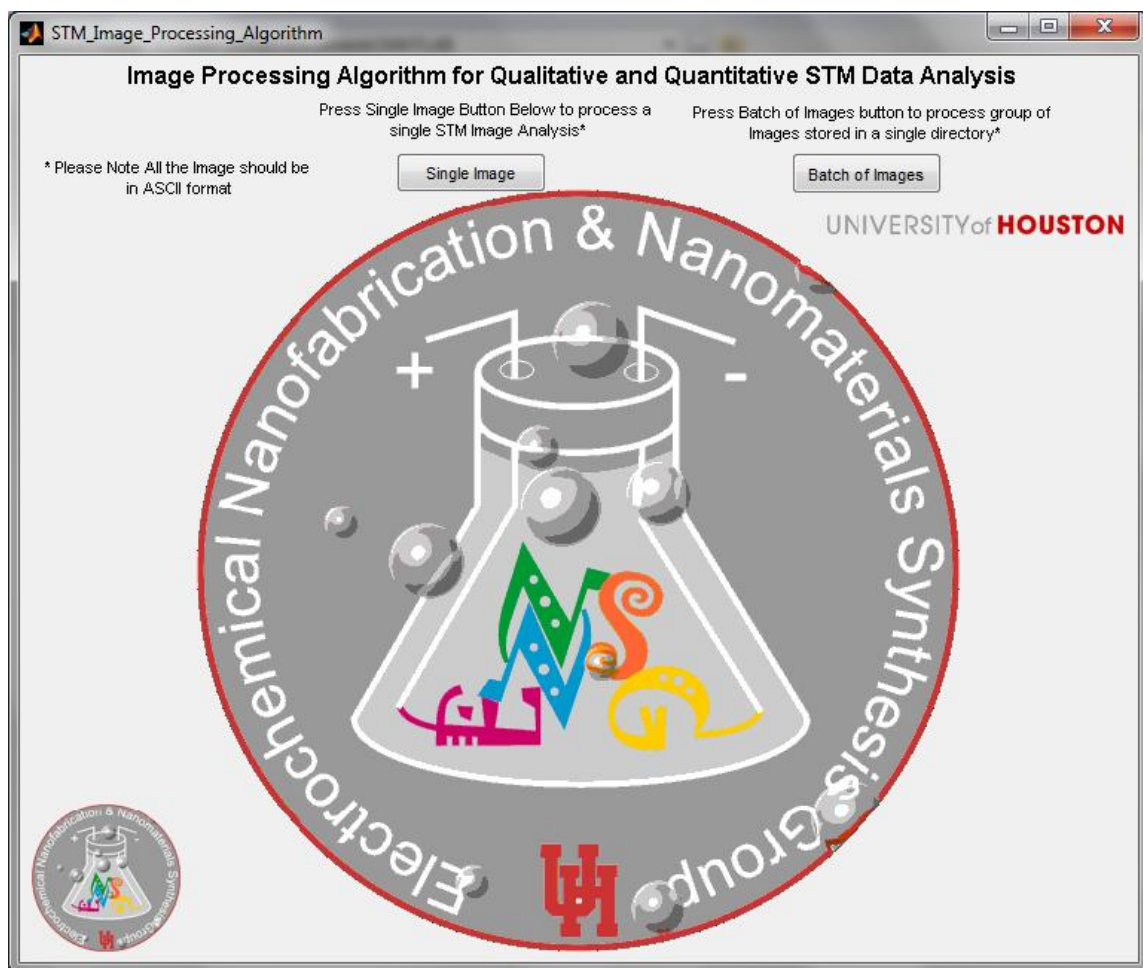


Figure 8.6 The GUI Screen with 'Single Image' and 'Batch of Images' button with their 'assist tag' and 'information tag' to inform user that input file should be in ASCII format.

The home screen of the GUI is provided with 'Task' button. As mentioned in the corresponding 'assist tag' it should be clicked by user to define a task the GUI needs to perform. If 'Task' button is clicked a new screen appears in same window with two more buttons 'Single Image' and 'Batch of Images.' 'Single Image' should be clicked if user

needs to perform image analysis on a single ASCII image. 'Batch of Images' should be clicked in order to perform image analysis on a batch of images in a directory or to perform image analysis on a group of batch of images stored in sub-folders.

### 8.2.1 Operation of the GUI on clicking 'Single Image'

If 'Single Image' button is clicked, 'Single Image' and 'Batch of Images' buttons disappear and a dialog box is prompted. The user is asked to select between 'Single image taken at one potential' and 'Group of single image taken at different potentials.' 'Single Image taken at one potential' button should be clicked to analyze a single STM file. To analyze a group of single image taken at different potentials, 'Group of single image taken at different potentials' button should be pressed. The dialog box can be seen in the Figure 8.7. As shown in the Figure 8.7 the default selected button is 'Single image taken at one potential.'

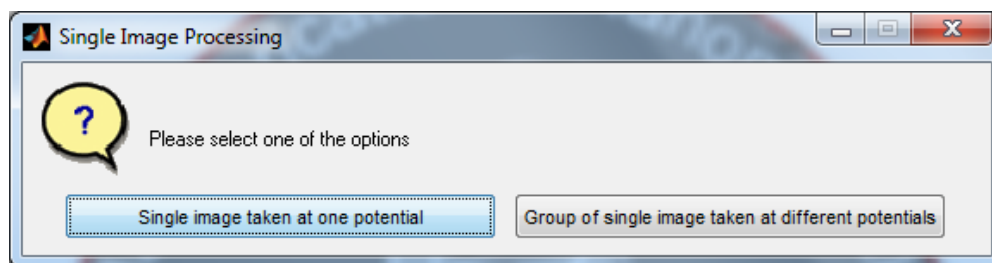


Figure 8.7 Dialog box after clicking 'Single Image' button.

#### 8.2.1.1 Single image taken at one potential

On selecting 'Single image taken at one potential,' a file manager window pops up. The default file type accepted by the GUI is .txt because most of the ASCII files are in text format. If the ASCII file has no extension that could be identified by the operating



system, select 'All Files' option from files of type drop down menu as shown in the Figure 8.8.

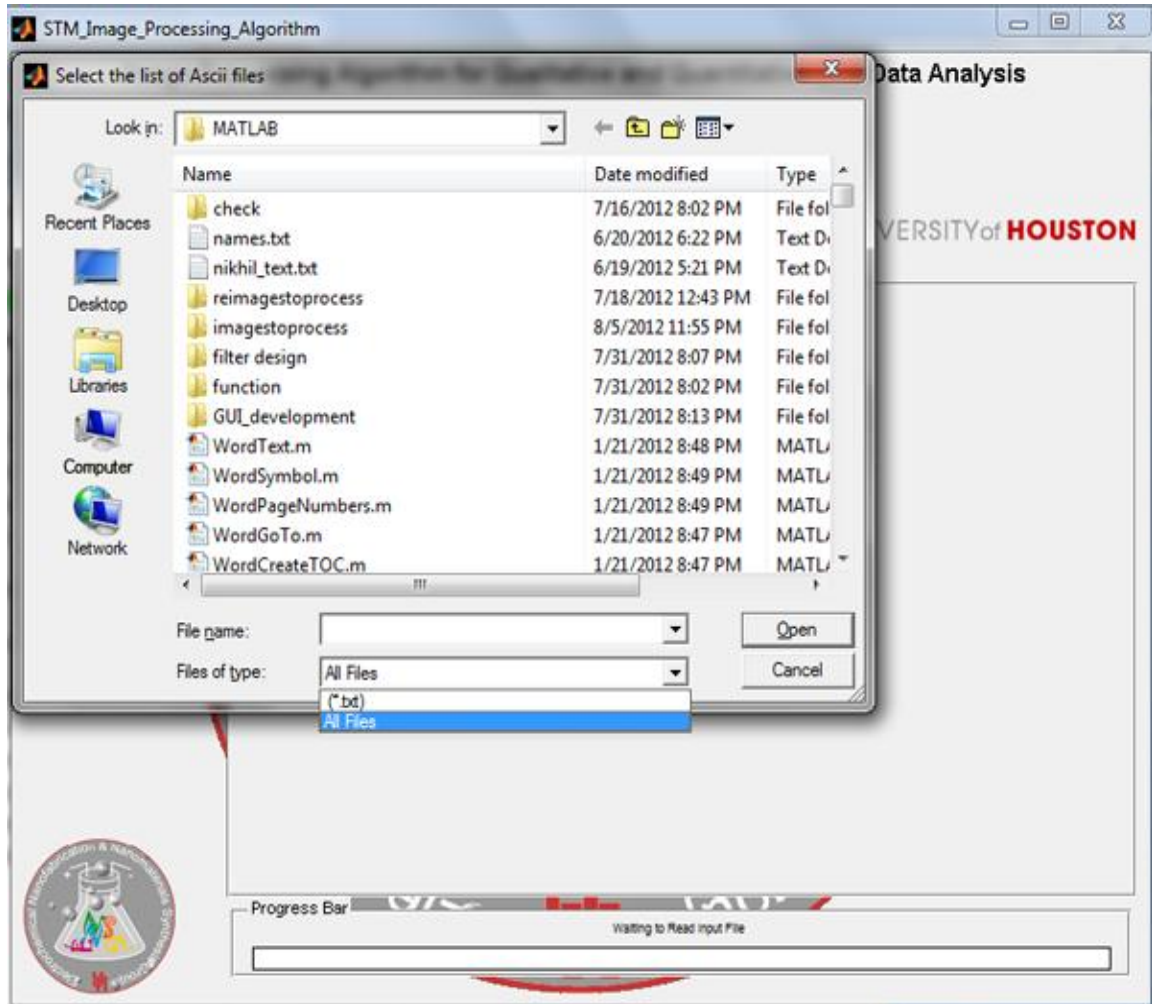


Figure 8.8 The GUI Screen after clicking single file button and the process to select ASCII files with no extension.

On selecting the appropriate input file, the GUI uses the algorithm to determine the cluster layer and displays this information to user in 'AlgorithmResult' window as shown in the Figure 8.9.



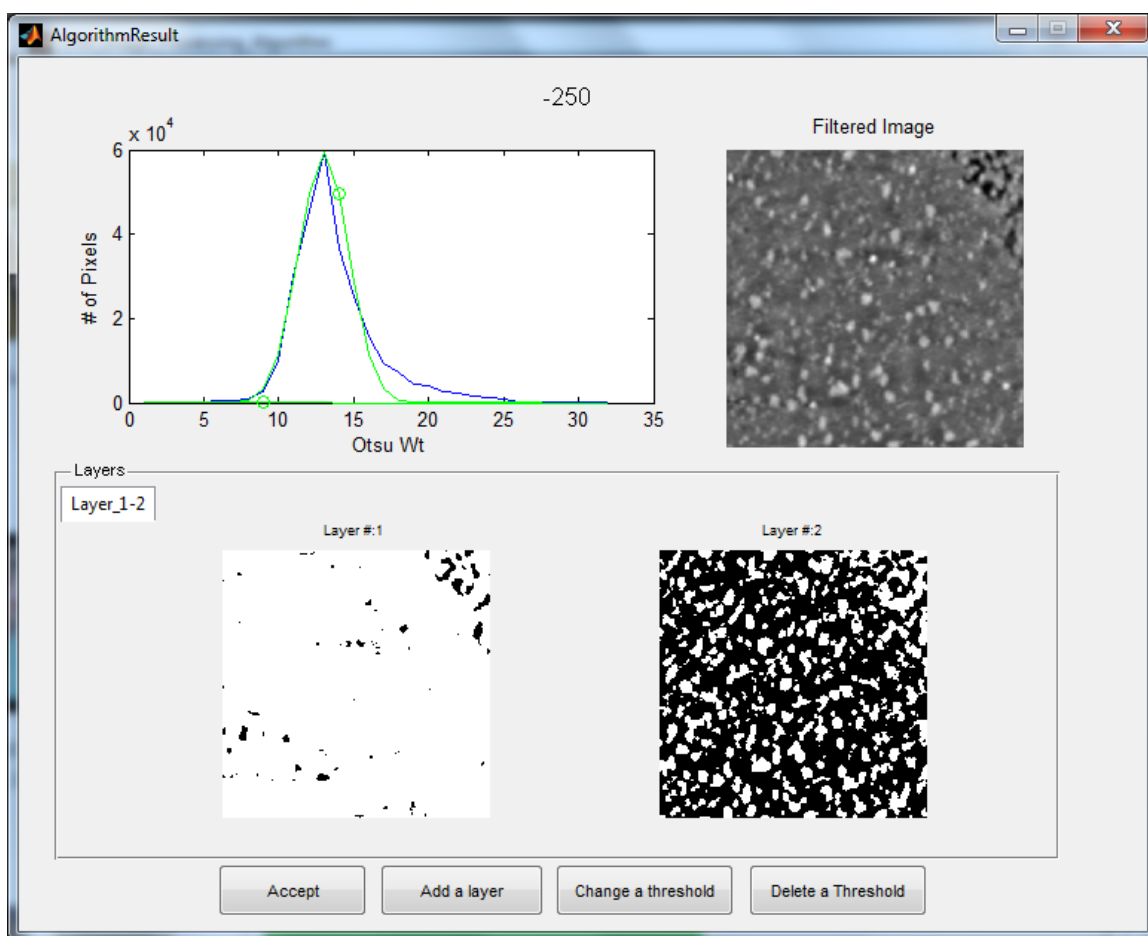


Figure 8.9 'AlgorithmResult' window displaying the cluster layer detected using 'Image processing algorithm for qualitative and quantitative STM data Analysis.'

The threshold level to determine the presence of a layer in an STM image for 'Image processing algorithm for qualitative and quantitative STM data Analysis' is based on empirical data. 'AlgorithmResult' window provides an easy option for user to accept and/or change the result using visual observation.

The 'AlgorithmResult' window displays the filename as its title at the top center on the window panel. In the Figure 8.9, '-250' at the top of the window panel is name of file processed by the GUI. The plot of 'number of cluster' v/s 'Otsu wt' is used to indicate layer detected by the 'Image processing algorithm for qualitative and quantitative STM

data Analysis.' The green dot(s) in plot represents the threshold level for each layer. As shown in the Figure 8.9, green dot can be observed for Otsu wt '9' and '14.'

The filtered image on top right of 'AlgorithmResult' is useful for visual observation. The user can use this image to decide if the result obtained through algorithm is acceptable. 'Layers' panel is used to display the binary image generated by the 'Image processing algorithm for qualitative and quantitative STM data Analysis.'

'AlgorithmResult' window is also provided with 'Add a layer,' 'Change a threshold,' 'Delete a threshold,' and 'Accept' buttons to either change or accept the result presented in 'AlgorithmResult.'

To add a layer user should click 'Add a layer.' A dialog box, as shown in the Figure 8.10, appears asking user to enter the Gaussian mean position for new layer and the threshold level in terms of percentage.

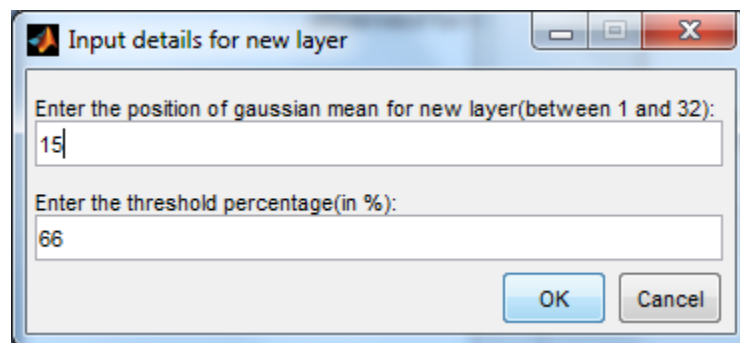


Figure 8.10 'Input details for new layer' dialog box asking user to enter the position of Gaussian mean for new layer and the threshold percentage.

When a valid input is provided through this dialog box. The 'AlgorithmResult' window is updated with the new layer information. This could be seen in the Figure 8.11.

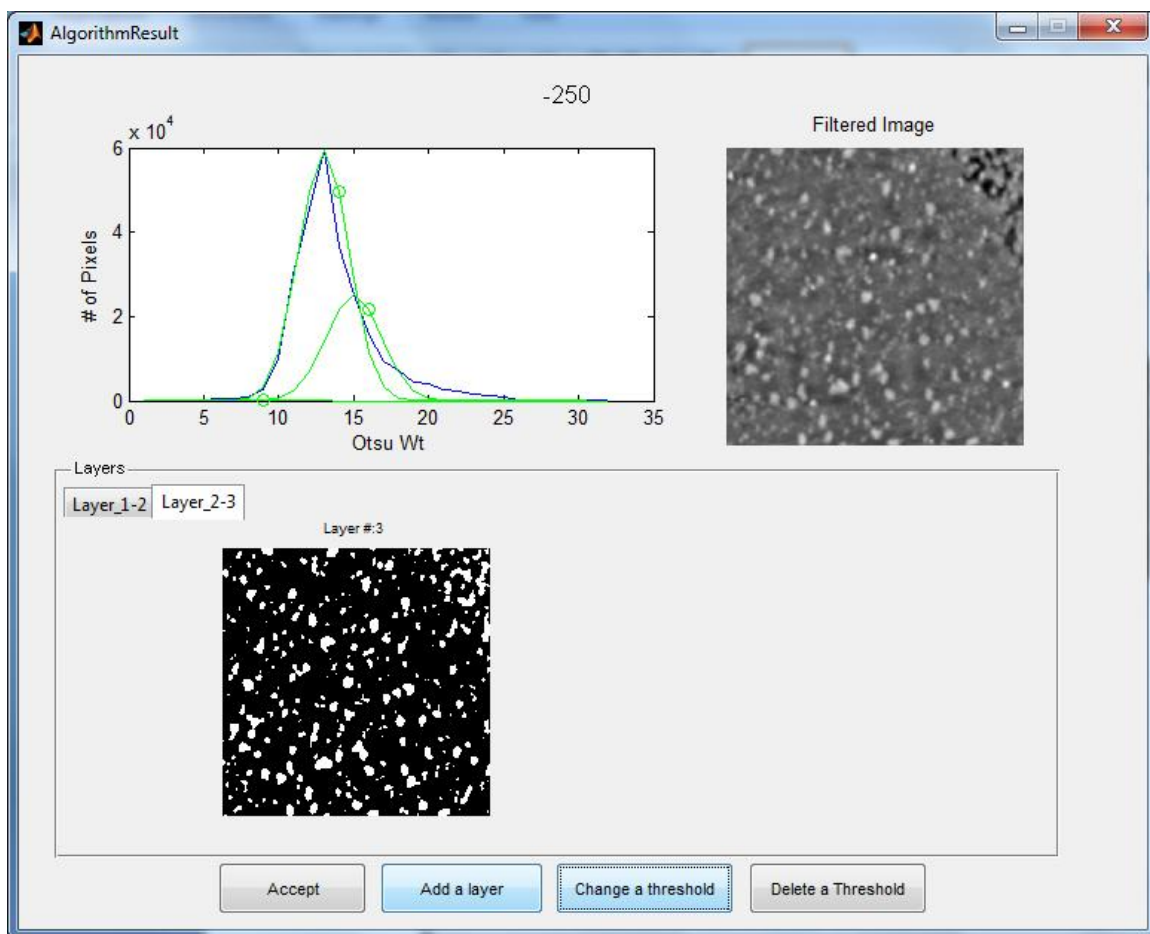


Figure 8.11 'AlgorithmResult' window displaying the binary image created using 'Add a layer' button. The plot of 'Number of pixels' v/s 'Otsu Wt' has been updated with Gaussian curve and threshold level for third layer.

