NE 201: Micro and Nano Characterization Methods

IDENTIFYING DIFFERENT MATERIALS IN A SPECIMEN USING LFM AND KPFM

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Abstract

Atomic force microscopy (AFM) is a powerful technique used to study samples at nanoscale. It is generally used to determine sample topography. Besides height information, availability of various modes like Lateral force microscopy (LFM) and Kelvin probe force microscopy (KPFM) helps us to know about sample's surface properties. LFM provides a way in extracting information regarding frictional properties whereas KPFM offers a method of distinguishing materials based on workfunction.

In the present work, we have made an attempt to identify surface compositional differences of various samples like Graphene on SiO_2, Graphene on Cu, Germanium and Gold, HOPG, Al_2O_3 using LFM and KPFM techniques.

Acknowledgement

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Contents

1. Introduction

Atomic force microscopy (AFM) is a technique for imaging the surface structure of a sample with unprecedented resolution and accuracy. It belongs to a larger family of instruments termed as scanning probe microscopes (SPMs). The common factor in all SPM techniques is the use of very sharp probe which is scanned across the surface of interest. The interactions between the probe and the sample is used to produce a very high resolution image of the sample, potentially to the sub-nanometre scale, depending upon the technique and sharpness of probe tip[1]. An AFM physically feels the sample surface with a sharp probe and builds a map of height of sample's surface. AFM can image all materials – hard or soft, synthetic or natural, conductive or non-conductive and transparent or opaque. In addition to imaging the topography of sample's surface, an AFM can also give information such as adhesion forces, friction forces, workfunction, surface potential, stiffness of the surface etc. There are various modes of operation that are available to extract different information related to the surface. In the present work, different materials on a sample are differentiated using two modes of AFM namely, Lateral Force Microscopy (LFM) and Kelvin Probe Force Microscopy (KPFM).

1.1. Lateral Force Microscopy

Lateral Force Microscopy (LFM) is an AFM mode where horizontal deflection of cantilever is measured. This lateral deflection is due to force applied on the cantilever as it moves horizontally across the sample surface. The magnitude of lateral deflection is determined by frictional coefficient, topography of sample surface, direction of cantilever movement and the lateral spring constant of the cantilever. The power of LFM lies in its ability to identify different components in a sample based on frictional characteristics even while the surface is relatively flat. This helps in gaining additional information about the sample.

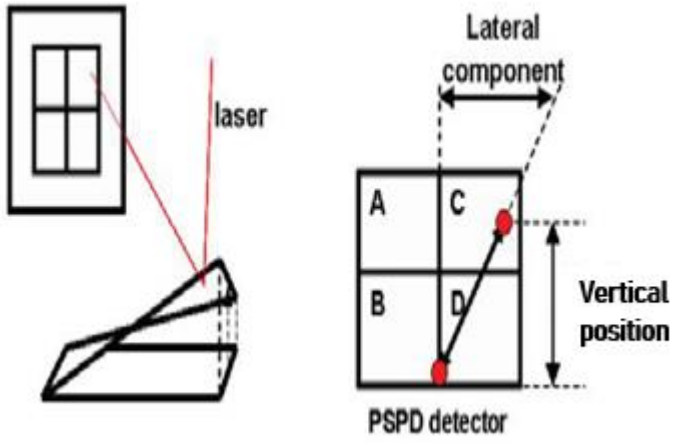


Figure 1.1 : Schematic representation of LFM operation

In LFM operation, the cantilever motion in both and vertical and horizontal direction is tracked via a position sensitive photo detector (PSPD) that consists of four domains (a quad-cell) as shown in figure 1.1[2]. The topographical information is related to difference between upper (A+C) and lower (B+D) cells while, frictional information of the surface is obtained from the difference between right (A+B) and left (C+D) cells.

1.2. Kelvin Probe Force Microscopy

Kelvin probe force microscopy (KPFM) is a technique that is capable of imaging surface potential of a sample. It measures the local contact potential difference between a conducting AFM tip and the sample, thereby mapping the workfunction or surface potential of the sample. The contact potential difference between tip and sample is given by $V_{CPD} = \frac{\varphi_{tip} - \varphi_{sample}}{e}$, where φ_{tip} and φ_{sample} are the workfunctions of tip and sample respectively and e is electronic charge. When AFM tip is brought close to the sample surface, an electrical force is generated between tip and sample surface due to difference in their Fermi energy levels. Figure 1.2(a) shows the electronic energy levels of tip and sample surface when separated by distance d and not electrically connected. The Fermi levels align through the flow of electrons and the system reaches an equilibrium state. Due to the flow of electrons, the tip and the sample surface gets charged and a contact potential difference develops which creates an electrical force on the contact area as shown in figure 1.2(b). This force can be nullified as depicted in figure 1.2(c) by applying an external bias V_{DC} with same magnitude as V_{CPD} but in opposite direction. The amount of external bias applied to nullify the electrical force due to contact potential difference gives the difference in workfunctions of tip and sample. By knowing the workfunction of tip, the workfunction of sample can be determined. KPFM is the best technique, at present, to characterize the electrical properties of nanostructures.