The 'Change a threshold' button is used when the cluster is detected in a layer by the 'Image processing algorithm for qualitative and quantitative STM data Analysis' is smaller or bigger than the actual cluster evident through visual observation. The user is asked to input the layer number through the 'Select layer to change threshold' dialog box as shown in the Figure 8.12.

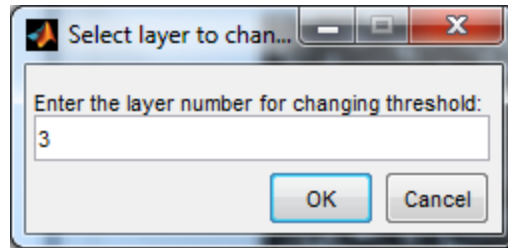


Figure 8.12 'Select layer to change threshold' dialog box asking user to enter the layer number for changing threshold.

On selecting a valid layer number, the 'ChangeLayerThreshold' window appears. The Figure 8.13 shows the 'ChangeLayerThreshold' window.

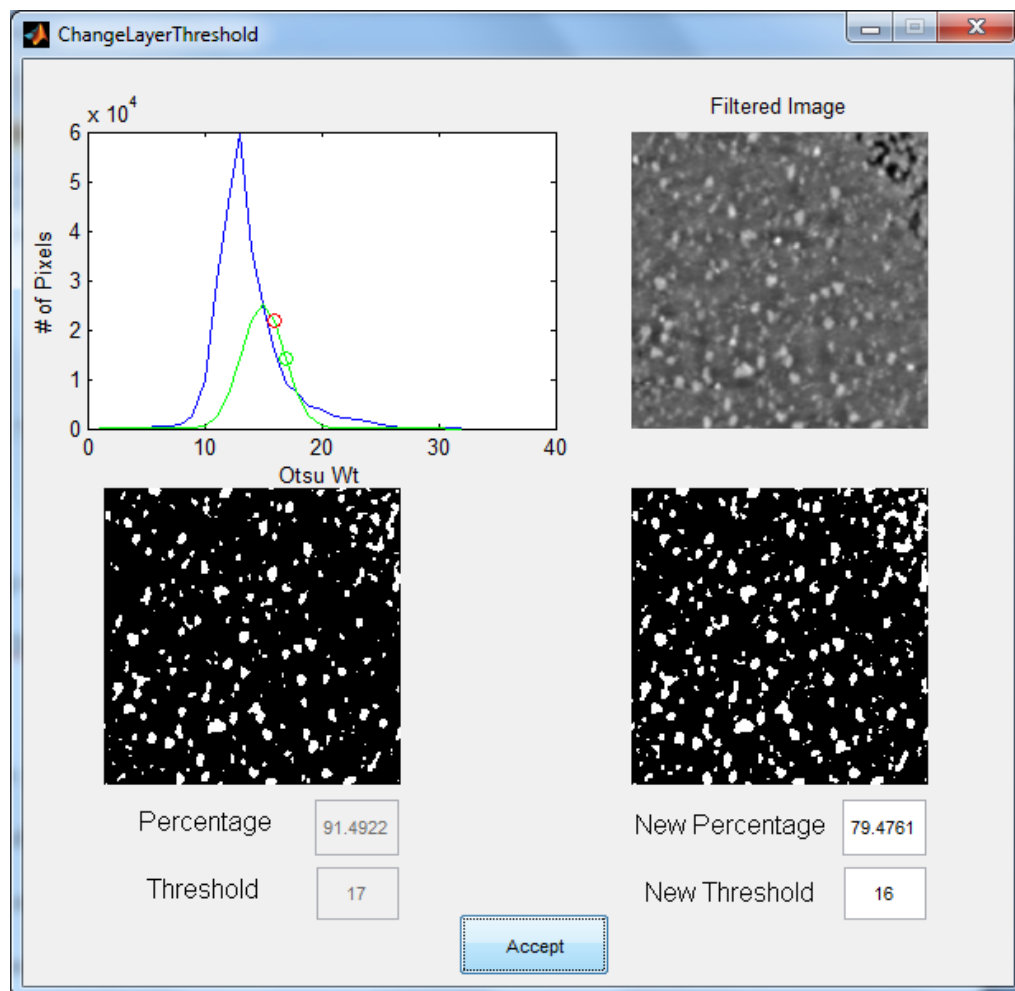


Figure 8.13 'ChangeLayerThreshold' window displaying the plot of 'Number of pixels' v/s 'Otsu Wt' with Gaussian curve for the layer selected to change the threshold.

As shown in the Figure 8.13, 'ChangeLayerThreshold' window contains a plot 'Number of Pixels' v/s 'Otsu Wt' with Gaussian curve of the layer selected for changing the threshold. The red circle is used to denote the new threshold level selected by user using edit box besides 'New Percentage' or 'New Threshold' label. The green circle is used to indicate the previously set threshold level. A 'filtered image' is provided to help user in selecting the most appropriate threshold level based on visual observation.

The binary image above the 'New Percentage' label in the 'ChangeLayerThreshold' window shows the user defined layer image. A user defined layer image is an image obtained by changing the edit box besides 'New Percentage' or 'New Threshold' label. It is necessary for the user to press the tab button after changing any edit box besides 'New Percentage' or 'New Threshold' label. The GUI will update the image above the 'New Percentage' edit box based on the new threshold level. Accept button should be clicked to use the new threshold level. Changes made to threshold level gets updated on 'Algorithm Result' window.

'Delete a threshold' button is used to delete a layer. This option will work if number of layer is more than one. When user clicks this button, a dialog box 'Select layer to delete' pops up, as shown in the Figure 8.14, asking user to input the layer number to be deleted. For a valid input this option deletes the selected layer.

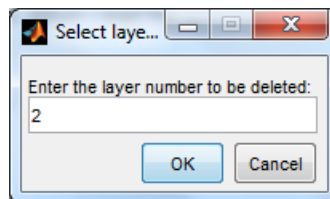


Figure 8.14 'Select layer to delete' dialog box asking user to enter the layer number to delete the corresponding layer.

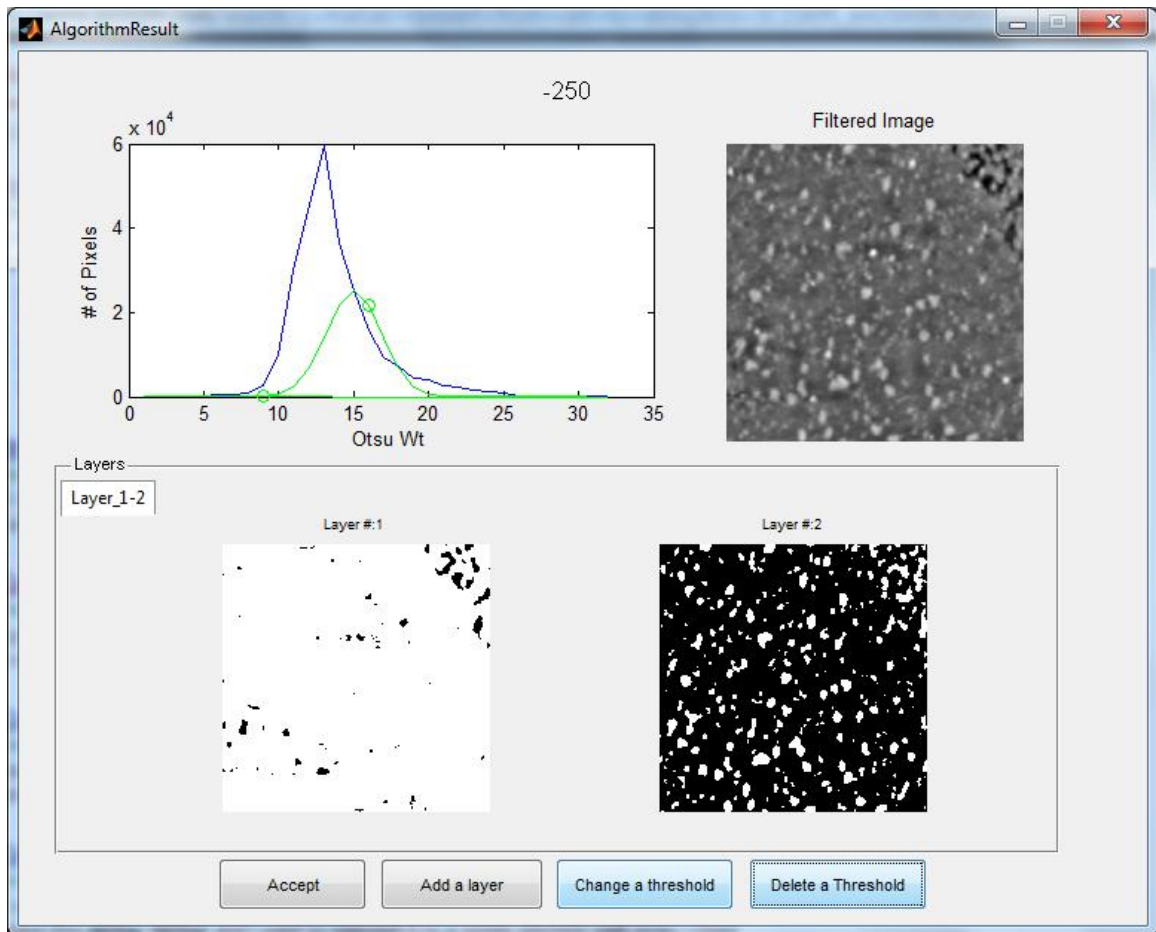


Figure 8.15 'Algorithm Result' window displaying the binary image for layer #: 1 and layer #: 2. when comparing the Figure 8.11, it can be concluded that a layer has been deleted. In the given the Figure layer #: 2 was deleted using 'Delete a threshold' button and layer #: 3 now becomes layer #: 2.

The 'Accept' button is used to accept the results displayed on the 'Algorithm Result' window. The GUI extracts the cluster area and displays a plot of numbers of cluster v/s cluster area in a separate window, 'PlotSumLogNormal,' as shown in the Figure 8.16.

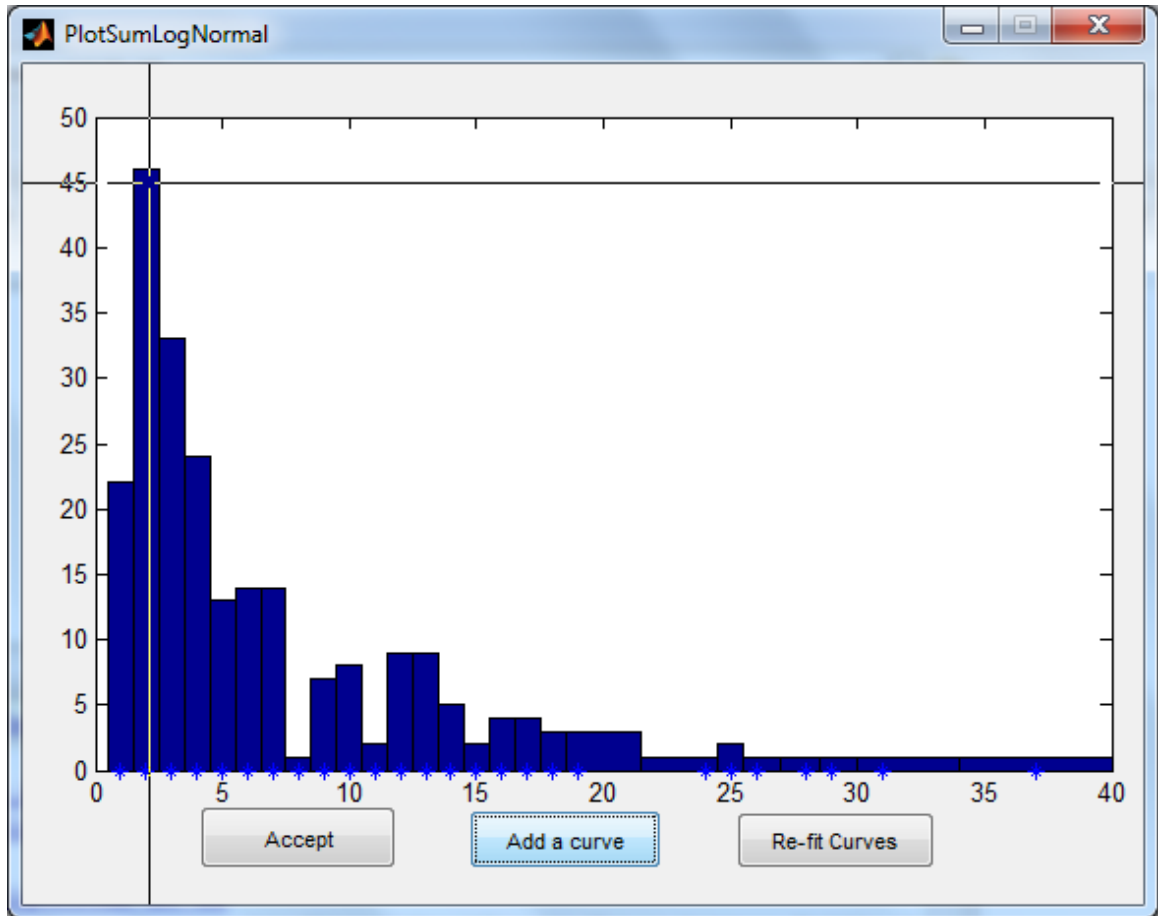


Figure 8.16 'PlotSumLogNormal' window displaying the plot of number of cluster v/s cluster area.

As shown in the Figure 8.16, the 'PlotSumLogNormal' window has three buttons 'Accept,' 'Add a curve,' 'Re-fit Curves.' This window helps user to select the maximum of plot by the user. A log normal curve is fitted to distribution based on user selected points. Using the 'Add a curve' button user can provide a co-ordinate based on his visual observation. The GUI treats the x co-ordinate as average (median) of log normal curve.

Log Normal distribution is a continuous distribution in which logarithm of a variable is a normal distribution. The probability density of function for a log normal distribution is given in Formula (8-a),

$$f_x(x; \mu, \sigma) = \frac{1}{x\sigma\sqrt{2\pi}} e^{-\frac{(\ln x - \mu)^2}{2\sigma^2}}, x > 0, \quad (8-a)$$

where notations have their usual meaning.  $\mu$  and  $\sigma$  is mean and standard deviation of normal distribution and it could be calculated using the following formula,

$$\sigma = \frac{1}{x.y.\sqrt{2\pi}}, \quad (8-b)$$

where  $x$  =  $x$  co-ordinate of a point selected by user,

$y$  = pdf of  $y$  co-ordinate of a point selected by user,

$$\mu = \log(x), \quad (8-c)$$

where  $x$  =  $x$  co-ordinate of a point selected by user.

$\mu_{\log \text{ normal}}$  and  $\sigma_{\log \text{ normal}}$  can be calculated using the following formula,

$$\mu_{\log \text{ normal}} = e^{\mu + \sigma^2 / 2}, \quad (8-d)$$

where  $\mu_{\log \text{ normal}}$  = mean of log normal curve,

$\mu$  = mean of normal distribution,

$\sigma$  = standard deviation of normal distribution.

Similarly,

$$\sigma_{\log \text{ normal}} = \sqrt{(e^{\sigma^2} - 1)e^{2\mu + \sigma^2}}, \quad (8-e)$$

where  $\sigma_{\log \text{ normal}}$  = standard deviation of log normal curve,

$\mu$  = mean of normal distribution,

$\sigma$  = standard deviation of normal distribution.

Maximum of log normal is calculated using the following formula,

$$\text{Maximum}_{\log \text{ normal}} = e^{\mu - \sigma^2}, \quad (8-f)$$



where  $\text{Maximum}_{\log \text{ normal}} = \text{maximum of log normal curve},$

$\mu = \text{mean of normal distribution},$

$\sigma = \text{standard deviation of normal distribution},$

the average of the log normal is calculated using the following formula,

$$\text{Average}_{\log \text{ normal}} = e^{\mu}, \quad (8-e)$$

where  $\text{Average}_{\log \text{ normal}} = \text{average of log normal curve},$

$\mu = \text{mean of normal distribution},$

A log normal distribution is fitted to the plot as shown in the Figure 8.17 using Formula

(8-a).

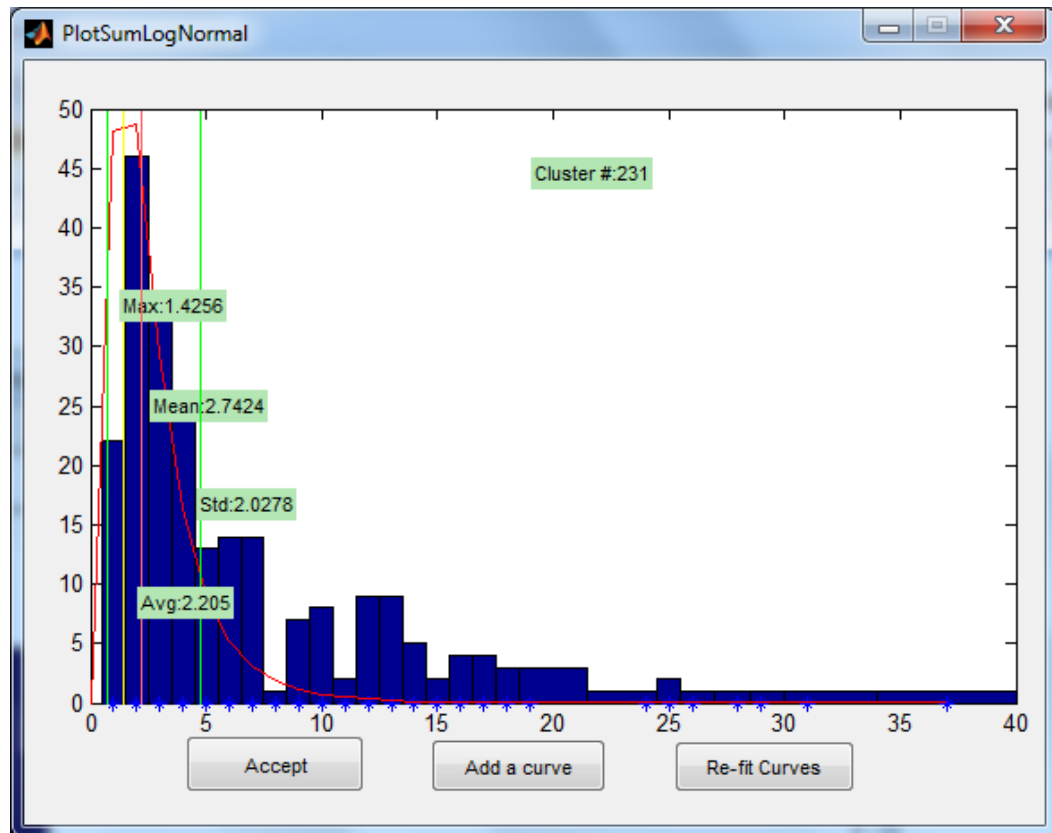


Figure 8.17 'PlotSumLogNormal' window displaying the distribution fitted to the plot of number of cluster v/s cluster area.

Using the 'PlotSumLogNormal,' user can fit maximum of two distributions in the plot. The 'Re-fit Curves' button should be clicked in case the user wants to refit the distribution. Once the distribution is fitted to a plot, user can click the 'Accept' button to continue processing.

In case of error, progress bar informs user about the error by displaying appropriate error message. The GUI sends an email to the developer indicating the error and the line at which the error was observed. In case if no internet connection is available the GUI updates 'errorLog.txt' with the error and line at which the error was observed. The 'errorLog.txt' is located in the working directory of Matlab.

Once the process is complete the GUI displays information as shown in the Figure 8.18. After completing the process, 'Task' button becomes visible to perform analysis on different image. Print Panel can be seen on the left side of GUI. Check boxes like 'Mean Plot,' 'Maximum Plot,' 'Average Plot,' 'Coverage Plot,' 'Density Plot,' in the 'Print Panel' are locked because plots can only be obtained for processing on more than one image at a time. The user can also observe different analysis done on image in different 'tab' under the 'Result' panel.

These tabs are,

1. ASCII Image File
2. Image in Gray Level
3. Image After Applying Filter
4. Determining Layers

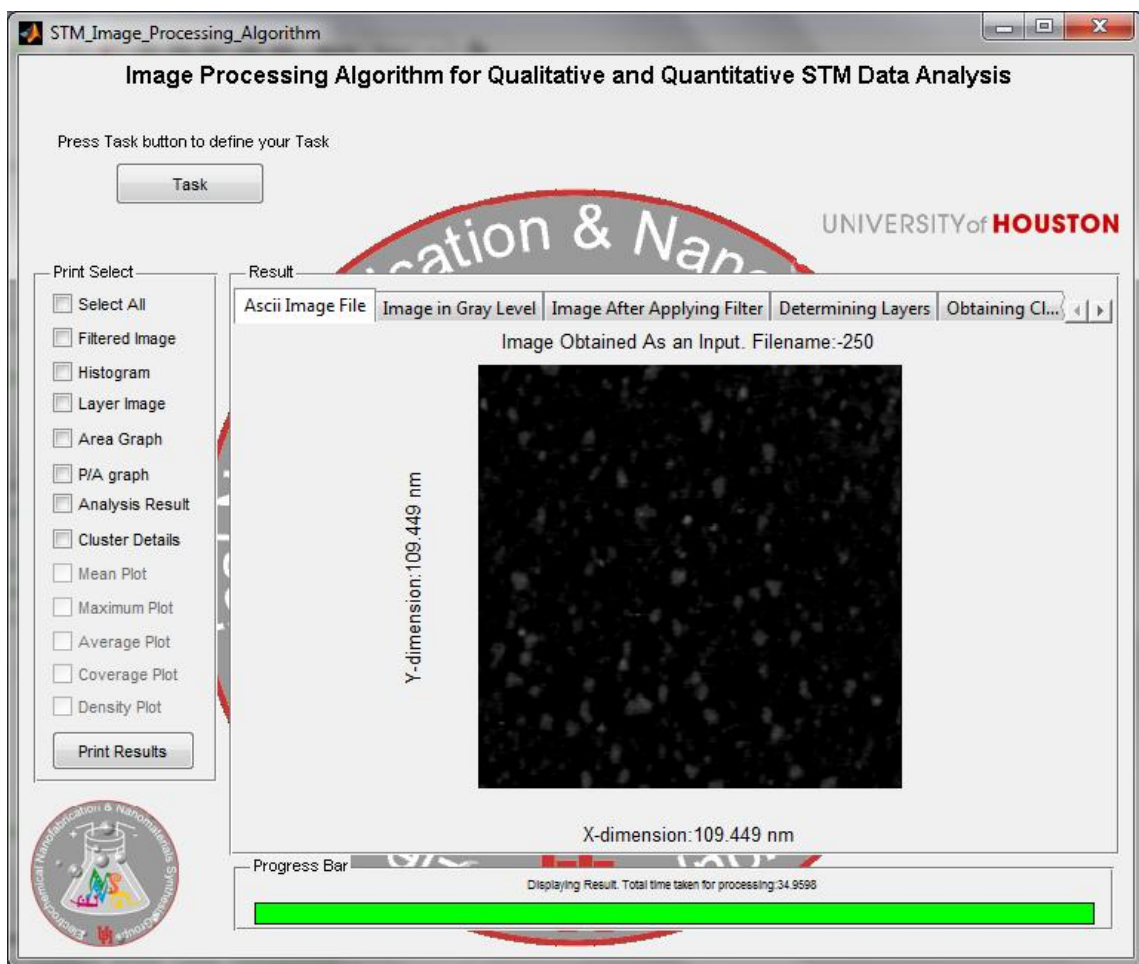


Figure 8.18 The GUI Screen after process of analyzing STM image is complete.

5. Obtaining Cluster (Layer Specific)
6. Analyzing the data (Layer Specific)
7. Result tab (Layer Specific)

#### 8.2.1.1.1 ASCII Image File

Figure 8.19 displays the 'ASCII Image File' tab. The 'ASCII Image File' tab displays the input image read by the GUI.

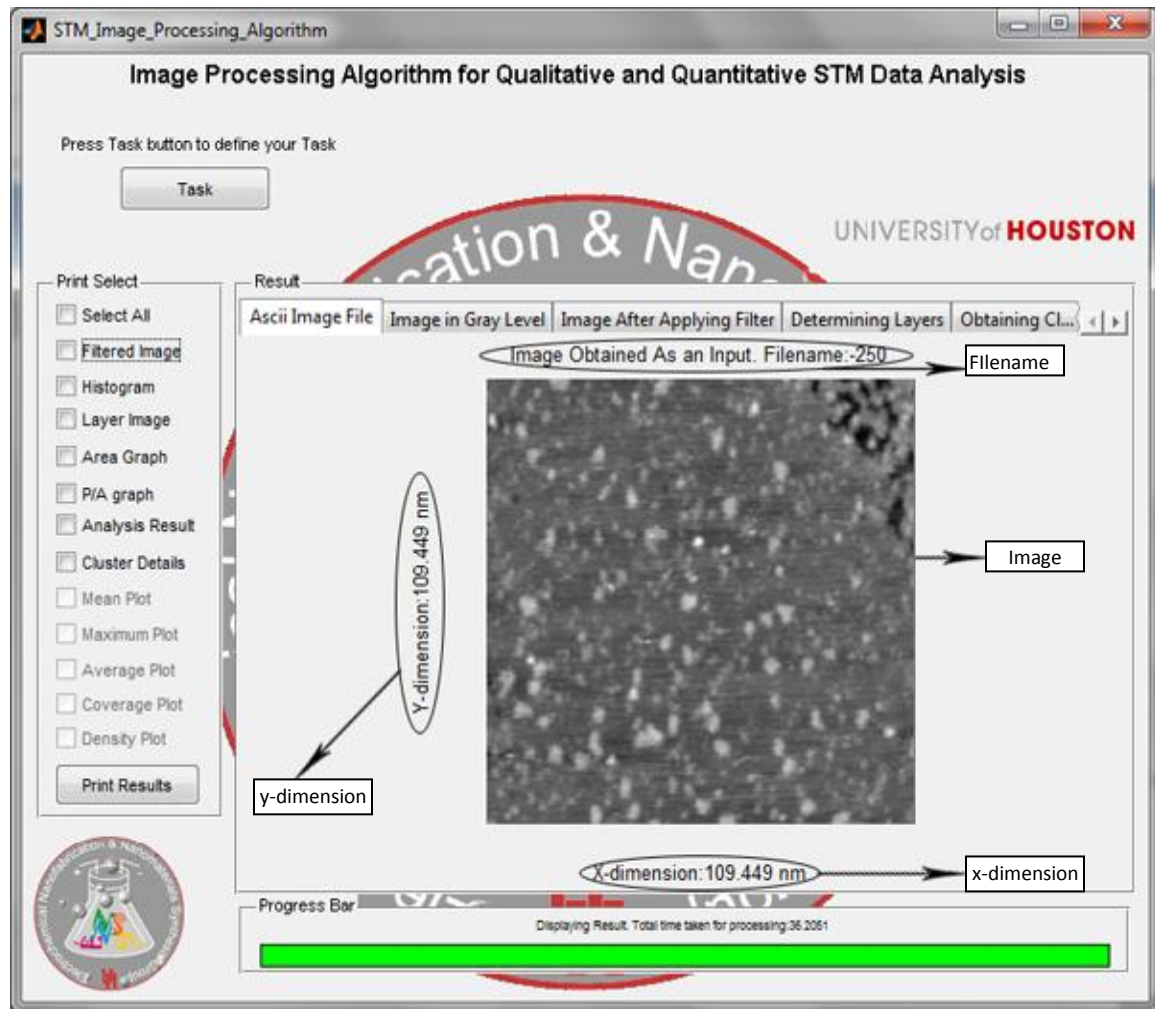


Figure 8.19 The GUI Screen displaying the 'ASCII Image File' tab.

As shown in the Figure 8.18, the 'ASCII Image File' tab displays the image read by the GUI. It contains the file name as title with image. If scan size is mentioned in the input file, it displays the x-dimension and y dimension as the scan size. The default unit assumed for scan size is nanometers. If ASCII file does not contains information about

image's scan size then the GUI uses the number of rows and columns of image matrix as y-dimension and x-dimension of image.

#### 8.2.1.1.2 Image in Gray Level

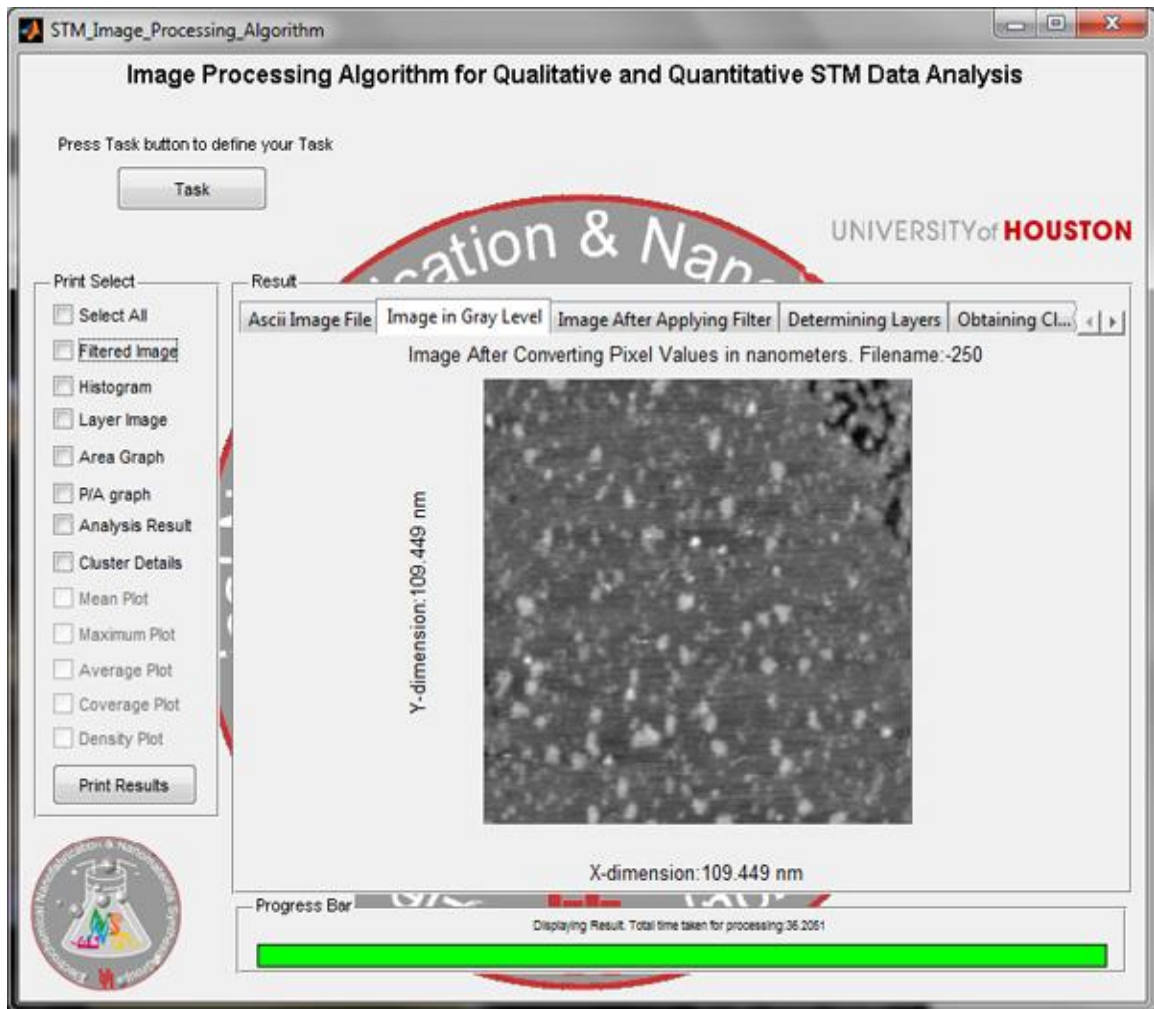


Figure 8.20 The GUI Screen displaying the 'Image in Gray Level' tab.

The 'Image in Gray Level' tab displays the image in gray level. It also contains the filename as title, x dimension as x-label and y dimension as y-label.

### 8.2.1.1.3 Image After Applying Filter

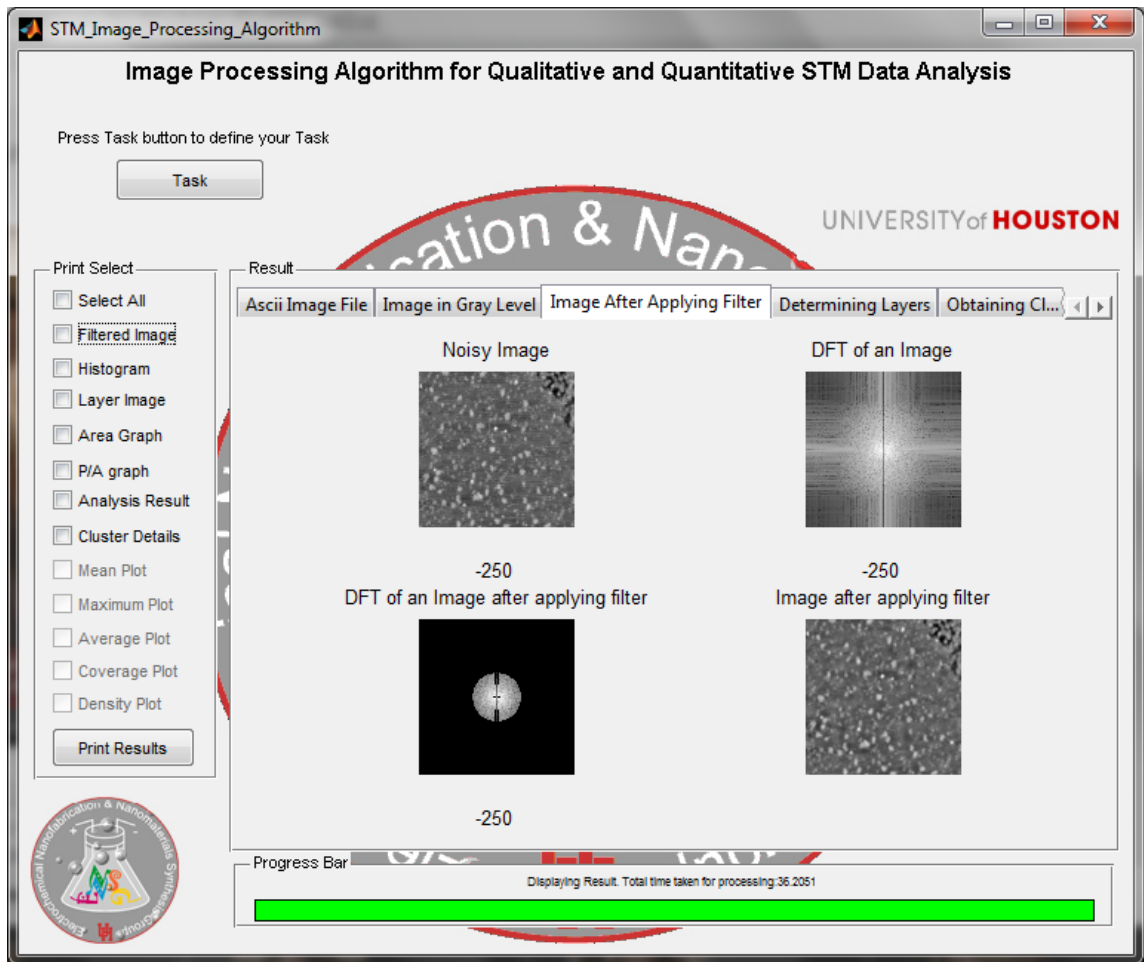


Figure 8.21 The GUI Screen displaying the 'Image After Applying Filter' tab.