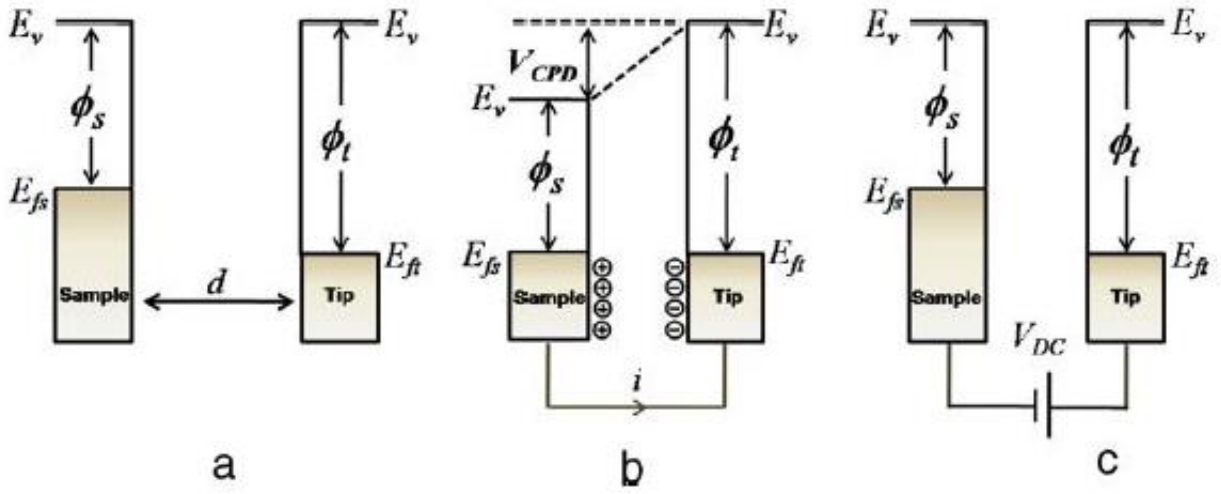


Figure 1.2 : Electronic energy levels of sample and tip when (a) tip and sample are separated by distance d and no electrical contact; (b) tip and sample are in electrical contact; (c) external bias (V_{dc}) is applied between tip and sample (E_v is vacuum energy level, E_{fs} and E_{ft} are Fermi energy levels of sample and tip respectively)[3].

2. Experimental details

Lateral Force Microscopy:

For LFM measurements, contact mode images were taken with scan angle perpendicular to AFM cantilever, so that frictional forces between tip and the sample causes lateral twist of the cantilever which is measured as lateral deflection. The map obtained by taking difference of lateral deflection image in trace and retrace directions gives a rough measure of friction coefficient of the sample. LFM studies were done on various samples to determine surface composition on the specimen based on their surface friction.

Kelvin Probe Force Microscopy:

KPFM study involved scanning of sample using Pt-Ir coated silicon cantilevers and the image processing was done using XEI software. The contact potential difference is calculated using the relation

$$eV_{CPD} = \varphi_t - \varphi_s \qquad 1$$

where $\varphi_t$and φ_s are the workfunctions of tip and sample respectively [4]. The sample is electrically grounded using silver paste and tip bias is applied. The contact potential difference between sample and tip is obtained during KPFM measurements. To get the absolute values of workfunction, calibration of AFM tip is necessary. The calibration is generally done using a standard sample of known workfunction like HOPG whose workfunction value is 4.47 eV [5]. By knowing the workfunction of the tip, workfunction of sample can be calculated from the measured contact potential difference value using equation 1.

3. Results and Discussions

3.1. Graphene on Silicon dioxide

The best quality graphene, in terms of structural integrity, is obtained by mechanical cleavage of highly oriented pyrolytic graphite (HOPG). First, HOPG is mechanically cleaved using scotch tape. Then the flakes of exfoliated graphene on scotch tape are transferred onto SiO_2 substrate. Mechanical and electrical properties vary with the thickness of graphene flakes. The image of area 19 µm x 19 µm is obtained by scanning the sample using a platinum coated cantilever of spring constant 2 N/m at a scan rate of 0.6 Hz.

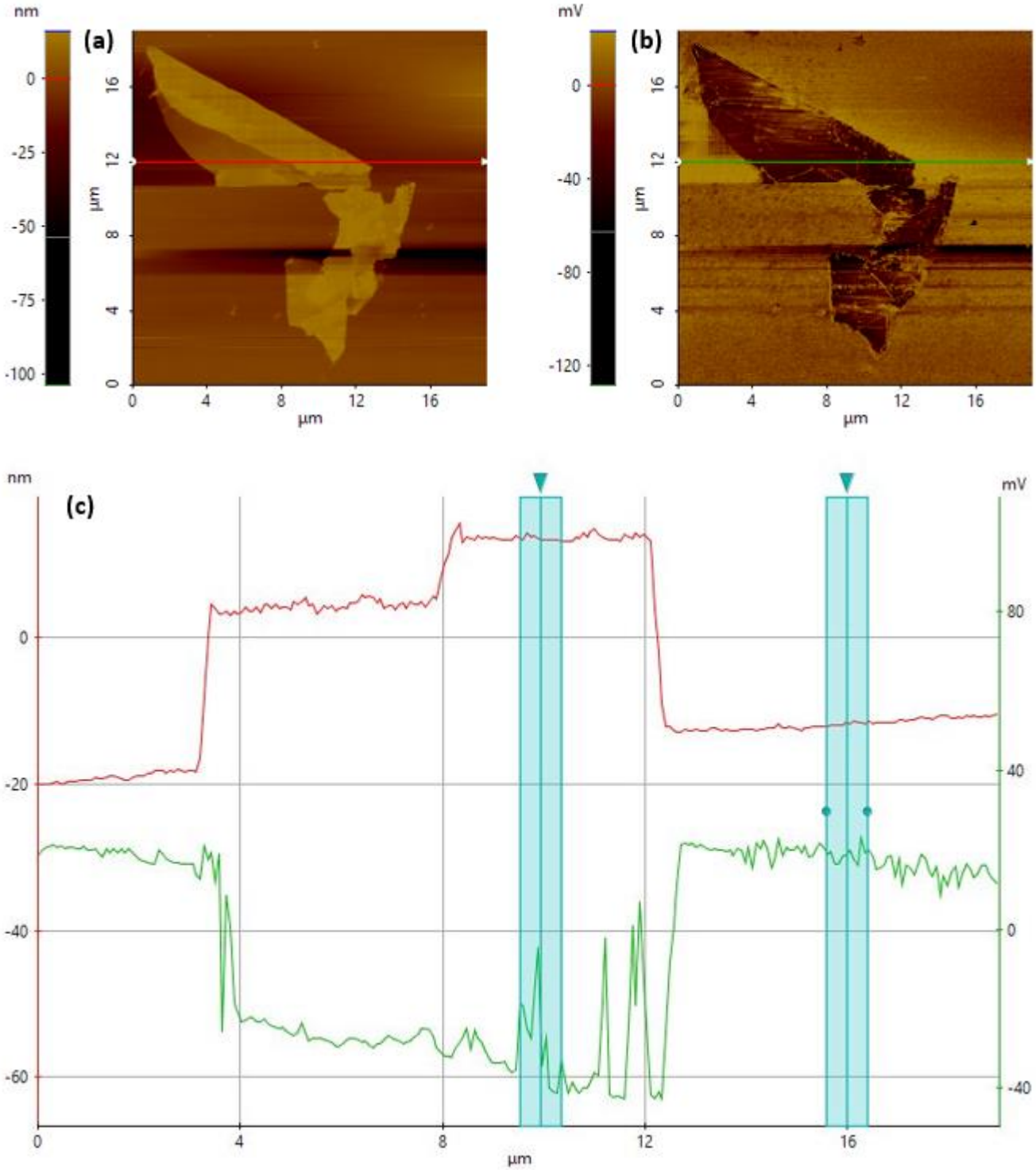


Figure 3.1 : (a) Height topography; (b) LFM image (c) Line profiles plotted along red line in 3.1(a) and green line in 3.1 (b).