In the Figure 8.21 as observed the 'Image After Applying Filter' tab displays Noisy Image on the top left side of tab, towards right is its equivalent DFT (Discrete Fourier Transform) of an Image. The image analysis algorithm applies a filter mask and the resultant DFT obtained after applying filter is shown on the bottom left side of tab. The resultant DFT is then converted to image, which is shown with the title 'Image after applying filter' in the bottom right of the tab. The filename of image being processed is

displayed at the bottom of 'Noisy image,' 'DFT of an image,' and 'DFT of an Image after applying filter.'

#### 8.2.1.1.4 Determining Layers

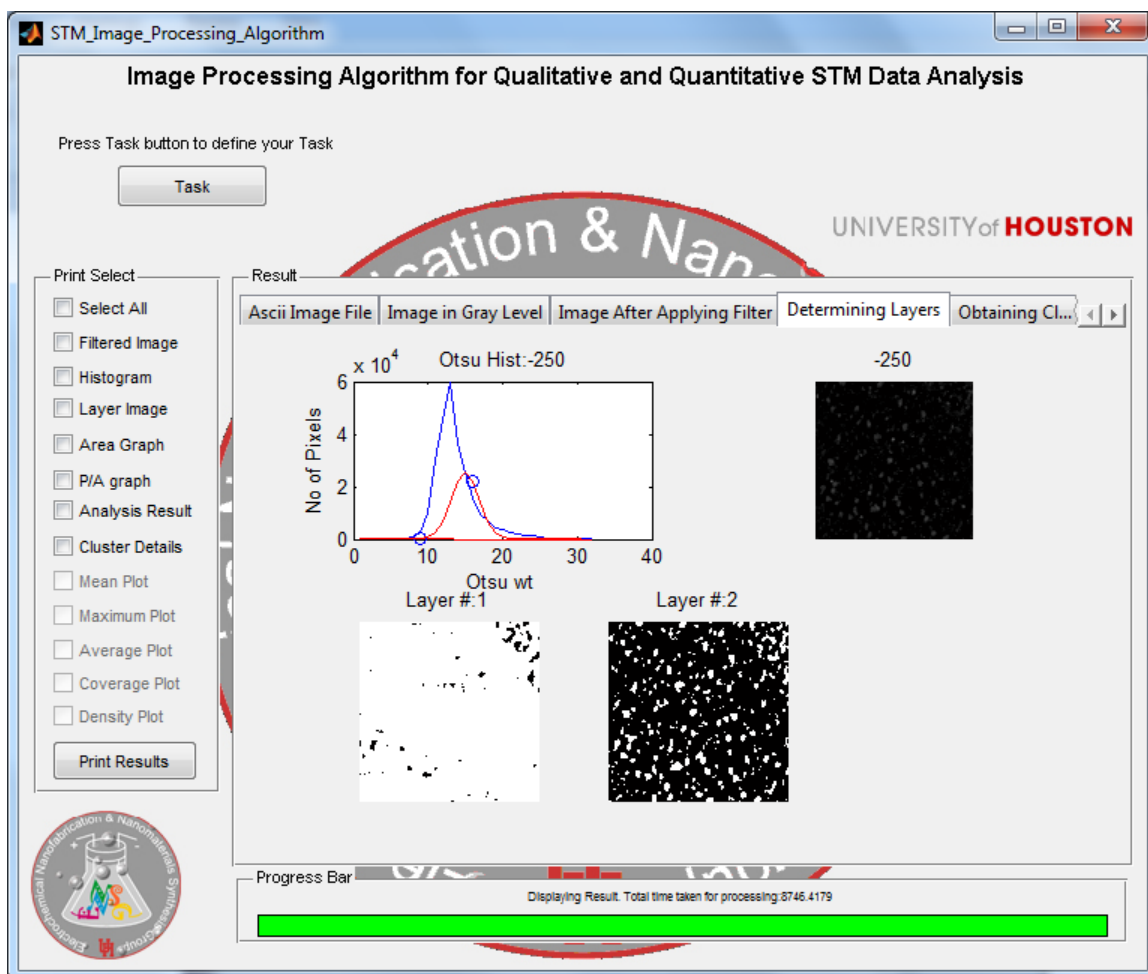


Figure 8.22 The GUI Screen displaying the 'Determining Layers' tab in STM Image of Pb UPD on  $\text{Pt}_{\text{SML}}/\text{Au}_{(111)}$  in  $10^{-2}$  M  $\text{Pb}^{2+}$  and 0.1 M  $\text{HClO}_4$  solution taken at -250 mV w.r.t. SCE (Standard Calomel Electrode).

The 'Determining layers' tab, as indicated in the Figure 8.22, shows OTSU histogram on the top left of the tab. This histogram shows Gaussian curve fitted to OTSU histogram. In this plot two 'blue circle' could be seen. This sign indicates the threshold used to create binary image for cluster layer. The image on bottom left indicates the

first layer detected and the image beside the first layer is the second cluster layer detected.

#### 8.2.1.1.5 Obtaining Cluster (Layer Specific)

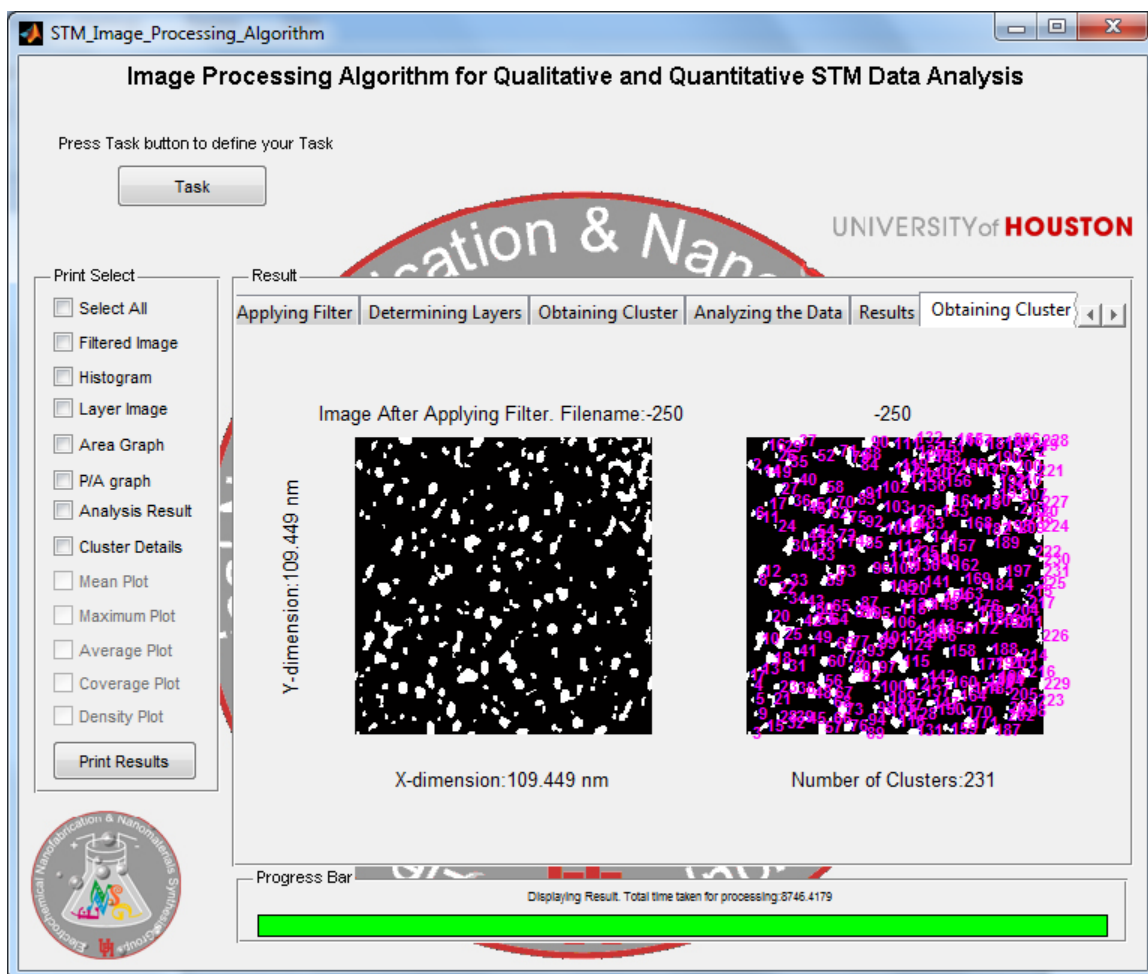


Figure 8.23 The GUI Screen displaying the 'Obtaining Cluster' tab for second layer of cluster in STM Image of Pb UPD on Pt<sub>SML</sub>/Au<sub>(111)</sub> in 10<sup>-2</sup> M Pb<sup>2+</sup> and 0.1 M HClO<sub>4</sub> solution taken at -250mV w.r.t. SCE (Standard Calomel Electrode).

It can be seen in the Figure 8.22 that 'Obtaining Cluster' tab consists of binary image. The binary image on left is generated by 'Determination of Threshold' module of algorithm and on the right side the binary image consists of labeled cluster. These





horizontal axis is in terms of nanometers if scan size is given in input ASCII file else it is in terms of pixels.

#### 8.2.1.1.7 Result (Layer Specific)

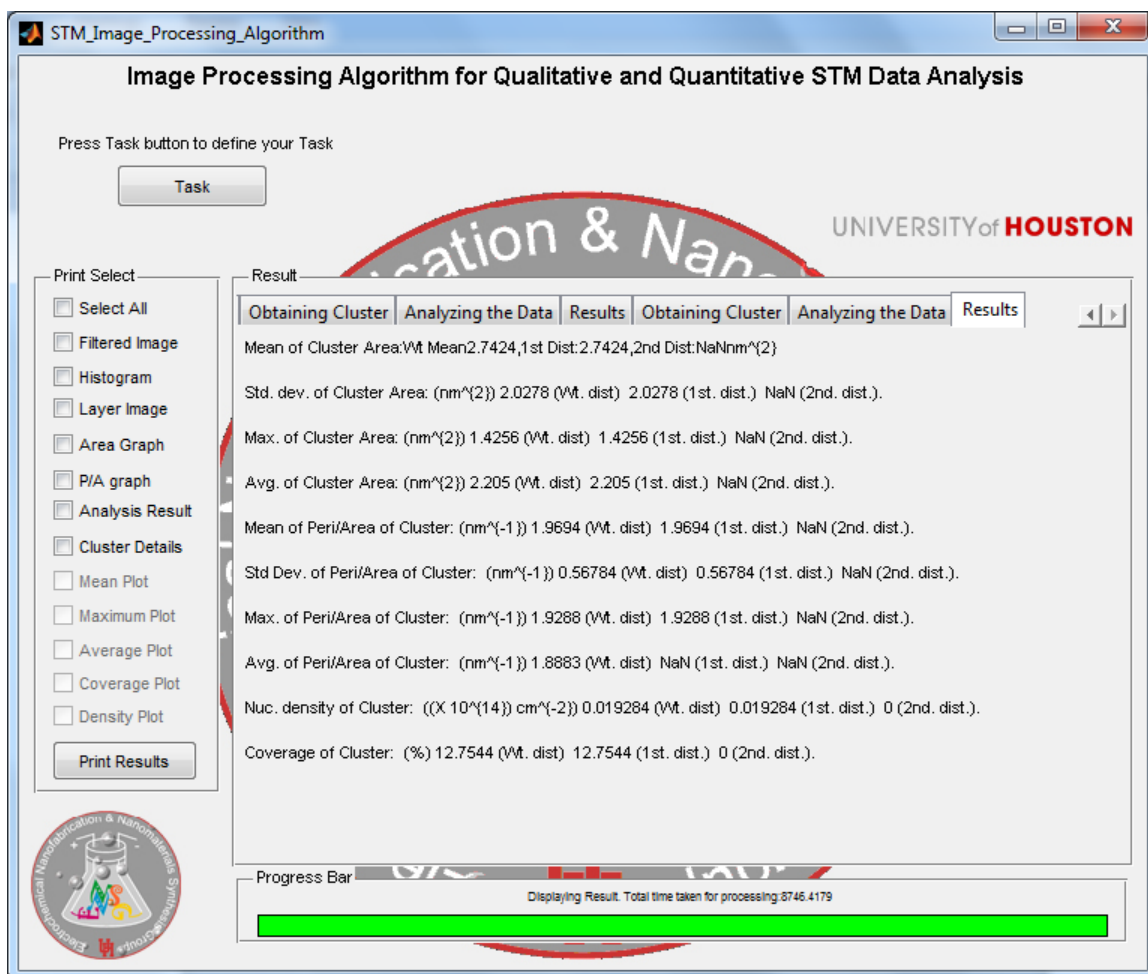


Figure 8.25 The GUI Screen displaying the 'Result' tab for second layer of cluster in STM Image of Pb UPD on Pt<sub>SML</sub>/Au<sub>(111)</sub> in 10<sup>-2</sup> M Pb<sup>2+</sup> and 0.1 M HClO<sub>4</sub> solution taken at -250 mV w.r.t. SCE (Standard Calomel Electrode).

The 'Result' tab has quantitative results of analysis perform on STM image. These quantitative result is layer specific as shown in the Figure 8.25. It gives information about mean, standard deviation, maximum, average of cluster area, and perimeter by area. It also gives a quantitative value of nucleation density and coverage of cluster.

The user can print a word file using 'Print Select' panel. This panel is discussed in the later section of this chapter.

#### 8.2.1.2 Group of Single image taken at different potentials

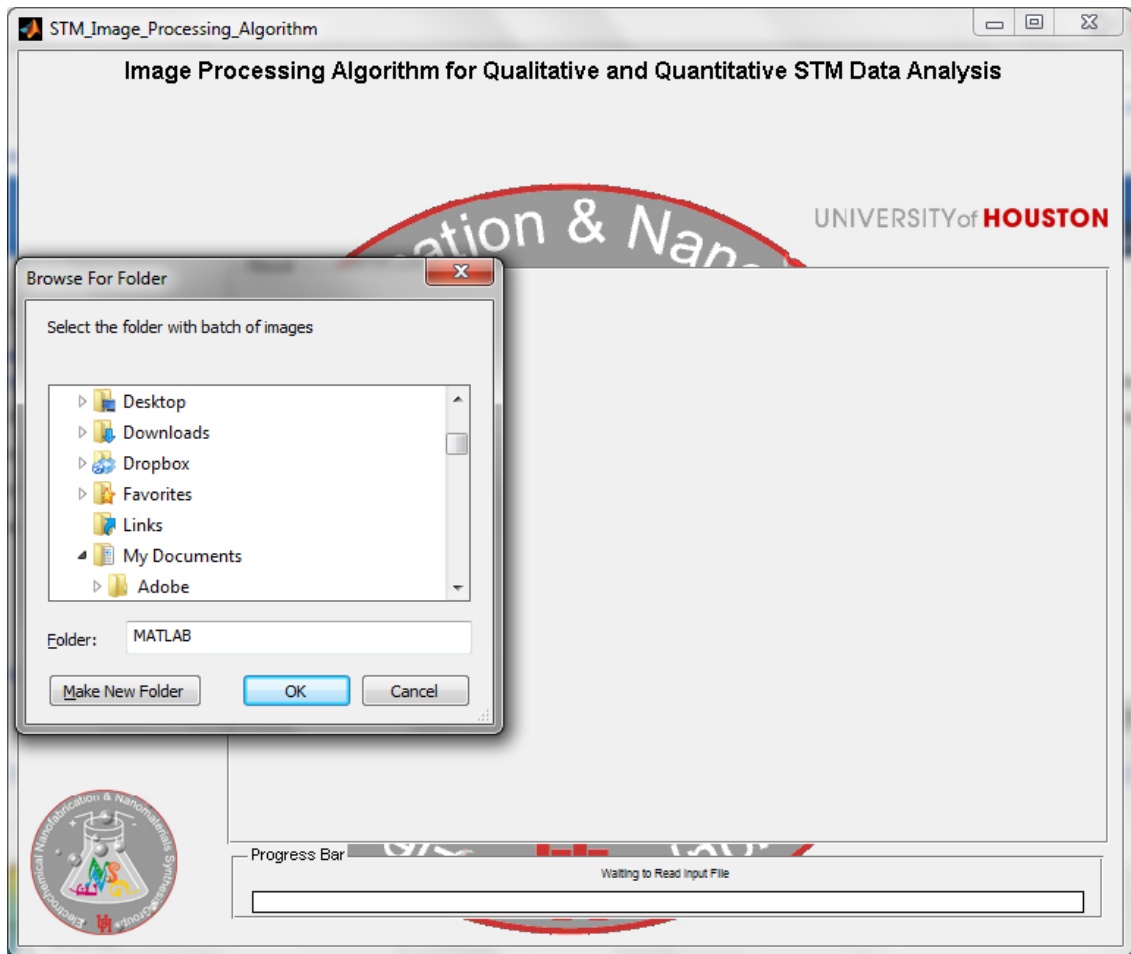


Figure 8.26 The GUI Screen after user clicks the 'Group of Single image taken at different potentials' button.

If the 'Group of single image taken at different potentials' button is clicked, user is asked to select a directory with the group of images for stand-alone processing. The 'Progress Bar' appears at the bottom the GUI window. It is an improved version of wait bar in Matlab. Developed by Ross Haton, it is used to inform user about the percentage of processing completed by the GUI [31-34]. In case of error, the 'Progress Bar' informs

user about the error by displaying appropriate error message as shown in the Figure 8.27.

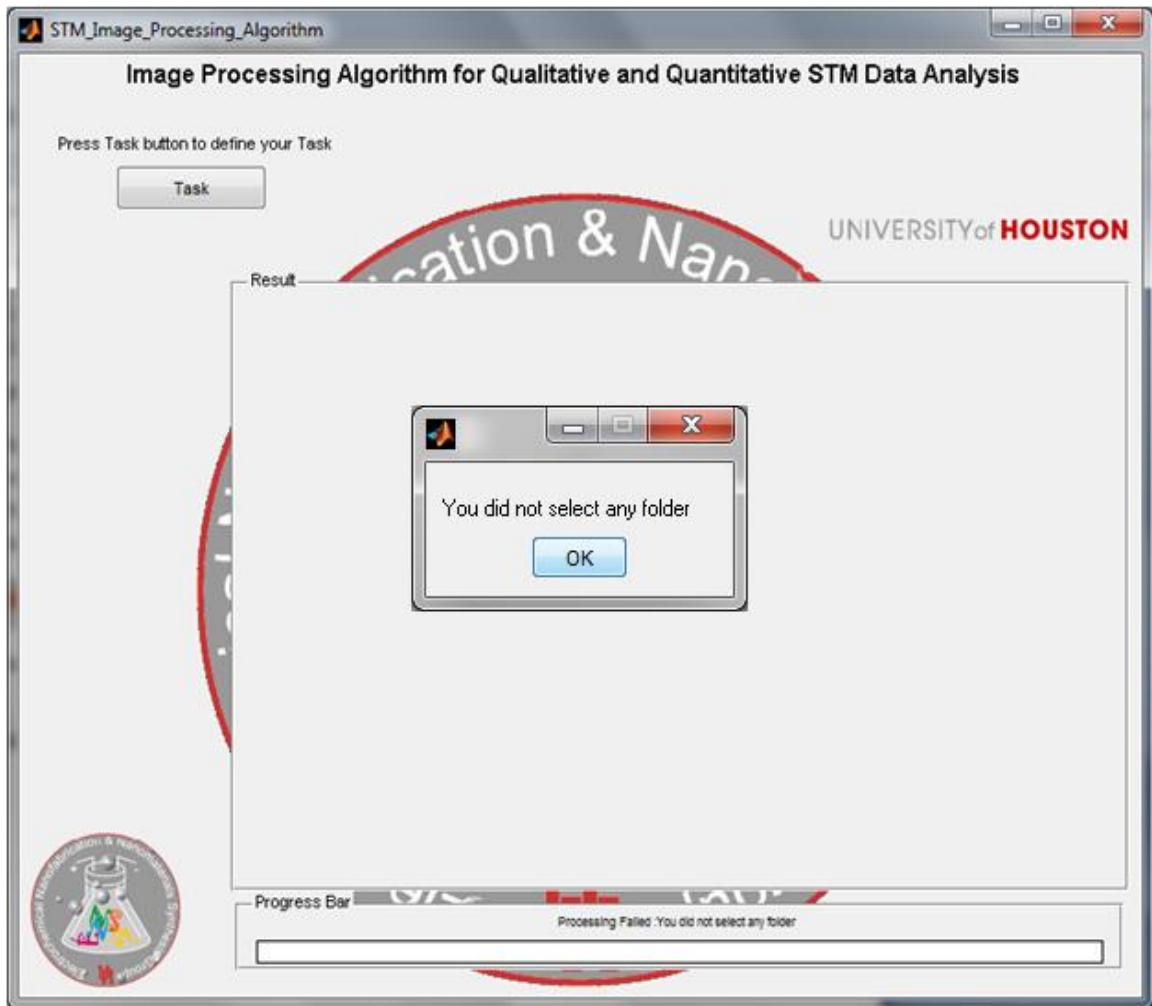


Figure 8.27 The GUI Screen when no directory is selected after user click 'Group of Single image taken at different potentials' button.

As shown in the Figure 8.27 if no selection is made the GUI throws an exception with subsequent error message and makes the 'Task button' visible to restart the process of image analysis. When the user selects a directory with batch of images, the GUI processes the information and at the end of processing it displays information as shown in the Figure 8.18.

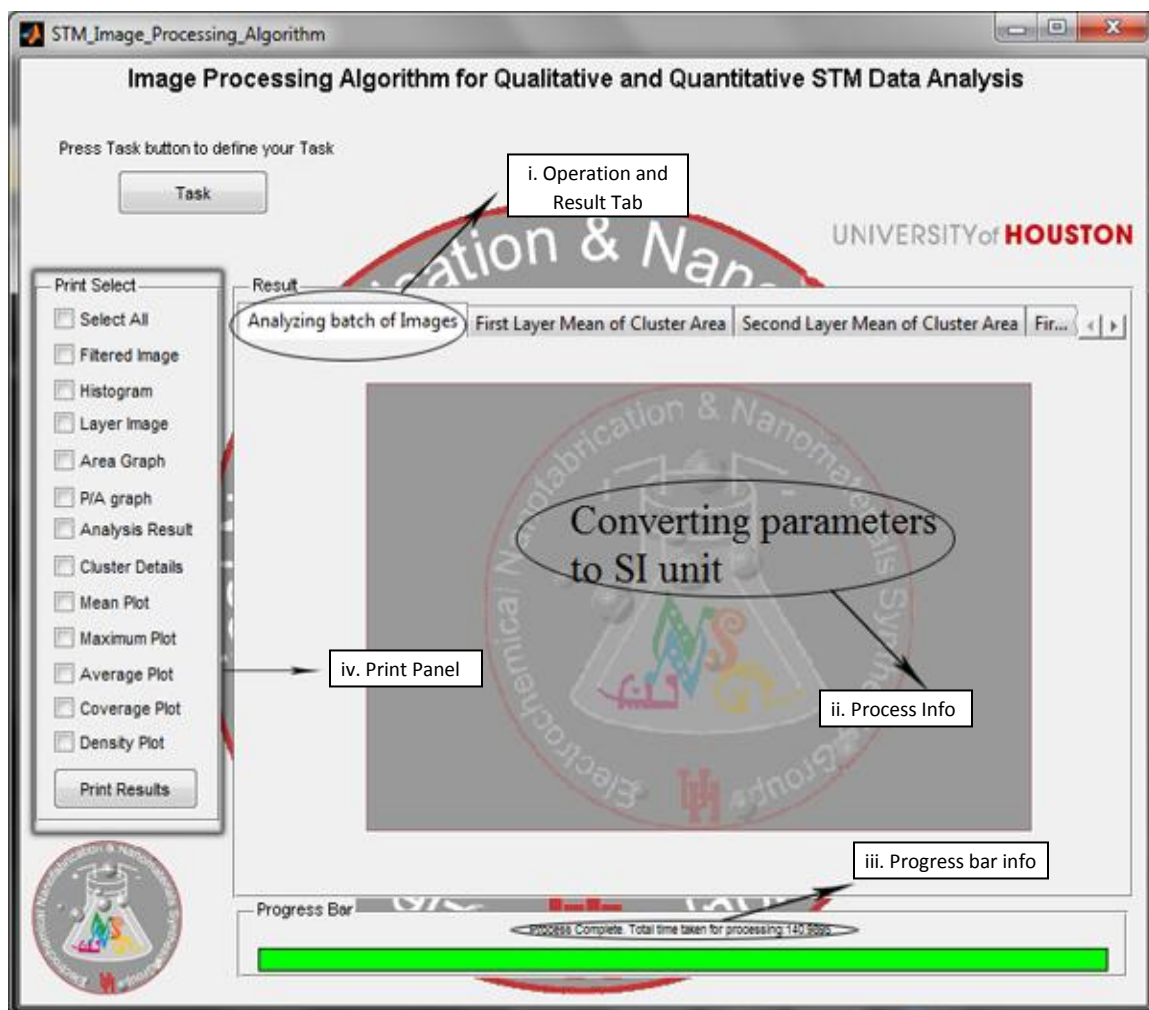


Figure 8.28 The GUI Screen after processing group of images.

Figure 8.28 displays the GUI after images has been processed. Once the processing is complete the 'Task button' becomes visible. This button should be clicked if the user wants to analyze another batch of images. The GUI screen displays 'Operation and Result tab' and 'Process info' in Result panel, 'Progress bar info' in 'Progress bar' panel and 'Print Panel' section. They are discussed in the next section of this chapter.

#### *8.2.1.2.1 Operation and Result tab*

The GUI uses the 'Operation and Result' tab to display the current or last performed operation on batch of images and to display result in form of graphs. It uses tab panel in Matlab to create a tab group [35]. If tab is used to display info regarding process, it loads an image on axes and update the text based on operation performed on batch of images. Operation tab is always visible to user by default and it is always active as seen in the Figure 8.28.

The result tab displays a plot on the axes. The plot contains cluster parameter versus file name or potential of file. If the file name contains potential at which the image was recorded, then the GUI extracts the potential from file name and uses it to plot cluster parameter versus potential at which STM image file was recorded.

The result tab is generated after all the cluster parameter is available to plot the graph. The GUI generates a plot of mean of cluster area, mean of perimeter by cluster area, maximum of cluster area, maximum of perimeter by area of the cluster, average of cluster area, average of perimeter by area of the cluster, layer density and layer coverage v/s potential or filename in the batch analyzed. This plot is generated for first distribution and/or second distribution as selected by the user in 'PlotSumLogNormal.'

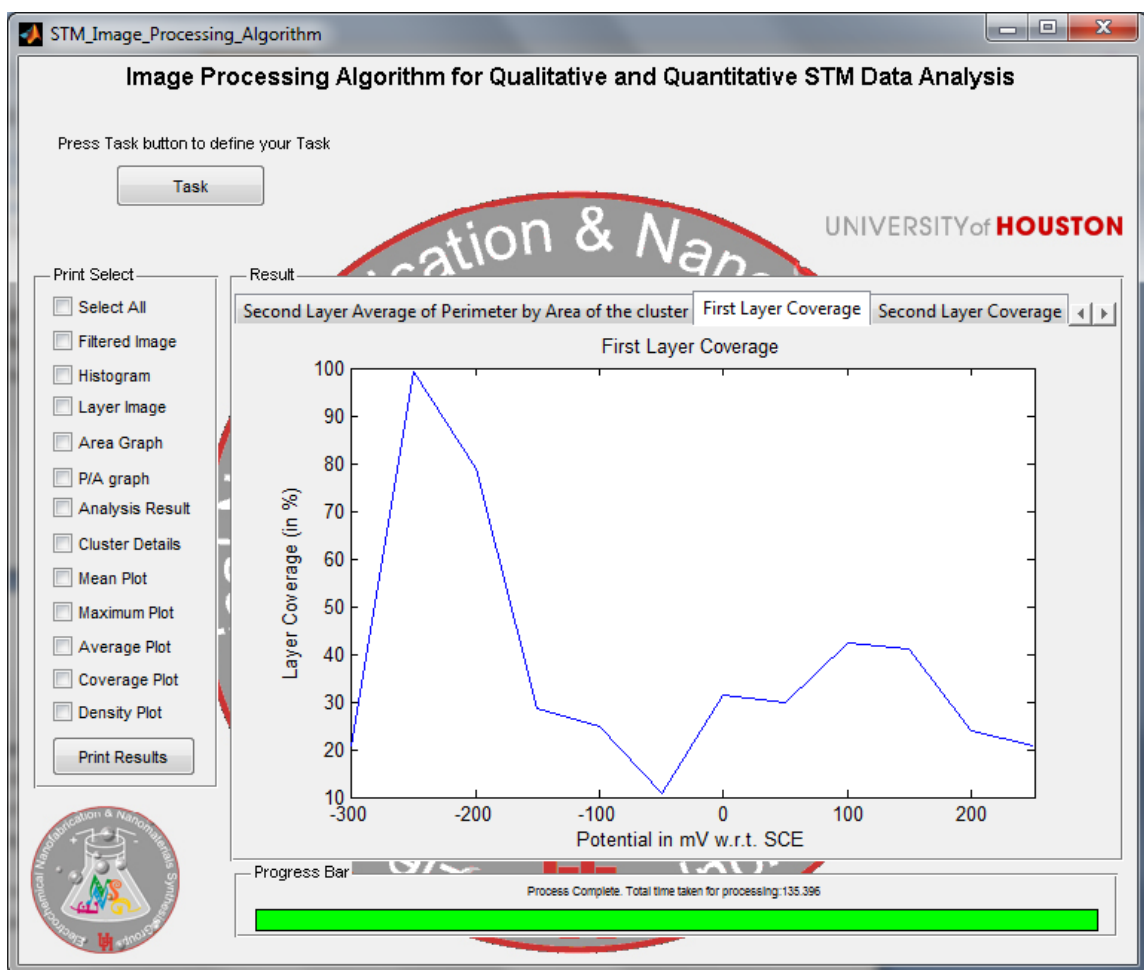


Figure 8.29 The GUI Screen with First layer coverage plot in result tab. Images of Pb UPD on PtSML/Au(111) in 10<sup>-2</sup> M Pb<sup>2+</sup> and 0.1 M HClO<sub>4</sub> solution were used to obtain the plot. The plot of layer coverage v/s Potential w.r.t. SCE is shown in the Figure.

#### 8.2.1.2.2 Process Info

Process info is a text bar and is updated based on the current operation performed on the group of images.

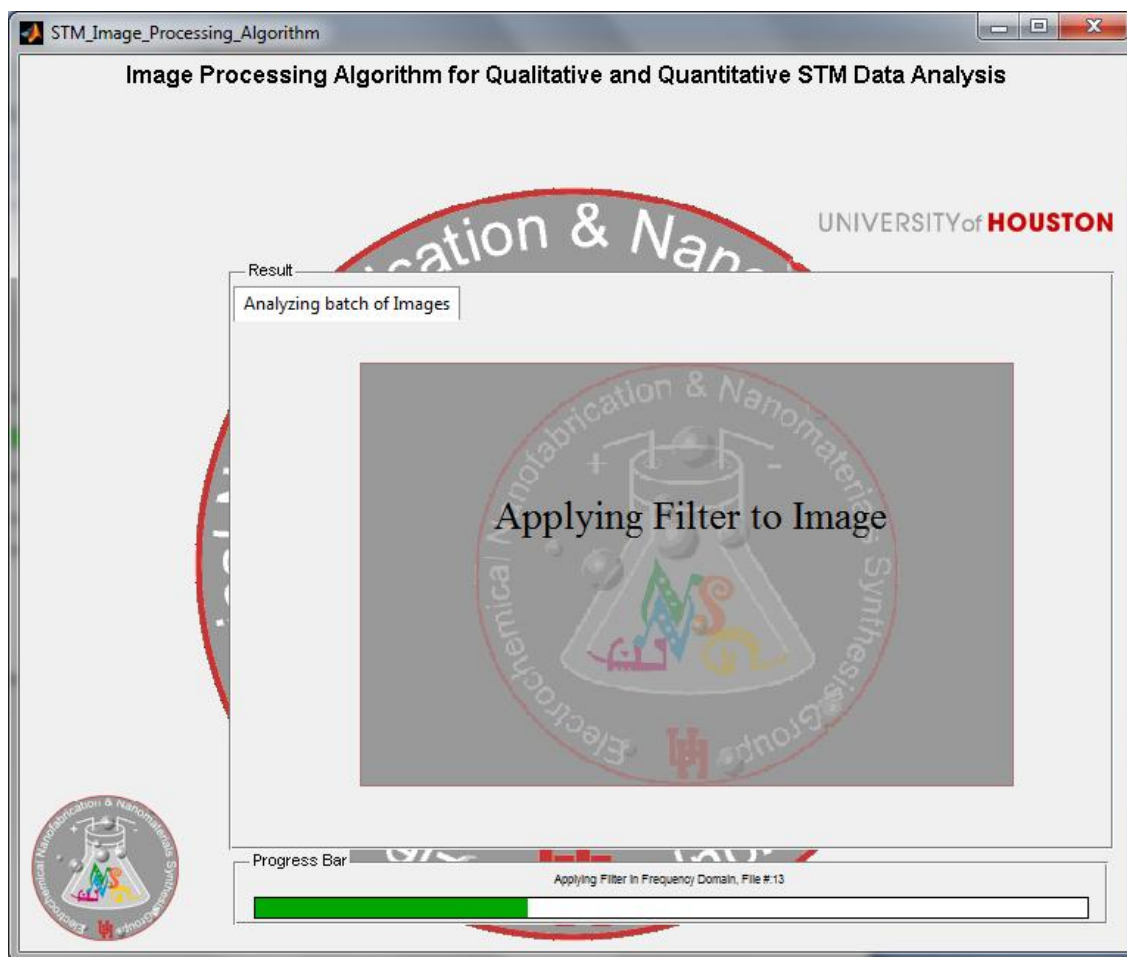


Figure 8.30 The GUI Screen during the Process info section displays 'Applying Filter to Image' and Progress info bar section displays 'Applying Filter in Frequency Domain File # 13.'

#### 8.2.1.2.3 Progress Bar Info

Progress Bar info is used to display the status of the GUI. It displays information such as 'Waiting to read input file' to indicate that the GUI has asked user to select an image or batch of image. This section updates the current status of the GUI as oppose to Process info section. In process info section, information pertaining to operation performed on batch of images is updated. At the end of processing it indicates the total time taken to complete the process. This could be observed in the Figure 8.29.



#### *8.2.1.2.4 Print Panel*

The print select panel contains following check boxes

1. Filtered Image: To print a word file of the image obtained after applying filter to the noisy input image. This check box is inactive when the GUI processes batch of image.
2. Histogram: To print a word file of the Otsu histogram along with thresholding point and Gaussian curve fitted on the histogram for layer detection. This check box is inactive when the GUI processes batch of image.
3. Layer Image: To print a word file of the binary image of first and second cluster layer detected in an image. In case of 'Batch of Image' this check box could be used to print the most suitable binary layer image.
4. Area graph: To print a word file of the plot of # of cluster v/s cluster area in an image.
5. P/A graph: To print a word file of the plot of # of cluster v/s perimeter by area in an image.
6. Analysis Result: To print a word file of the numerical value of mean, standard deviation, maximum, average of cluster area and P/A of cluster in an image along with coverage density and layer coverage.
7. Cluster Detail: To print a word file of the area and perimeter by area values of each cluster in an image.
8. Mean Plot: To print a word file of the plot of mean of cluster area v/s potential (based on file name) and mean of perimeter by area of cluster v/s potential (based on file name). This check box is inactive when the GUI processes a single image.