Figure 3.1(a) shows the topography image. The lighter region represents greater Z height which is the exfoliated graphene. The darker region is the SiO_2 substrate. The graph represented in green (nm) represents topography signal. The average cursor pair on graphene and SiO_2 gives a height difference of 25.320 nm.

In LFM image shown in figure 3.1(b), the graphene flake is represented by the darker region (lower coefficient of friction with tip) and SiO_2 is represented by the lighter region (higher coefficient of friction with tip). The graph depicted in red (mV) represents friction signal. The average cursor pair on Graphene and SiO_2 gives a signal difference of 46.083 nm representing the difference in friction forces of the two materials.

3.2. Graphene on Copper

Graphene is grown on copper using Chemical Vapour Deposition (CVD) process with methane and hydrogen as precursors. The image scan size was 25 µm x 25 µm, scan rate was 0.5 Hz and a platinum coated cantilever of spring constant 2 N/m was used.

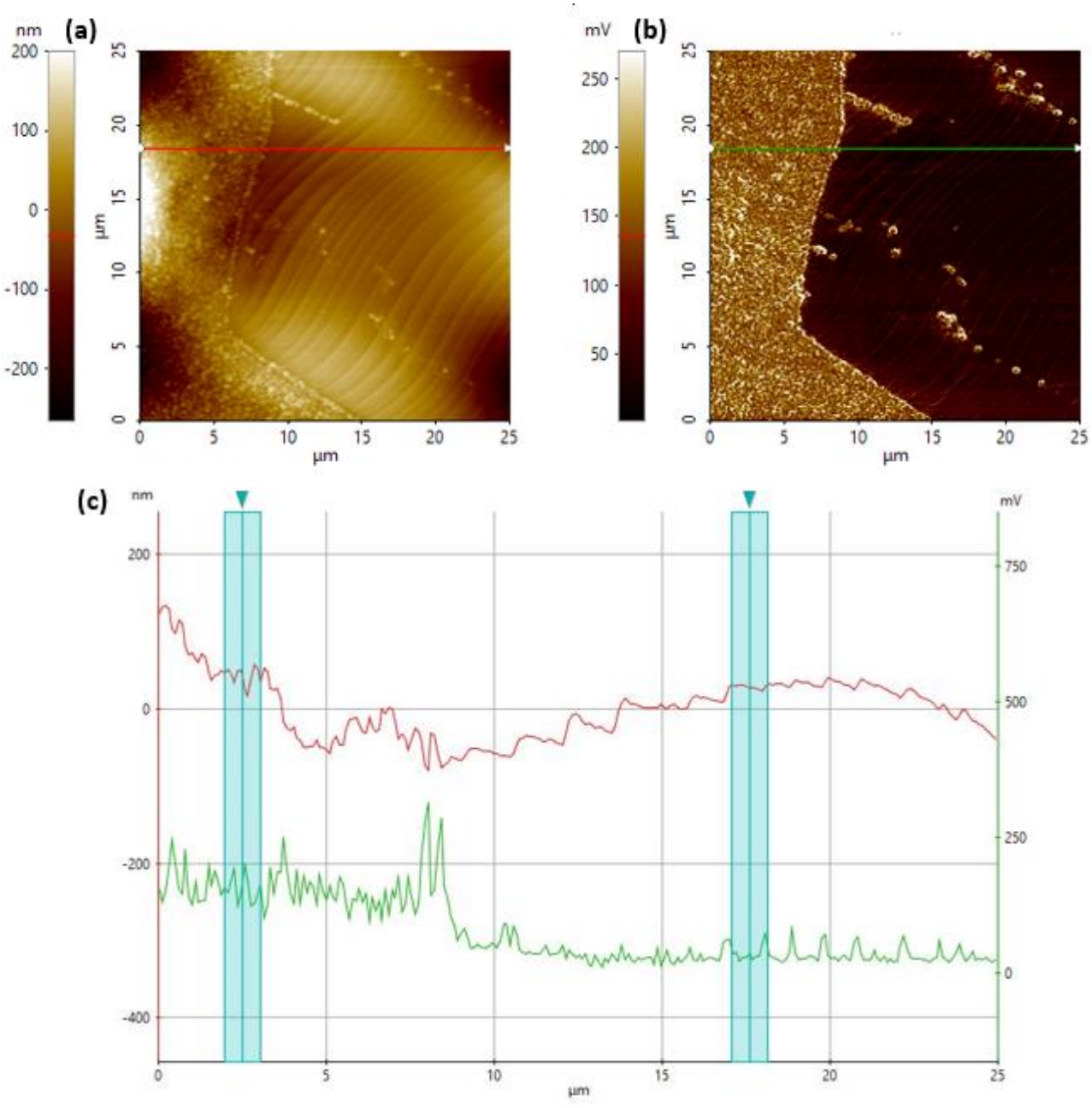


Figure 3.2: (a) Height topography; (b) LFM image (c) Line profiles plotted along red line in 3.2(a) and green line in 3.2 (b).

Topography image is shown in figure 3.2(a) with lighter region representing greater Z height. The graph shown in red (nm) represents topography signal. A height difference of 13.039 nm is observed between copper and graphene which is obtained from line profile along red line.

The high and low friction regions can be clearly distinguished in the friction image shown in figure 3.2(b). Graphene with lower coefficient of friction appears darker than copper which has higher coefficient of friction. The corresponding line profile in figure 3.2(c) gives a signal difference of 119.771 mV representing the difference in friction forces of the two materials.