9. Maximum Plot: To print a word file of the plot of the maximum of cluster area v/s potential (based on file name) and maximum of perimeter by area of cluster v/s potential (based on file name). This check box is inactive when the GUI processes a single image.

10. Average Plot: To print a word file of the plot of the average of cluster area v/s potential (based on file name) and average of perimeter by area of cluster v/s potential (based on file name). This check box is inactive when the GUI processes a single image.

11. Coverage Plot: To print a word file of the plot of the layer coverage in % v/s potential (based on file name). This check box is inactive when the GUI processes a single image.

12. Density Plot: To print a word file of the plot of the coverage density v/s potential (based on file name). This check box is inactive when the GUI processes a single image.

Apart from this, there is a 'Select All' check box. If this checkbox is selected then all the checkboxes mentioned from 1-12 will be selected and is basically used to print all the details pertaining to image analysis. It is basically used to save user's time.

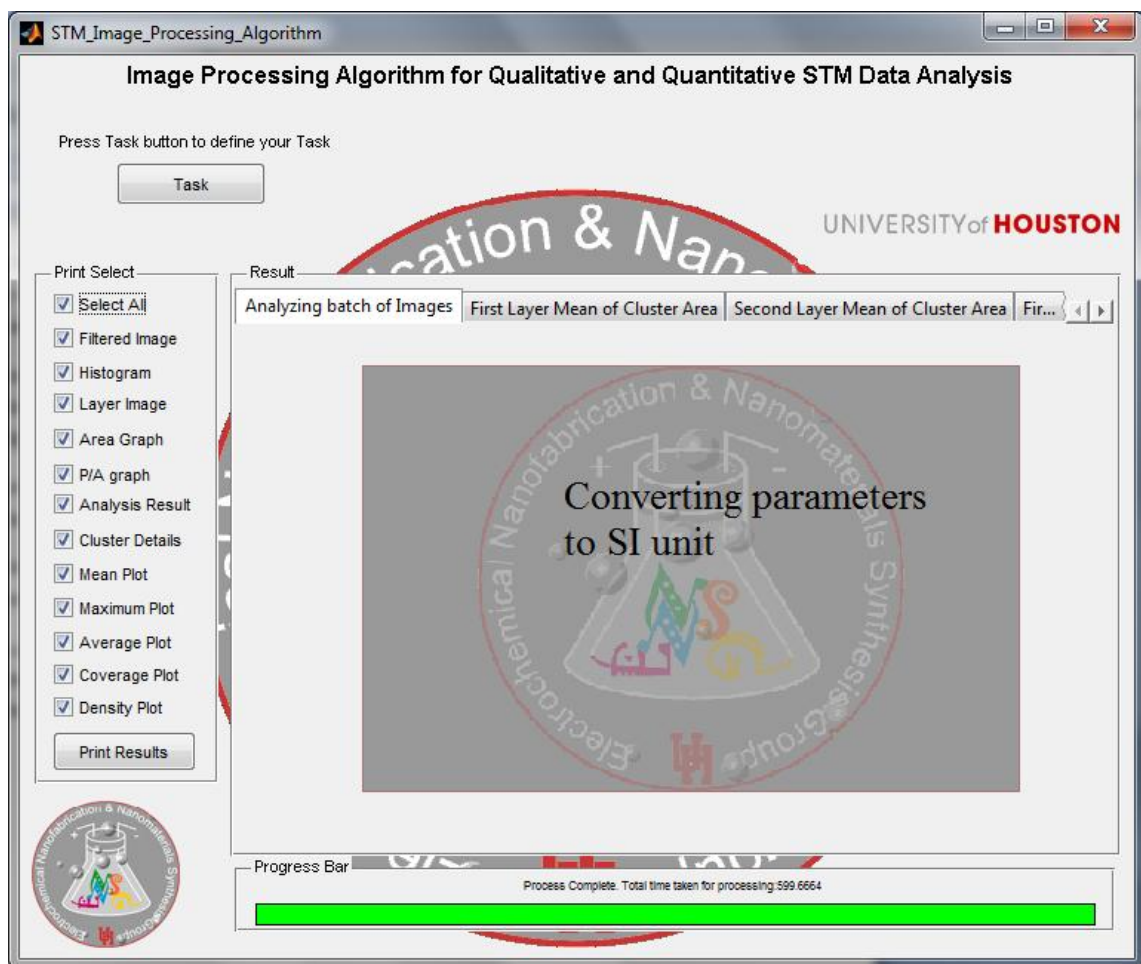


Figure 8.31 The GUI when 'Select All' check Box.

Once the 'Print Results' button is clicked the GUI creates a word file and asks the user to input a filename for the word file created along with a location to save the word file.

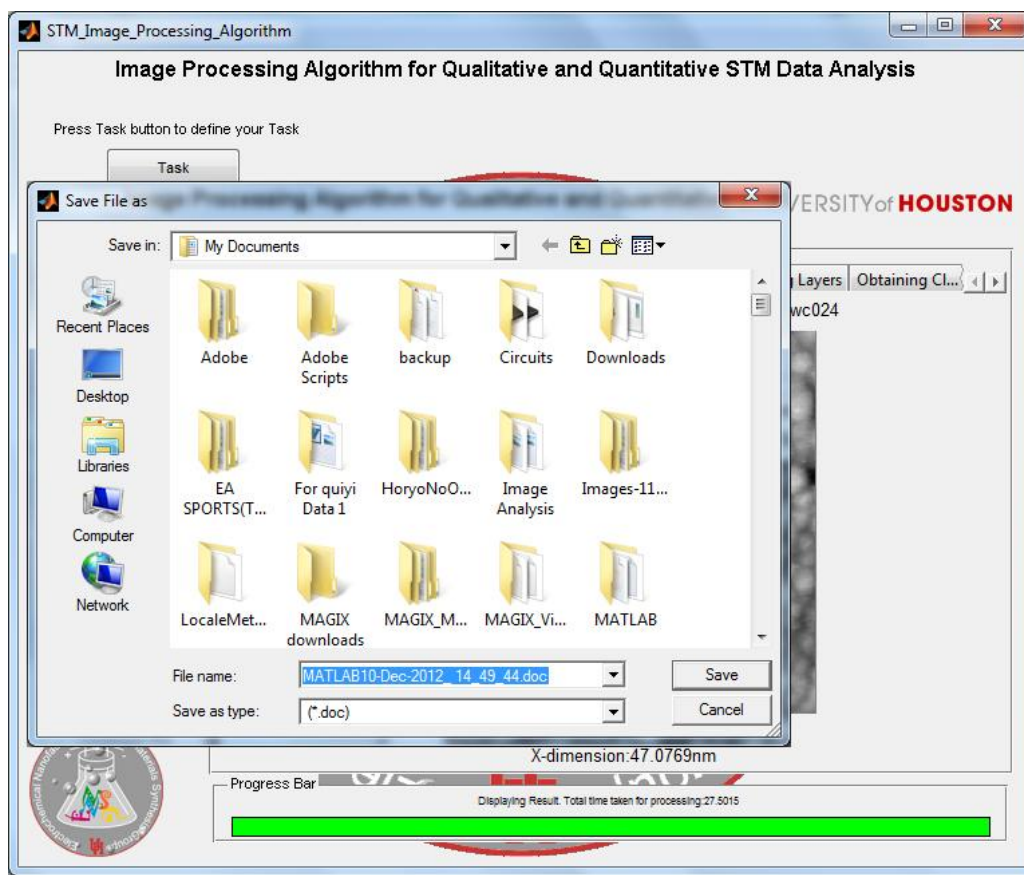


Figure 8.32 The GUI Screen after 'Print Select' button is pressed depicting the user dialog window to save word file generated by the GUI.

As shown in the Figure 8.32, the GUI provides a default file name to the word file and prints the data based on checkbox selected, the word document contains all the information pertaining to analysis performed on batch of images. To generate word file the GUI uses an inbuilt subroutine 'WriteToWordFromMatlab' by Andreas Karlsson [36]. The GUI prints a word file of the parameter checked inside 'Print Select.'

Once the word file is saved the GUI asks user if the word file is to be mailed. For this purpose the GUI uses 'questdlg' function in Matlab [36-37].

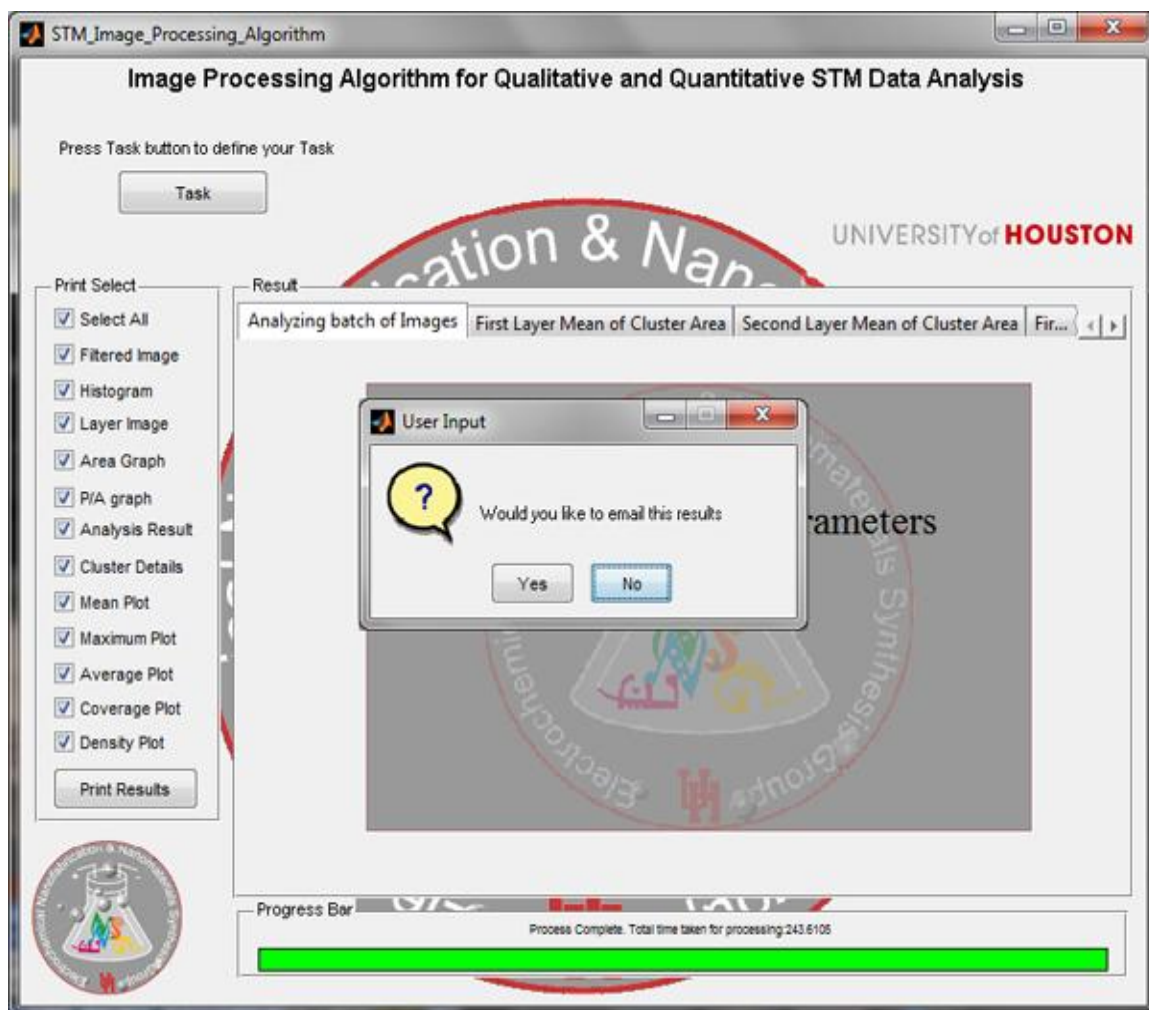


Figure 8.33 The GUI Screen after word file is saved a dialog box appears asking user if results should be emailed.

As shown in the Figure 8.33 if user clicks yes. The GUI uses 'inputdlg' function in matlab to create 'send email dialog box' as shown in the Figure 8.34 [38].

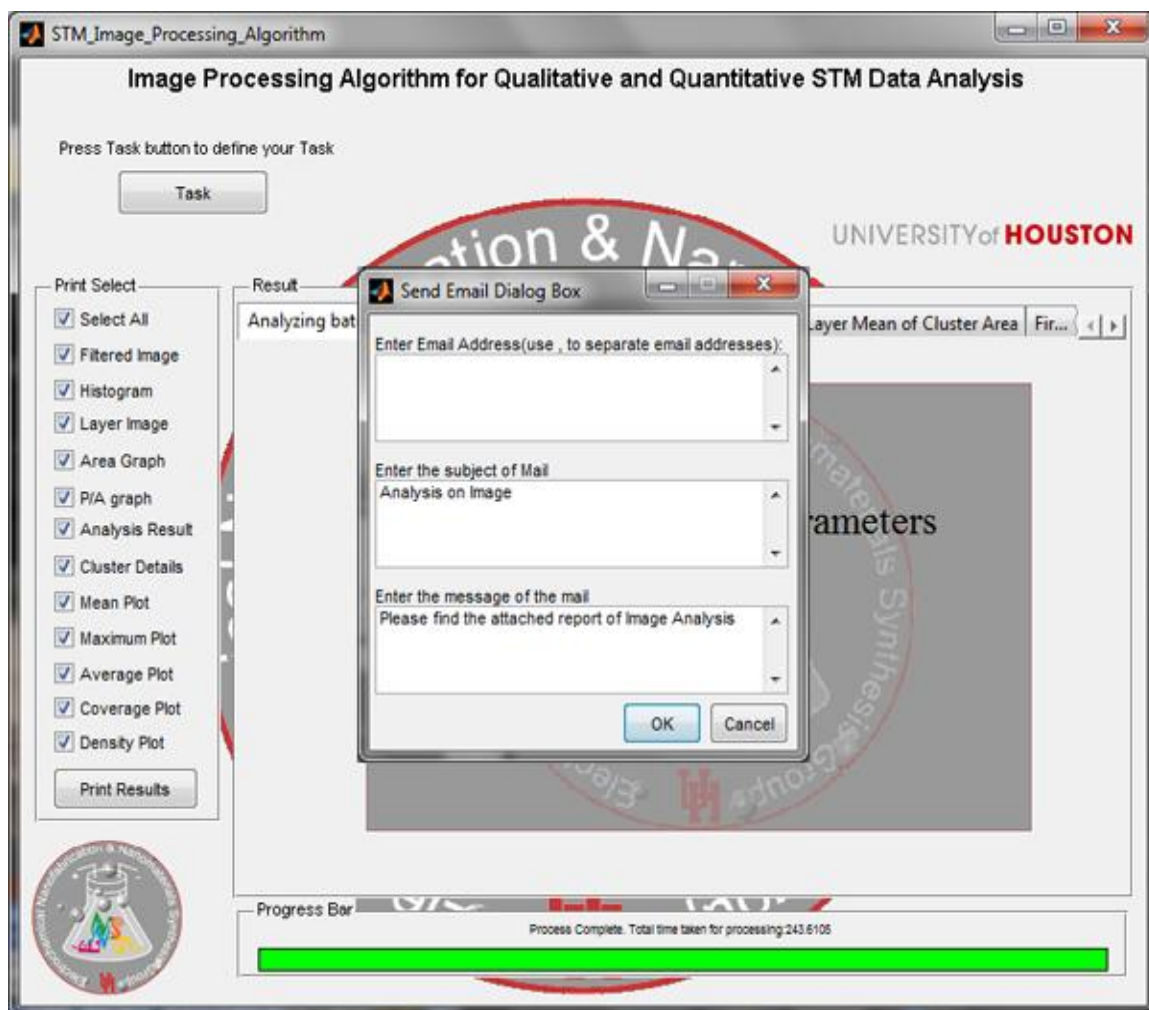


Figure 8.34 The GUI Screen 'Send Email Dialog Box.'

Figure 8.34 displays the 'Send Email Dialog Box.' It has three input textbox to enter email address, subject of the mail and message. The GUI provides an option of sending this mail to multiple email address. On clicking 'OK' button in the dialog box, The GUI uses 'sendmail' function in Matlab to send email with the result as an attachment [39].

### 8.2.2 Operation of the GUI on clicking 'Batch of Images'

'Batch of Images' is used to analyze a batch of image. The user will be asked to select the folder for batch processing. Images to be processed should be inside a sub folder as shown in the Figure 8.34.

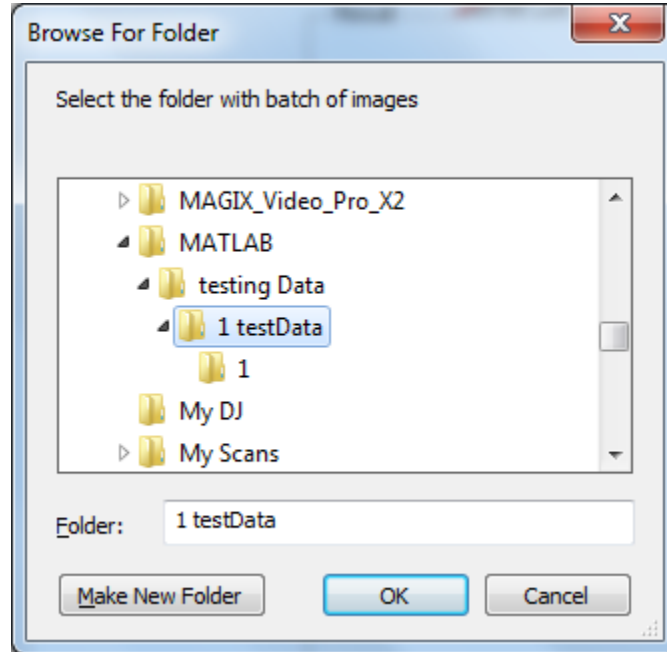


Figure 8.35 Windows explorer to select images for batch processing.

As shown in the Figure 8.35, the subfolder '1' contains the images for batch processing. In order to initiate the batch processing user needs to select '1 testData' from 'Browse For Folder' dialog box. The process flow for Batch of Images is similar to 'Group of single image taken at different potentials.' While processing a dialog box is used to ask user if file name represents the potential at which image was captured.