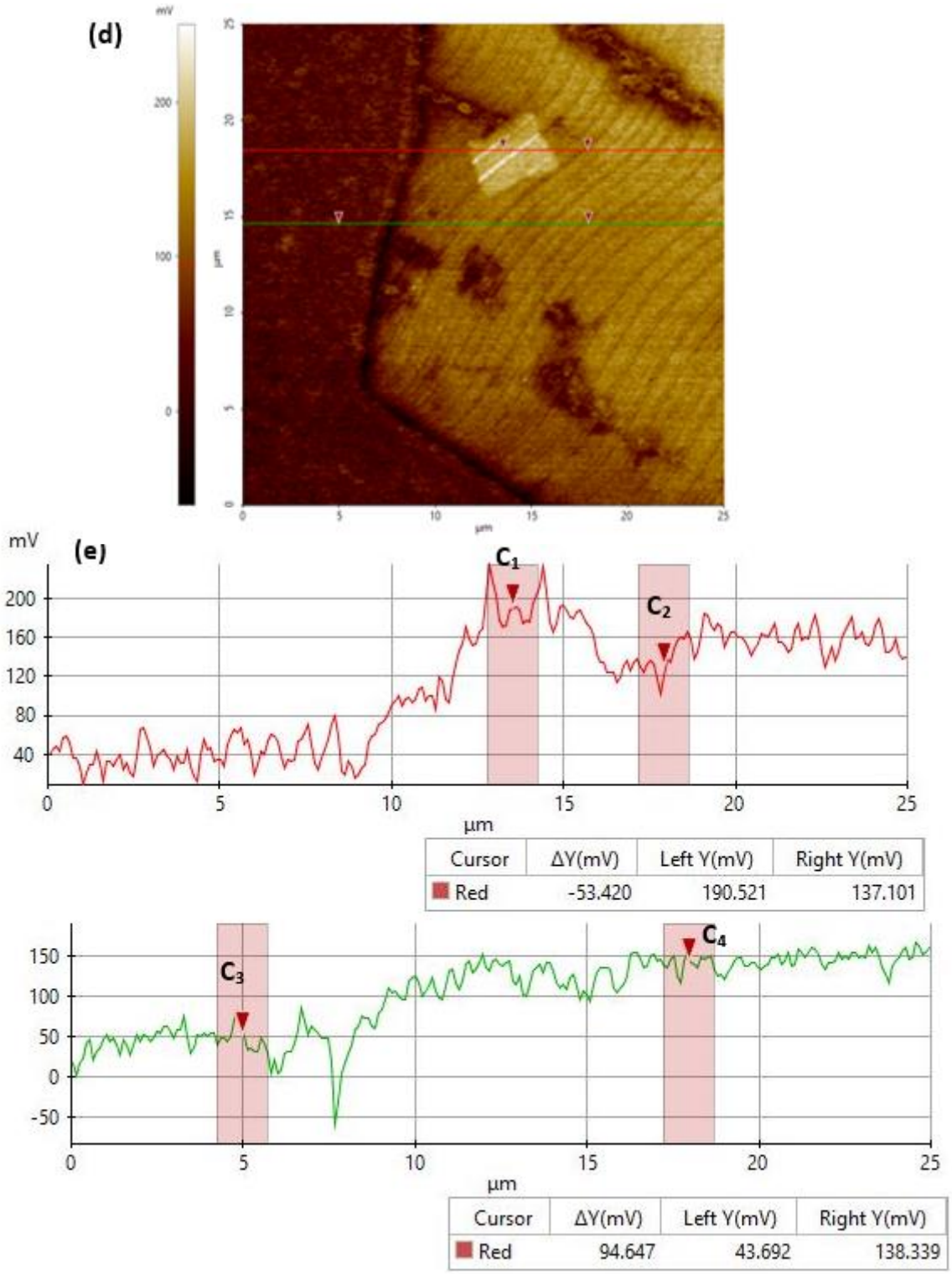


Figure 3.2: (d) KPFM surface potential; (e) Line profiles plotted along red line in 3.2(d) and green line in 3.2 (d).

Surface potential image obtained using KPFM is shown in figure 3.2 (d) and corresponding line profile is represented in figure 3.2 (e). From the contact potential values obtained, calculated workfunction values are 6.159 eV, 6.21 eV, 6.306 eV at the cursor positions C_1, C_2 and C_3 respectively. The region corresponding to lower workfunction indicates the presence of multilayer which had not shown up in either topography or friction image. It is interesting to note that even a small difference of 0.1 eV in workfunction value can be clearly differentiated in the figure.

3.3. Germanium and gold

The deposition is done by RF sputtering gold and germanium successively on silicon substrate. The thickness of germanium and gold are 160 nm and 25 nm respectively. The AFM images for the sample are acquired using a platinum coated cantilever of spring constant 3 N/m at scan rate of 0.5 Hz and a scan size of 10 µm × 10 µm.

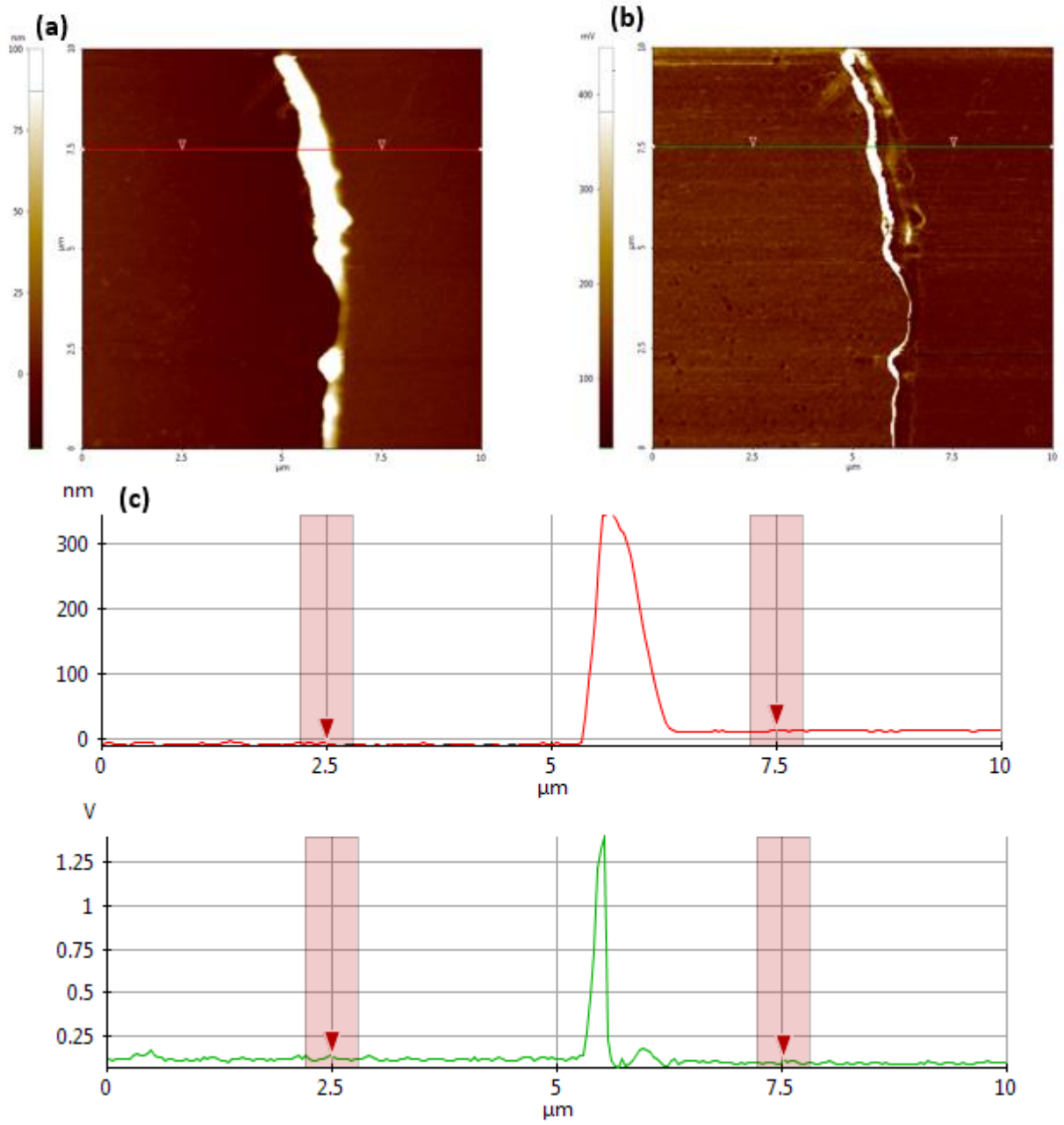


Figure 3.3: (a) Height topography; (b) LFM image (c) Line profiles plotted along red line in 3.2(a) and green line in 3.2 (b).

The topographic image is shown in figure 3.1(a). A height difference of 20 nm is observed between germanium and gold from the line profile depicted in figure 3.1(c).

The LFM image of the sample is shown in figure 3.1(b). The line profile in figure 3.1(c) shows a signal difference of 21.619 mV between germanium and gold. However, there is no significant contrast between the two materials in the LFM image. Hence, in this case, distinguishing two materials using this technique becomes challenging.

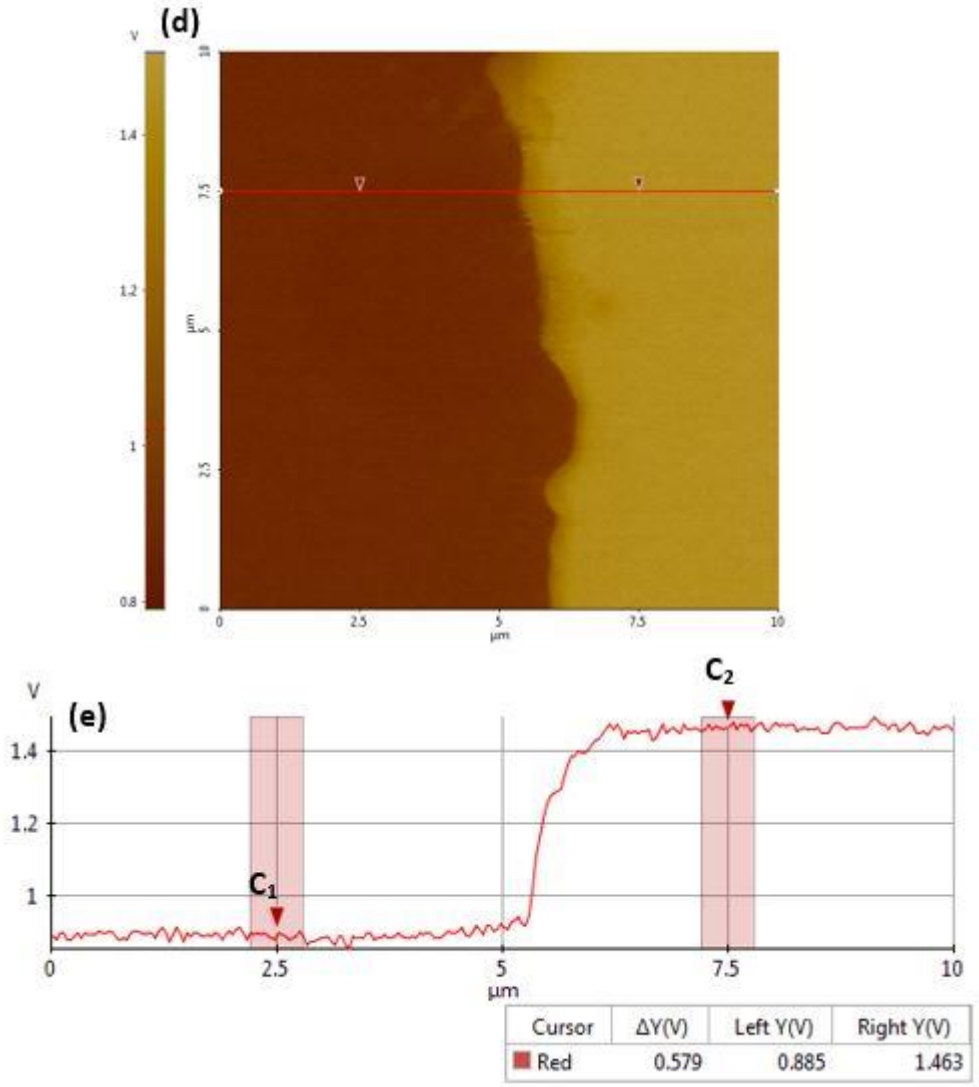


Figure 3.3: (d) KPFM surface potential; (e) Line profiles plotted along red line in 3.2(d).