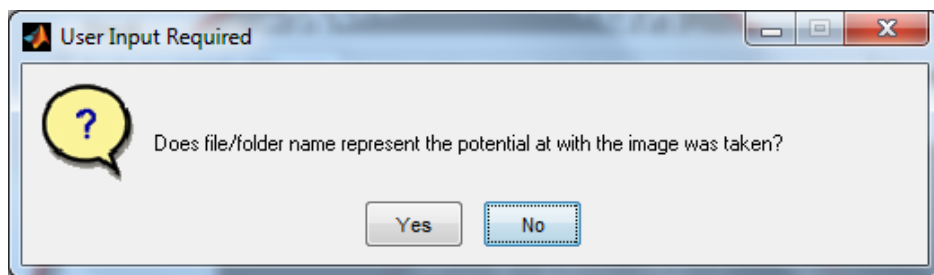


Figure 8.36 A dialog box asking user if the image name represents the potential.

After analysis, cluster parameters are extracted from these images and a cumulative plot of number of clusters v/s cluster area is obtained. Parameters of log normal distribution is obtained using the 'PlotSumLogNormal.' The 'Filtered Image' and 'Histogram' check box is disabled in the print select section. This is visible in the Figure 8.37.

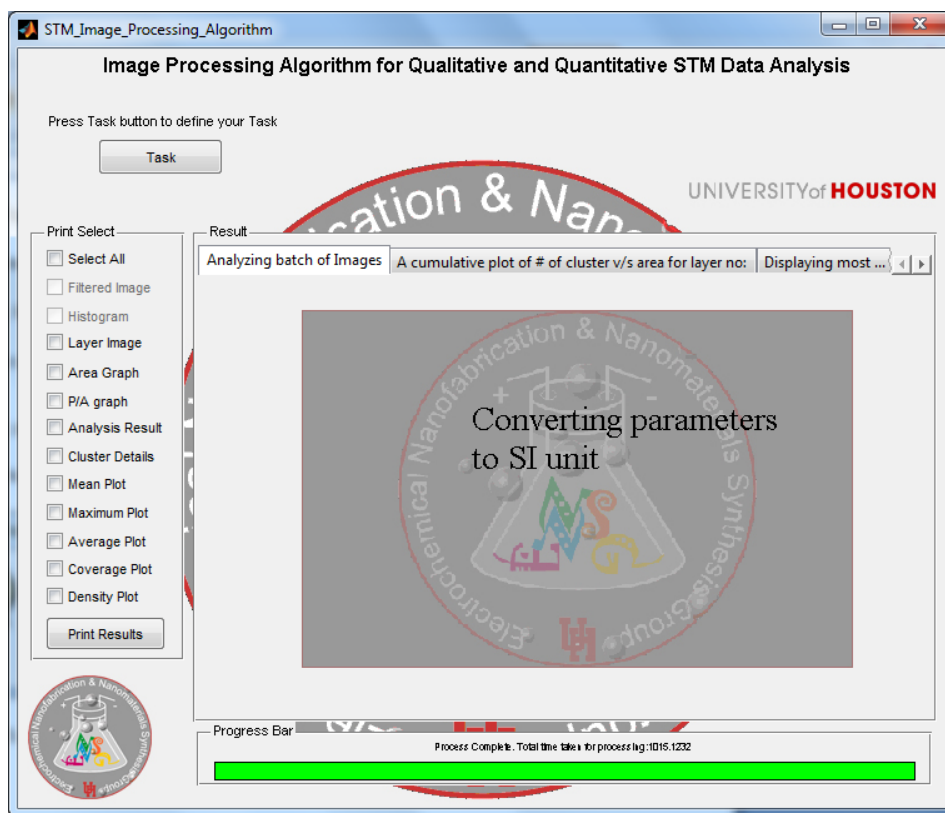


Figure 8.37 Status of the GUI after analyzing batch of images.



The GUI discussed in this chapter, uses the 'Image Processing Algorithm for Qualitative and Quantitative STM Data Analysis' to perform analysis on single image or on batch of images and displays the analysis in user friendly manner. It provides an option to save the result in form of word file. The user can choose parameters to print in word file and can mail it to an email address.

## CHAPTER 9 OBSERVATION AND RESULT

The GUI was used for quantification of morphological change during Pb underpotential deposition on Pt-modified Au<sub>(111)</sub> as a function of applied underpotential. To understand the conclusion drawn from the quantification of data, it is imperative to know the process of underpotential deposition.

### 9.1 Underpotential Deposition

The UPD process is an adsorption process, highly dependent on potential along with sensitivity and selectivity towards the surface of material. It also depends upon the demography of metal surface [40-41]. It is used as a decoration technique for surface characterization in corrosion studies [42], measurement of surface area [43] or characterization of thin film quality and surface roughness [44-45].

The UPD process is used to deposit monolayer on metal surface. Monolayer is layer of one atom thick deposition on metal surface. UPD monolayer can be used for enhancement of selectivity towards certain reactions [46]. It can also be used to develop monolayer catalyst for achieving ultimate specific activity with minimum loading of precious metals hence it plays a crucial step in the development of protocol for fuel cell catalyst synthesis. Further development of UPD based catalyst synthesis protocol requires that the studies of the UPD process be extended in the areas where surface is modified with sub monolayer of different noble metal.

## 9.2 Study of Pb UPD on Pt<sub>SML</sub>/Au<sub>(111)</sub> surfaces

The GUI, developed as a part of this thesis, was used to quantify parameters like areal density, cluster size etc., to understand Pb UPD on Au<sub>(111)</sub> modified by Pt. The two-dimensional Pt submonolayers were deposited by spontaneous Pt deposition on freshly annealed Au<sub>(111)</sub> surface [47-48]. The Pb UPD on Au<sub>(111)</sub> modified by Pt was obtained by using custom electrochemical cell where reference electrode is Pb wire of diameter 1mm, counter electrode was 0.5 mm diameter of Pt wire and Au<sub>(111)</sub> single crystal disk with the diameter of 10 mm as working electrode [49]. In order to understand the importance of data quantified using the GUI, it is imperative to understand Pb UPD on Au<sub>(111)</sub> and Pt UPD on Au<sub>(111)</sub> with the help of CV (cyclic voltammetry). CV (cyclic voltammetry) is a type of potentiodynamic electrochemical measurement used to study the electrochemical properties of an component in the solution. To obtain CV, the working electrode potential is ramped linearly verses time which ends after the potential reaches a particular point. Once it reaches a certain set of potential, the working electrode potential ramp is inverted [50].

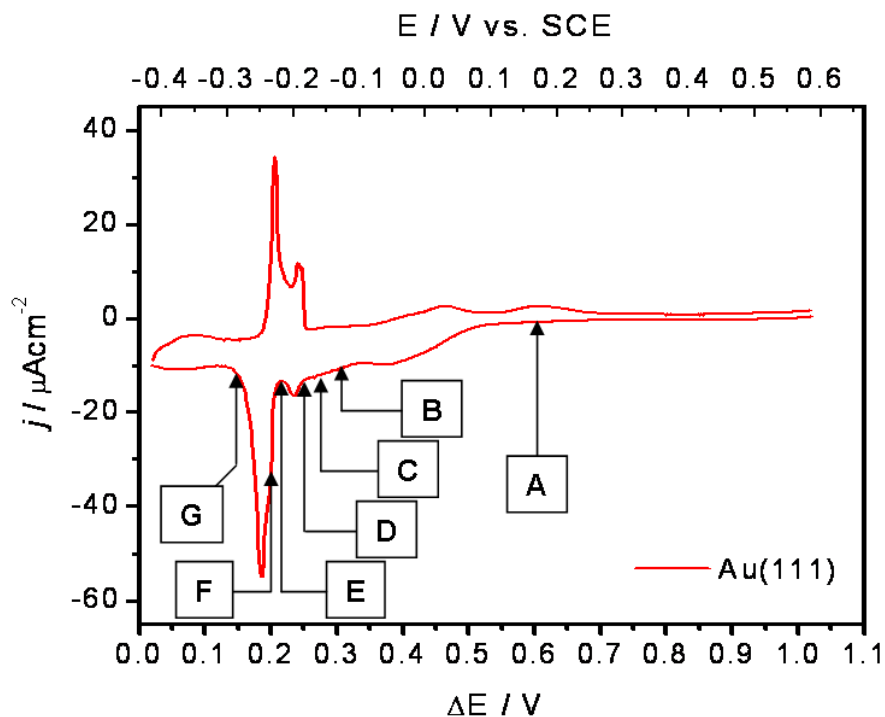


Figure 9.1 The cyclic voltammetry of Pb UPD on Au<sub>(111)</sub> surface in 10<sup>-2</sup> M Pb<sup>2+</sup> + 0.1 M HClO<sub>4</sub> with sweep rate 0.02 Vs<sup>-1</sup>. The underpotential, at which each STM image is recorded in Figure 9.2, is indicated in the graph.

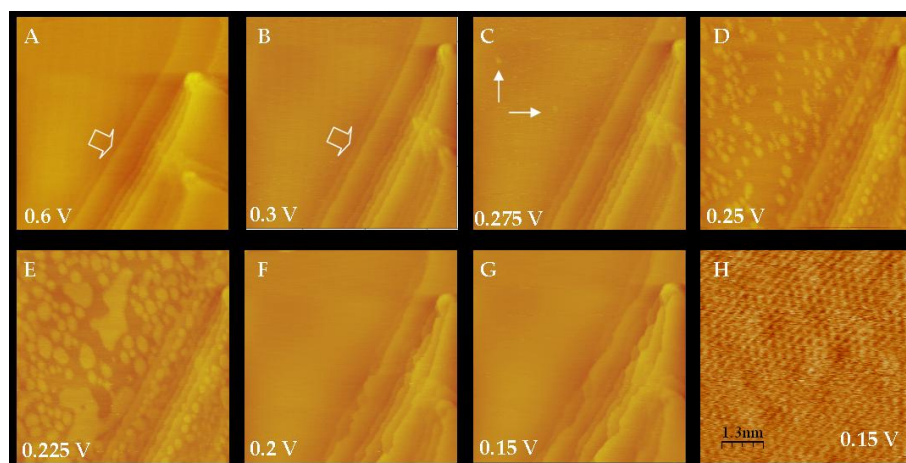


Figure 9.2 The 175 nm x 175 nm in situ STM images of Pb UPD on Au<sub>(111)</sub> surface. The underpotential of the Au<sub>(111)</sub> surface is indicated in the lower left corner of each image. Solution: 10<sup>-2</sup> M Pb<sup>2+</sup> + 0.1 M HClO<sub>4</sub>.

As shown in the Figure 9.1, a sharp peak could be observed at +0.18V underpotential. Several smaller and broader peak precedes this peak at higher

underpotential. They could be observed at 0.35V and 0.24V. The onset of UPD of Pb on Au<sub>(111)</sub> in perchloric acid electrolyte vary, depending on the quality of Au<sub>(111)</sub> surface and preparation routine. The general agreement is that UPD process starts with adsorption of Pb or Pb-OH species on the surface defects such as steps and dislocations. Au<sub>(111)</sub> at  $\Delta E = 0.6V$  could be observed in the Figure 9.2 A. At this potential no Pb UPD layer is present on Au surface.

Once the potential changes to  $\Delta E = 0.3V$ , a significant change of contrast in STM image is observed at steps which is associated with the Pb step decoration and the onset of Pb UPD on Au<sub>(111)</sub>. This is in conjunction with the broader peak at  $\Delta E = 0.375V$  observed in CV (Figure 9.1) of Pb UPD on Au<sub>(111)</sub> surface in  $10^{-2} M Pb^{2+} + 0.1 M HClO_4$ . At  $\Delta E = 0.275V$ , first Pb UPD nuclei at the Au<sub>(111)</sub> terraces. The nucleation process advances further as the underpotential is changed to  $\Delta E = 0.250V$ . At this potential, the significant portion of the Au<sub>(111)</sub> terrace is covered with Pb UPD nuclei in the Figure 9.2 E. These Pb UPD began to coalesce and an incomplete but continuous layer can be seen. This is in conjunction with the broad shoulder and cathodic peak obtained at  $\Delta E \approx 0.235V$  in the Figure 9.1. As the potential is further reduced to  $\Delta E = 0.2V$ , complete change on Au<sub>(111)</sub> surface could be observed. This is in agreement with the peak observed at  $\Delta E = 0.18V$  in the Figure 9.1. No change in morphology is observed if the potential is further reduced to  $\Delta E = 0.15V$  and it could be seen in the Figure 9.2 G. From the peak at  $\Delta E = 0.18V$  in the Figure 9.1, it could be concluded that most of the current charge associated with main Pb UPD peak is related to densification of the UPD layer which initially nucleates and grows as low-density phase [41]. From the STM image taken at  $\Delta E = 0.6V$  (Figure 9.2 A) and the

images at  $\Delta E = 0.15\text{V}$  (Figure 9.2 G) the similarities in demographic topography of the surface could be observed. Also from the Figure 9.2 H, taken at  $\Delta E = 0.1\text{V}$ , the presence of moiré pattern indicates the compression in Pb-UPD layer. Thus it can be concluded that a fully dense Pb UPD phase forms having an incommensurate hexagonal structure and  $\approx 7\%$  smaller inter-atomic distance than bulk Pb [51].

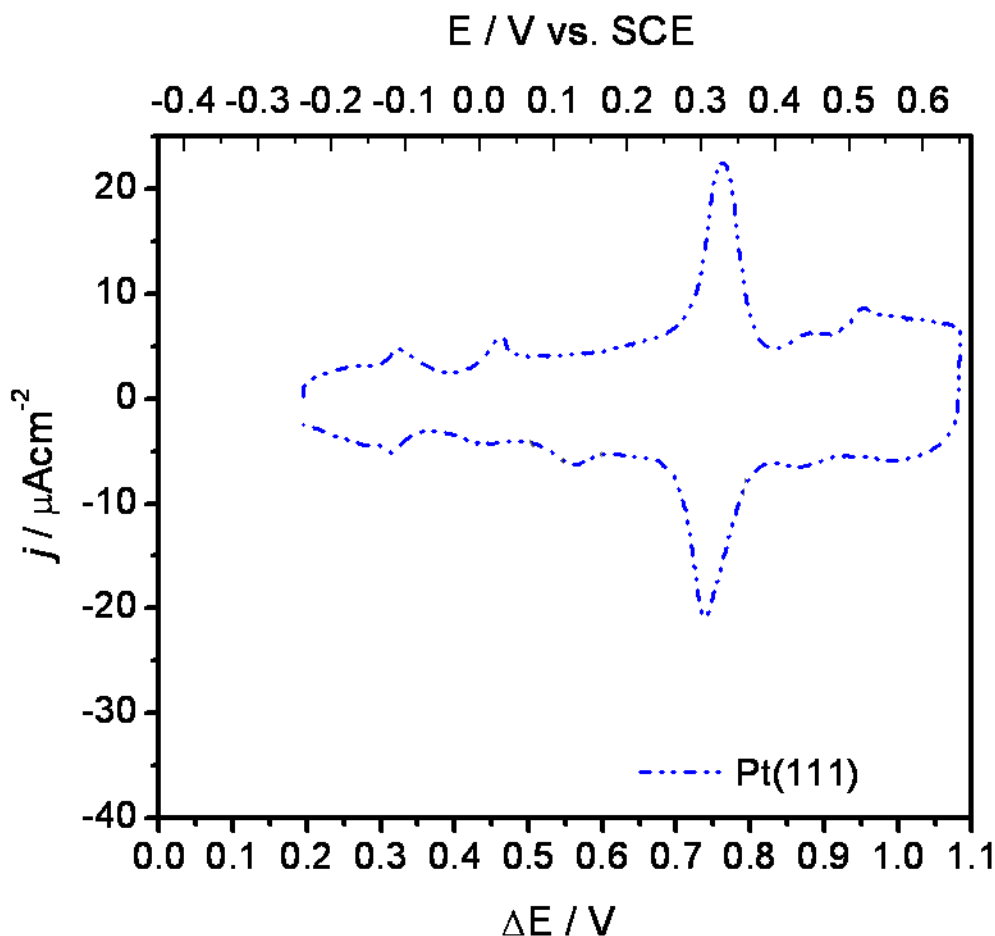


Figure 9.3 The cyclic voltammetry of Pb UPD on  $\text{Pt}_{(111)}$  surfaces. Solution:  $10^{-2}\text{ M Pb}^{2+} + 0.1\text{ M HClO}_4$ , sweep rate  $0.02\text{ Vs}^{-1}$ .

As observed in the Figure 9.3. The main Pb UPD peak occurs approximately at  $\Delta E \approx 0.75\text{V}$ . It is preceded by two smaller and broader peaks occurring at higher

underpotentials related to Pt-OH reduction and probable Pb-OH adsorption as a prelude to the Pb UPD process [52]. The smaller deposition peaks occurring at lower potential are associated with gradual densification of the Pb UPD layer and formation of different phases. The  $\sqrt{3} \times \sqrt{3}$  has been identified as the densest one forming at 0.3V underpotential [52].