The Contact potential difference between the tip and the sample, shown in figure 3.1(d) are 0.885 V and 1.463 V at cursor positions C_1 and C_2 respectively. Taking the work function of platinum coated tip as 6.35, we get work function of the sample at C_1 and C_2 as 5.465 eV and 4.887 eV. The difference in work function values helps us to differentiate between the two materials.

3.4. HOPG (Highly Oriented Pyrolytic Graphite)

It is a highly pure and ordered form of synthetic graphite. It is a layered material with the layers being held together by Van der Waal's forces and the surface contains atomic layer steps. The sample area 5 µm x 5 µm is scanned using cantilever of spring constant 3 N/m at a scan rate of 0.5 Hz. The scanning is repeated for varied set points (0.5 V, 1V, 1.5V, 2V) and their effect on friction image is studied. The friction images for set points 0.5 V, 1V, 1.5V and 2V are shown in figures 3.4 (a), (b), (c) and (d) respectively. The line plot corresponding to friction signal in all the four cases is depicted in figure 3.4(e). Increasing the set-point will result in increasing the imaging force

while reducing the set-point will result in reduced imaging forces. This can be very important for a number of reasons. If the set-point is too low, then the tip may not be able to track the surface properly and could come out of feedback if not enough force is applied. However, if too much force is applied to the surface then the tip could damage the sample surface, or in time damage to the tip itself can result in image artefacts e.g. double tipping.

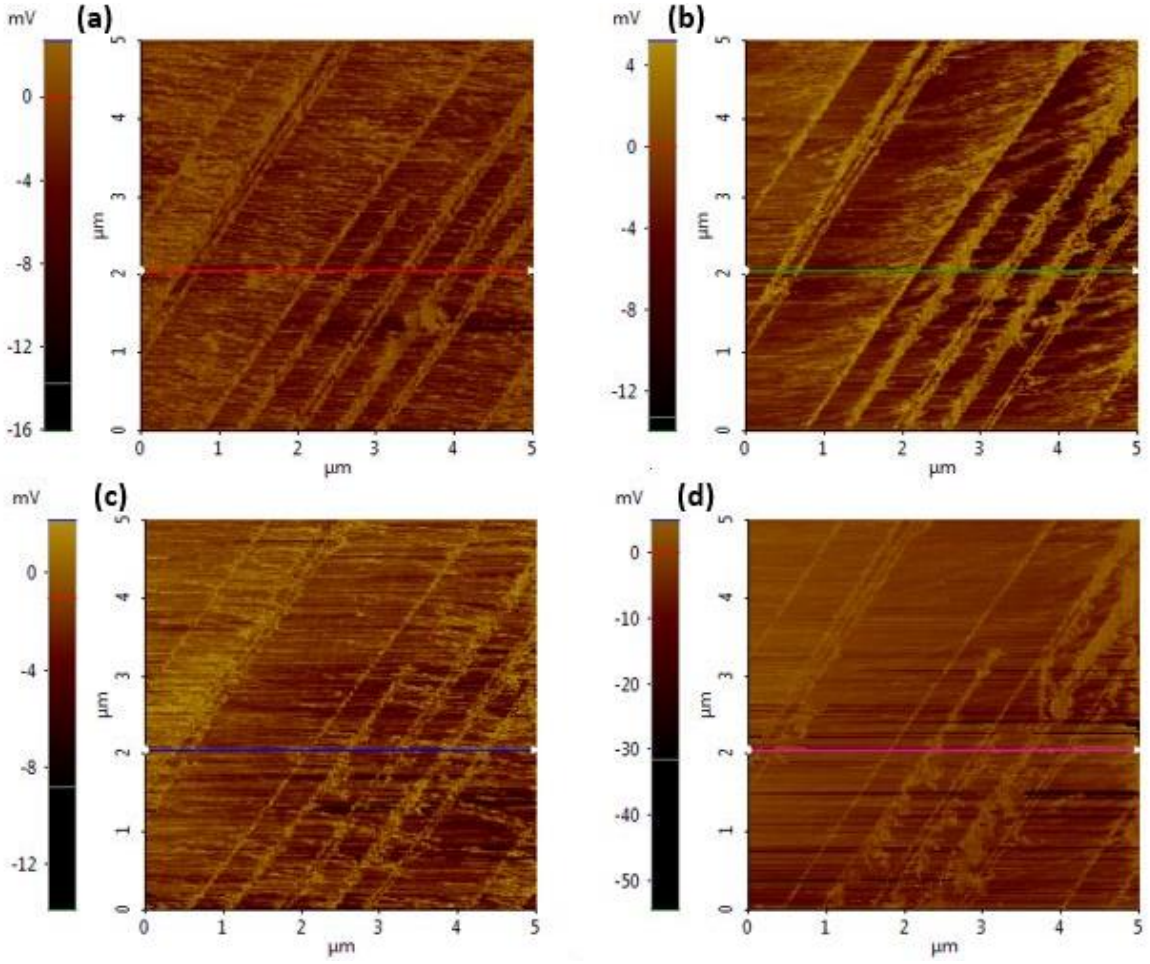


Figure 3.4: LFM image with set point (a) 0.5 V; (b) 1 V ; (c) 1.5 V; (d) 2V.