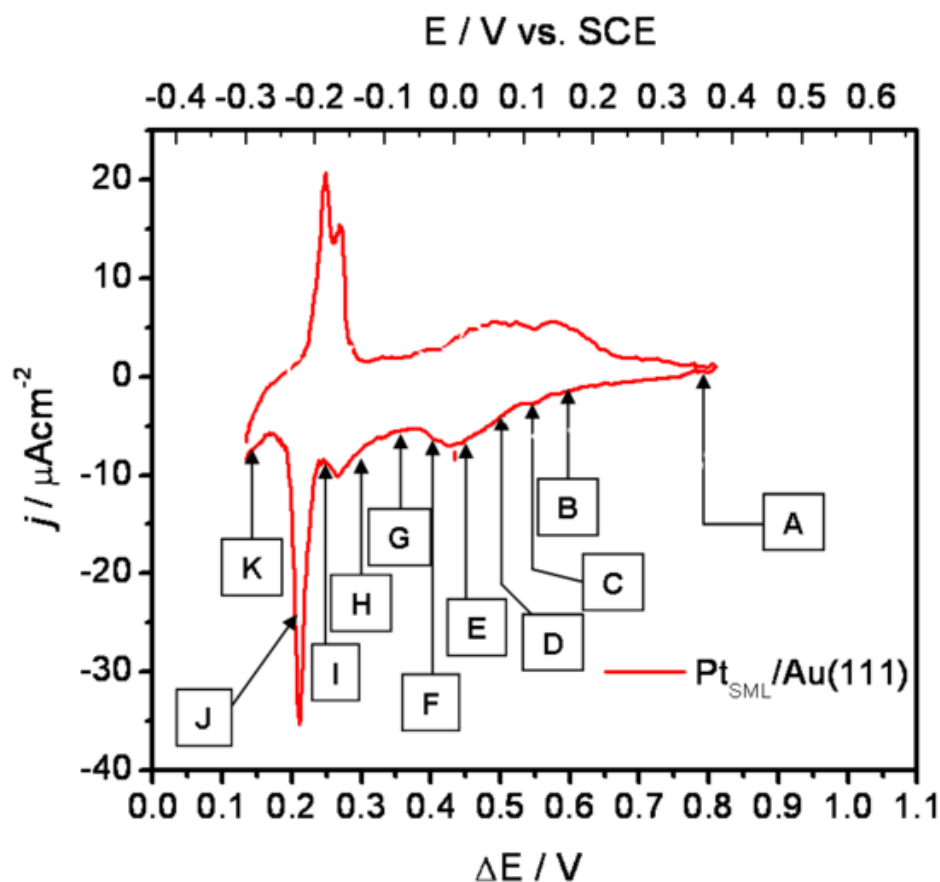


Figure 9.4 The cyclic voltammetry of Pb UPD on  $\text{Pt}_{\text{SML}}/\text{Au}(111)$  surfaces. Solution:  $10^{-2} \text{ M Pb}^{2+} + 0.1 \text{ M HClO}_4$ , sweep rate  $0.02 \text{ Vs}^{-1}$ . The underpotentials at which each STM image is recorded in the Figure 9.6, is indicated in the graph.

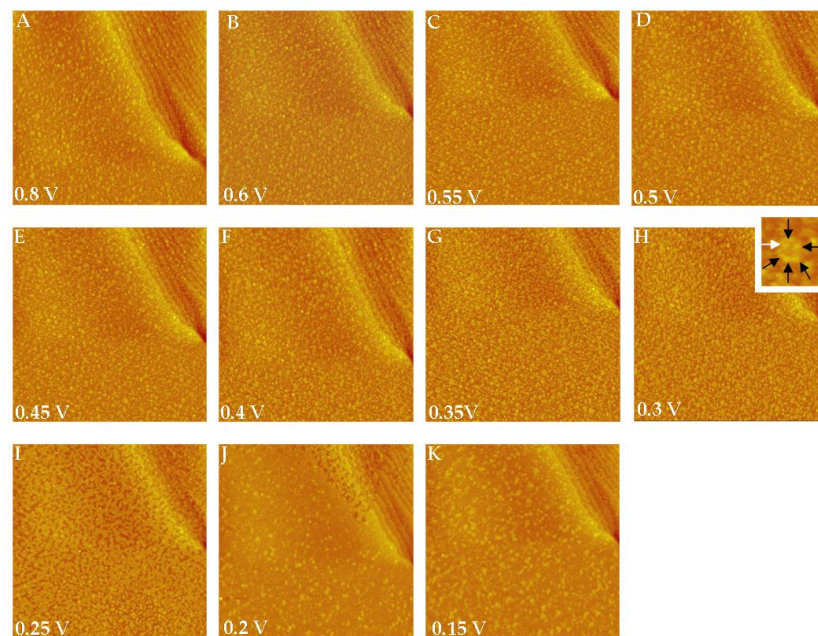


Figure 9.5 The 225 nm x 225 nm insitu STM images of Pb UPD on  $\text{Pt}_{\text{SML}}/\text{Au}_{(111)}$  surface. The underpotential of the surface is indicated in the lower left corner of each image. Solution:  $10^{-2}$  M  $\text{Pb}^{2+}$  + 0.1 M  $\text{HClO}_4$ .

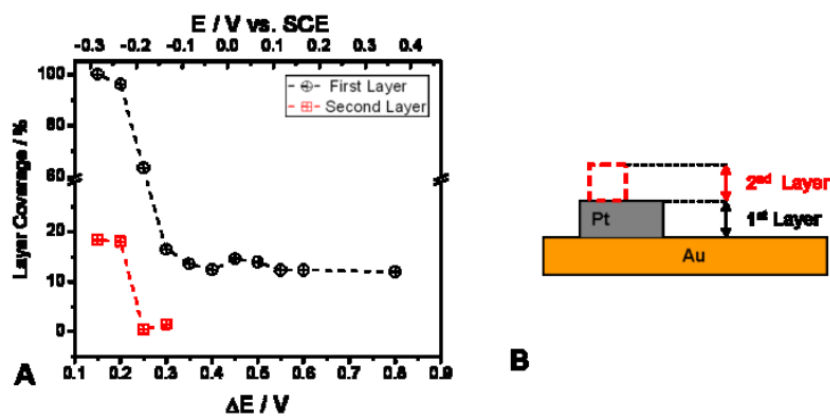


Figure 9.6 (A) The coverage of 1st and 2nd layer extracted from STM images in the Figure 9.5 A-K as a function of underpotential. (B) The schematics of 1st and 2nd layer in relation to the morphology of  $\text{Pt}_{\text{SML}}/\text{Au}_{(111)}$  surface. The data in (A) extracted from STM images in the Figure 9.5 using DIP algorithm.



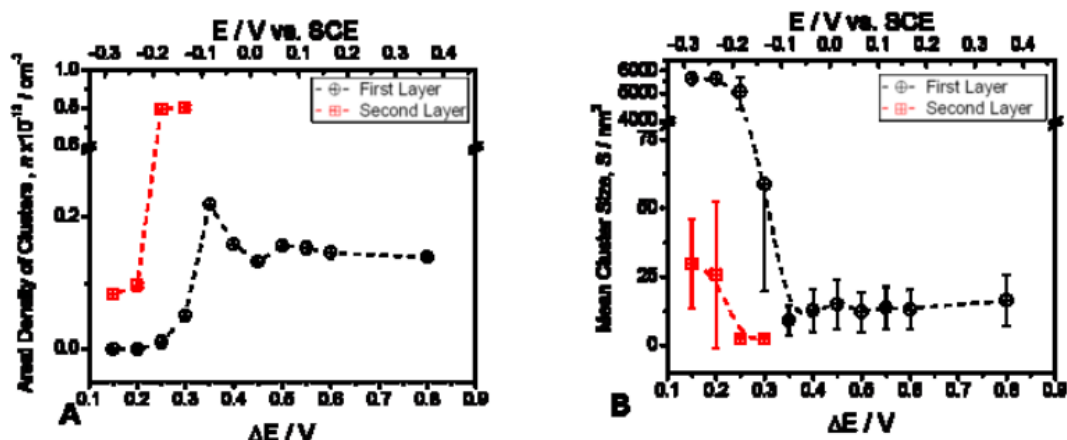


Figure 9.7: (A) The areal density of the clusters,  $n$ , in 1st and 2nd layer as a function of underpotential, (B) The mean of the nanocluster population,  $S$ , in 1st and 2nd layer as a function of the surface underpotential. All data extracted from STM images in the Figure 9.5 using DIP algorithm.

From the Figure 9.4, it can be observed that CV for Pb UPD on  $\text{Pt}_{\text{SML}}/\text{Au}_{(111)}$  surfaces in a solution of  $10^{-2} \text{ M Pb}^{2+} + 0.1 \text{ M HClO}_4$  has main Pb UPD peak at  $\Delta E \approx 0.215 \text{ V}$  and it is very close to the main Pb UPD peak for Pb UPD on  $\text{Au}_{(111)}$  in the Figure 9.1. The broad cathodic peak is obtained at  $\Delta E = 0.440 \text{ V}$  and smaller one at  $\Delta E = 0.260 \text{ V}$ . They are around the same potential as observed in CV for Pb UPD on  $\text{Au}_{(111)}$  in the Figure 9.1.

The Figure 9.4 shows the cyclic voltammetry of Pb UPD on  $\text{Pt}_{\text{SML}}/\text{Au}_{(111)}$  surfaces in  $10^{-2} \text{ M Pb}^{2+} + 0.1 \text{ M HClO}_4$  solution. It consists of tags that indicates the underpotential at which STM images were taken. As per the graphs plotted from quantitative data obtained from the GUI, at  $\Delta E = 0.8 \text{ V}$  i.e., at the beginning of underpotential deposition. The population of 2D Pt nanoclusters on the surface of  $\text{Pt}_{\text{SML}}/\text{Au}_{(111)}$  has a mean size of  $16 \pm 4 \text{ nm}^2$  and Pt coverage of  $0.14 \times 10^{13} \text{ cm}^{-2}$  which means that the average distance between the centers of neighboring nanoclusters is  $\langle l_{\text{pt}} \rangle \approx 8.5 \text{ nm}$ . The perimeter/area ratio for deposited Pt nanoclusters shows that great majority of

them have compact shape. The areal density of Pt on Au<sub>(111)</sub> is 12%, this explains the difference between CV observed in the Figure 9.4 and CV observed for Pb UPD on Pt<sub>(111)</sub> surfaces in 10<sup>-2</sup> M Pb<sup>2+</sup> + 0.1 M HClO<sub>4</sub> solution in the Figure 9.3. Also it should be observed that no Pb is present on the top of Pt nanoclusters and on top of Au<sub>(111)</sub> surface at  $\Delta E = 0.8V$ .

The average height of Pt nanoclusters is 0.33nm, which is slightly higher than expected monolayer high Pt nanocluster. This might be the indication that absorbed OH layer is present on top of the Pt. nanocluster at this underpotential. The small size and high curvature of 2D Pt. nanoclusters promote their reactivity.

As the underpotential is reduced further to  $\Delta E = 0.6V$ , no morphological change is observed in the Figure 9.5 B. This is also evident from data of areal density, mean cluster size and layer coverage. There is no indication of appreciable change in height or size of Pt nanoclusters. If the Figure 9.3 is observed than around  $\Delta E = 0.6V$ , CV shows main peak which indicates Pb UPD on Pt however no such peak is observed in the CV of Pb UPD on Pt<sub>SML</sub>/Au<sub>(111)</sub> surfaces the Figure 9.4. The Figure 9.5 B also shows no significant change in contrast in image. This could be due to presence of Pt-OH layer or it could be due to ligand effect of Au Substrate in modifying the electrosorption properties of Pt. nanodeposit [7]. Further reduction of underpotential to  $\Delta E = 0.55V$  and  $\Delta E = 0.5V$  also does not cause any visible changes in morphology of Pt<sub>SML</sub>/Au<sub>(111)</sub> surface. However at  $\Delta E = 0.45V$ , the GUI results shows decrease in areal density and layer coverage followed by increase in same parameters at  $\Delta E = 0.4V$ . The CV data in the

Figure 9.4 shows a broad cathodic peak at  $\Delta E = 0.440\text{V}$  underpotential. In electrochemical sense, the cathodic peak/current indicates the reduction process and it could be associated with reduction of Pt-OH phase to clean Pt nanocluster surface or it could attributed to reduction of  $\text{Pb}^{2+}$  ions to Pb adatoms. According to the CV data for Pb UPD on  $\text{Au}_{(111)}$  decoration of Au surface defects by Pb adatoms could start for any  $\Delta E < 0.5\text{ V}$  we should expect the same to occur at defect sites present on portion of the Au surface free from Pt nanoclusters. The charge associated with the cathodic peak centered at  $\Delta E = 0.44\text{V}$  for  $\text{Pt}_{\text{SML}}/\text{Au}_{(111)}$  is larger than the corresponding peak observed in CV for Pb UPD on  $\text{Au}_{(111)}$ . This means an additional reduction process takes place in parallel to the onset of Pb UPD process. Also the relative height of Pt monolayers on  $\text{Au}_{(111)}$  reduces to  $0.27\text{nm}$  which indicates that a simultaneous reduction of the Pt-OH phase along with the decoration of Au defects with Pb UPD adatoms.

Further decrease of underpotential below  $\Delta E = 0.4\text{V}$  produces significant change is morphology of  $\text{Pt}_{\text{SML}}/\text{Au}_{(111)}$  surface. At  $\Delta E = 0.35\text{V}$ , the areal density of the nanoclusters in 1st layer increases by 30% and simultaneous decrease in mean size of the nanocluster population can be observed in the Figure 9.7 B. These morphological changes indicates the beginning of Pb UPD on free  $\text{Au}_{(111)}$  terrace. At  $\Delta E = 0.3\text{ V}$  and  $\Delta E = 0.25\text{V}$  the growth of Pb UPD phase on Au surface with  $\approx 20\%$  and  $40\%$  increase in the first layer coverage could be seen and there is increase of 500 times in the mean size of the nanoclusters population in the first layer. At the same potential the nucleation of the second layer is observed and the areal density in the second layer is  $\approx 7\%$  larger than the initial density of Pt nanoclusters on  $\text{Au}_{(111)}$  since several Pb nuclei form per one Pt

nanocluster. The mean size of Pb nanoclusters nucleating in the second layer is  $\approx 2 \text{ nm}^2$  on pre-existing  $20 \text{ nm}^2$  large Pt nanocluster. Thus the cathodic peak at  $\Delta E = 0.26 \text{ V}$  in CV of Pb UPD  $\text{Pt}_{\text{SML}}/\text{Au}_{(111)}$  as shown in the Figure 9.4 is associated mainly with the nucleation and growth of Pb UPD monolayer on top of the Pt nanocluster and their lateral decoration with Pb UPD adatoms in the first layer.

The reduction of underpotential to  $\Delta E = 0.2 \text{ V}$  and  $\Delta E = 0.15 \text{ V}$  in morphological changes on  $\text{Pt}_{\text{SML}}/\text{Au}_{(111)}$  and it is related to completion of Pb-UPD process on Pt-free Au surface and on top of existing Pt nanoclusters. The coverage of first layer increases to 100% while the nanocluster density drops to 1 indicating morphology of a full Pb UPD layer filling the space on Au terraces in between the pre-existing Pt nanoclusters. In the second layer areal density is 40% less than the initial areal density of Pt nanoclusters on the starting  $\text{Pt}_{\text{SML}}/\text{Au}_{(111)}$  surface ( $0.14 \times 10^{13} \text{ cm}^{-2}$ ). The mean size of nanocluster in the second layer is around  $30 \pm 7 \text{ nm}^2$  and it is approximately two times as large the initial population of Pt nanoclusters on  $\text{Pt}_{\text{SML}}/\text{Au}_{(111)}$  surface and the second layer coverage is approximately 50% larger than that observed for the initial coverage of the Pt sub-monolayer in the first layer as shown in the Figure 9.5 A. The smaller number but larger size of Pb UPD on the top of the pre-existing Pt nanoclusters indicates they replicate a similar morphology. This is due to difference in size of Pt i.e.,  $0.27 \text{ nm}$  and Pb atoms i.e.,  $0.36 \text{ nm}$ . The second layer coverage is 46% larger than Pt monocluster layer on  $\text{Au}_{(111)}$  because deposition of Pb monolayers in second layer follows  $\sqrt{3} \times 3$  packing density and due to the merging of two or more Pb monolayers sitting on the top of two or more smaller Pt nanocluster. This assumption is assumed since platinum nanocluster

has very small nearest neighbor center to center spacing,  $\langle l_{pt} \rangle = 8.5 \text{ nm}$ . Most of Pt. clusters are compact in size hence it could be assumed that these cluster have disk like shape and their equivalent diameter is same as mean linear dimension ( $d_{Pt-mean} = \sqrt{\frac{4}{\pi} S_{Pt-mean}} = 4.5 \text{ nm}$ ). Thus if Pb UPD cluster on top of Pt one has 50% larger area and  $\approx 23\%$  larger diameter then local variation in the areal density and nearest neighbor distance within the Pt nanocluster population can lead to scenario where the corresponding Pb UPD clusters forming on top of Pt are merged due to their bigger size. This case is possible when center to center distance between neighboring Pt nanoclusters diameter ( $l_{pt} = \sqrt{n_{pt}^{-1}}$ ), is less than 1.2 times the sum of the neighboring Pt nanoclusters diameters ( $l_{pt} < 1.2 \times \sum_1^n d_{pt,i}$ ). If this condition is fulfilled Pb nanoclusters nucleate into a single Pb UPD nanocluster which does not replicate the exact morphology of the underlying Pt. deposit.

Thus, with the help of quantitative data obtained from the GUI, it was concluded that during Pb UPD on  $Pt_{SML}/Au_{(111)}$  surfaces in  $10^{-2} \text{ M Pb}^{2+} + 0.1 \text{ M HClO}_4$  solution, Pb underpotential deposition process is initiated by deposition of Pb on Au steps and other surface deformation. As the process proceeds, nucleation of Pb monolayer takes place on the Au terraces till a complete layer of Pb is obtained over Au. During the nucleation of Pb layer on Au terraces, Pb UPD monolayer also start to nucleate on the top of pre-existing Pt nanoclusters. The process completes by formation of compact Pb-nanoclusters on the top of the pre-existing Pt nanoclusters. The morphology of

underpotentially deposited Pb monolayer on Pt modified Au<sub>(111)</sub> is similar to the starting surface in terms of areal density of nanoclusters, their size and shape.

## CHAPTER 10 FUTURE SCOPE

The GUI (Graphical User Interface) for 'Image Processing Algorithm for Qualitative and Quantitative STM Data Analysis' is used for quantification of metallic surface morphology. It is designed for the user with knowledge of underpotential deposition to study UPD where substrate is a metallic surface with submonolayer of different noble metal. The GUI measures parameters like cluster area, perimeter by area, layer coverage, and layer density for a layer of cluster in an image.

The image provided to the image processing algorithm as an input should be free of any drift. The STM image may appear distorted due to thermal deformation and due to the creep of piezomanipulators applied. Such distortion is termed as drift. Research shows an automatic drift elimination technique could be applied to such image. In future an algorithm could be embedded in the GUI for automatic rectification of STM image drift [53].

The image processing algorithm deals with measuring two dimensional parameters for a layer of cluster. However, the STM image are by default range information image which means every image data points explicitly represent scene surface geometry as sampled points [54]. It could be used to calculate the height of cluster layers. This can help in understanding the mechanism of layer formation on substrate. In future the GUI is expected to measure the approximate height of a layer of cluster in an image.

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