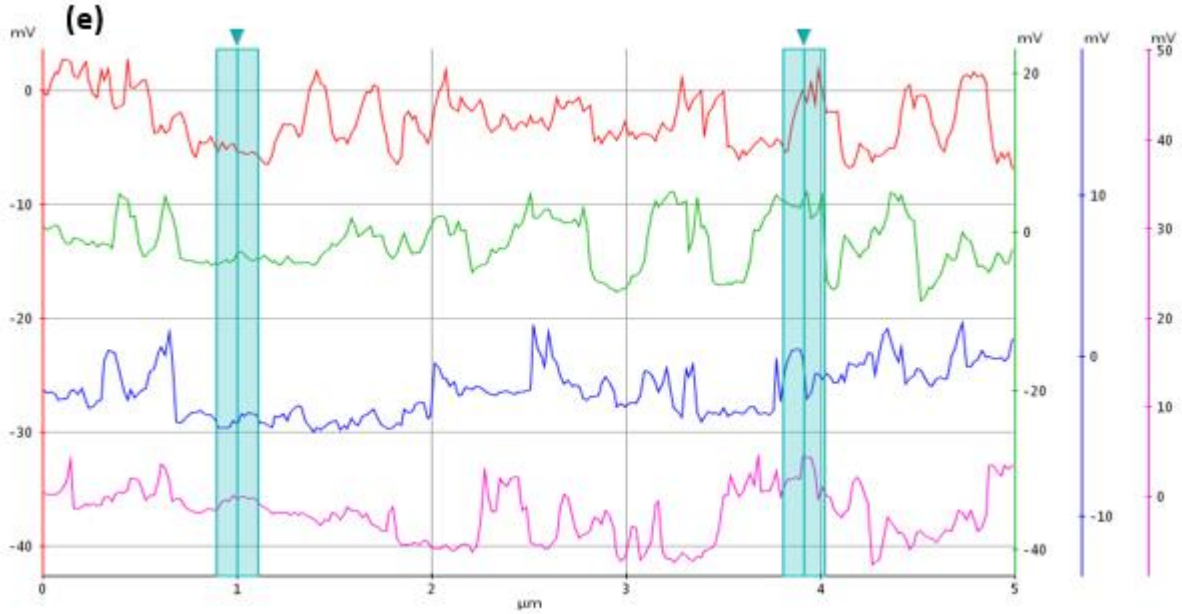


Figure 3.4:(e) Line profiles of friction signal for varied set points.

HOPG steps are hydrophilic and the water layer gets adsorbed on these steps[6]. Hence we observe a difference in lateral force on the steps and flat surface. From LFM images with different set points, we have deduced that set point value of 1 V gives a good contrast in the image

3.5. Al_2O_3 sample

Al_2O_3 is uniformly deposited on a flat silicon wafer using Atomic Layer Deposition (ALD). The ALD films are grown using alternate exposures to trimethyl aluminium and water at 250^0C and 10^{-3}bar. Four such samples with different thicknesses (5nm, 10nm, 20nm, 30nm) of Al_2O_3 deposited on Si are studied using Lateral Force Microscopy (LFM). The LFM image of samples are acquired using a platinum coated cantilever of spring constant 2 N/m at scan rate of 0.6 Hz and a scan size of 50 μm × 50 μm.

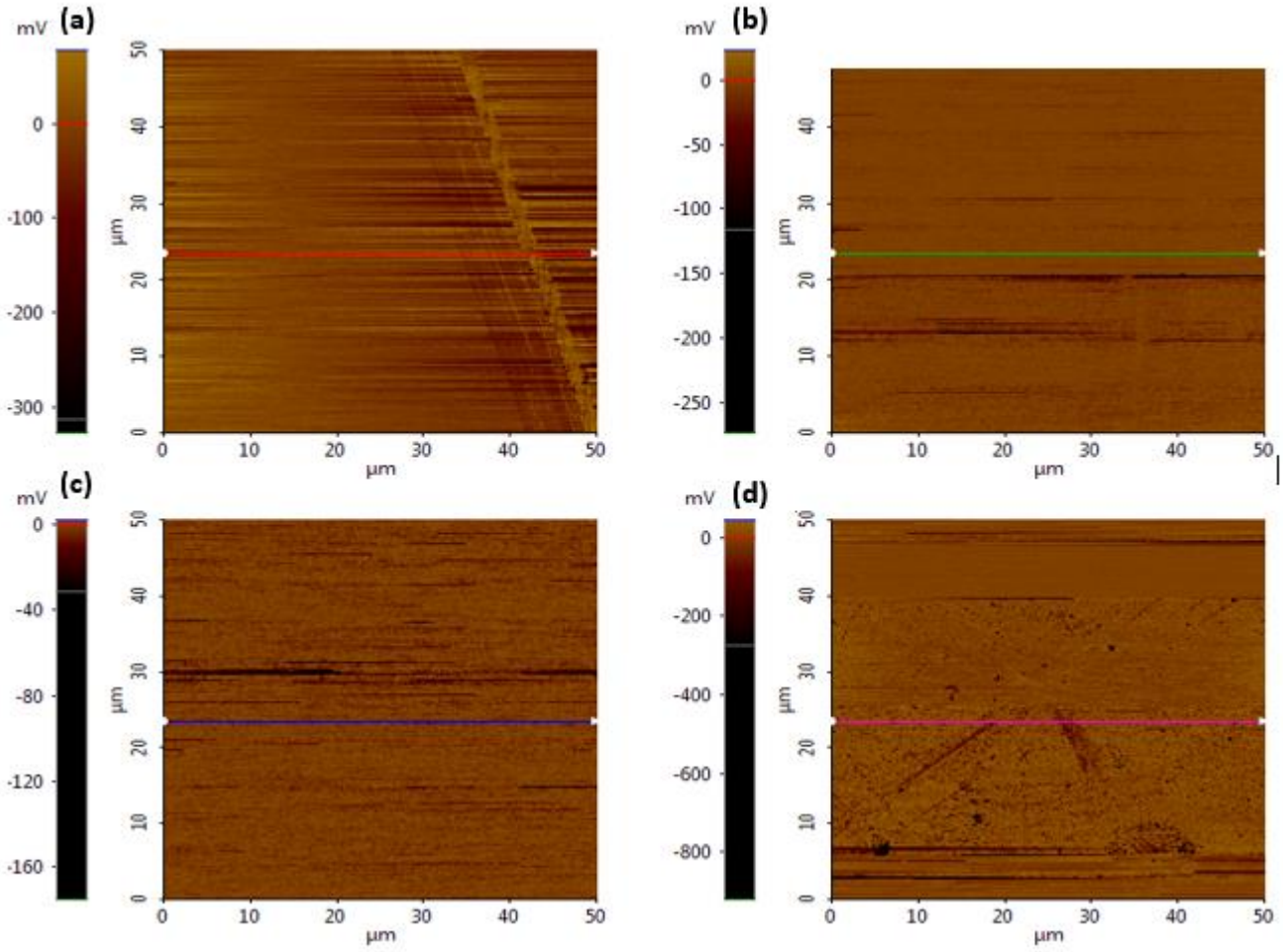


Figure 3.5: LFM image of sample of thickness (a) 5 nm; (b) 10 nm; (c) 20 nm; (d) 30 nm

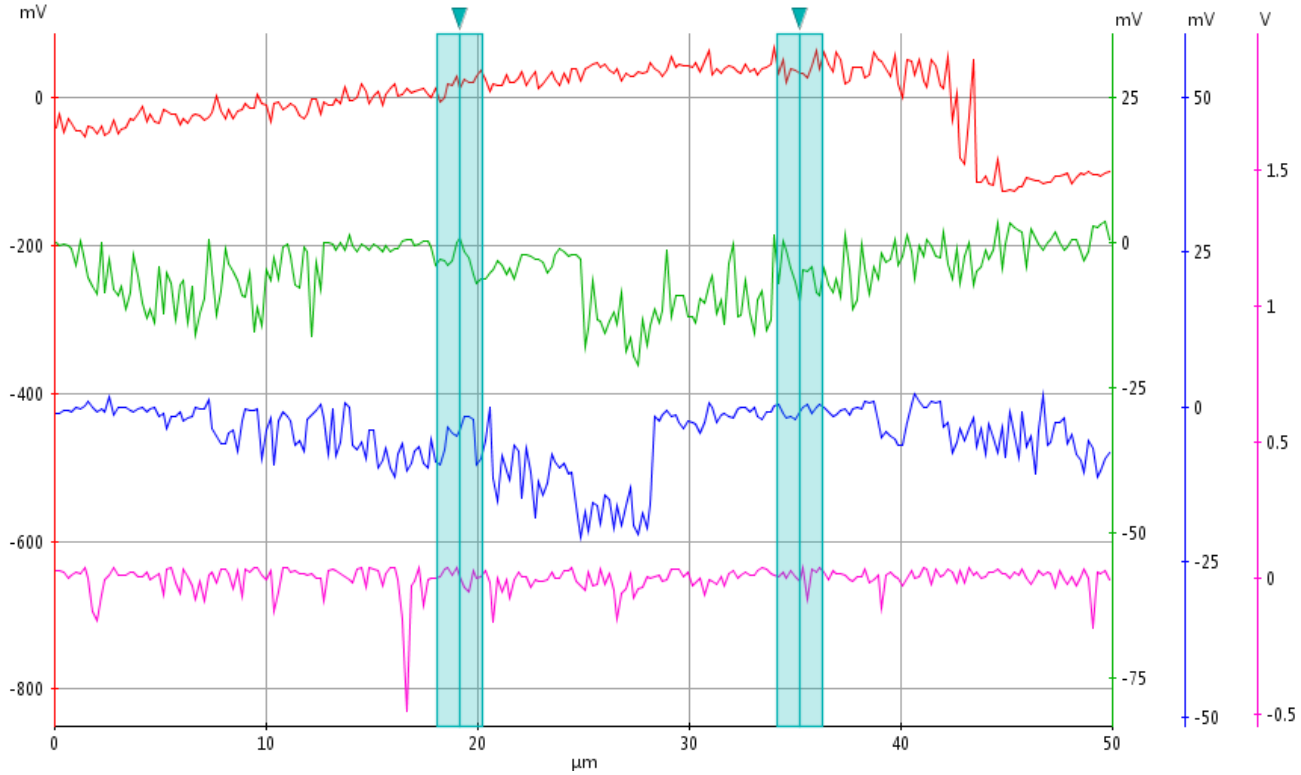
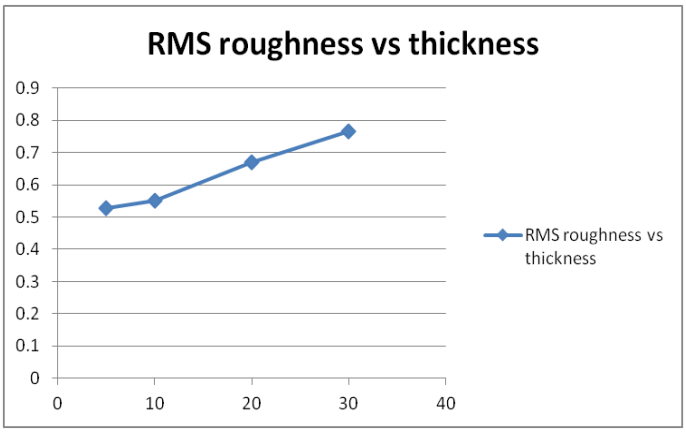
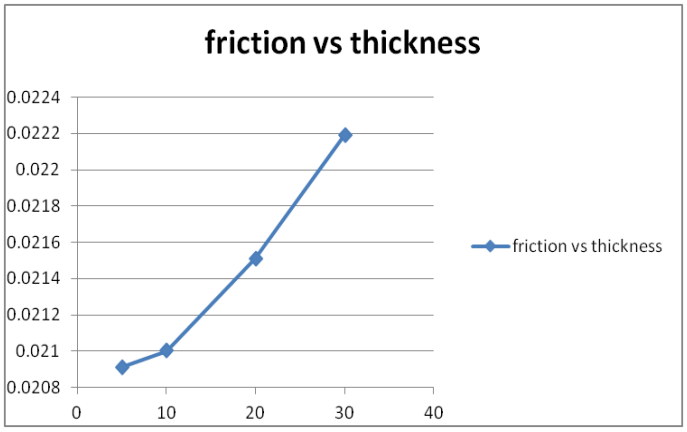


Figure 3.5: (e) Line profile of friction signal for samples of various thicknesses.

LFM images of samples of various thicknesses are shown in figure 3.5 (a), (b), (c) and (d). Corresponding line profiles are depicted in figure 3.5 (e). Plots of RMS roughness versus thickness and friction versus thickness are shown below.





We have studied the effect of ALD thickness on Root Mean Square Roughness (Rq) and Friction. The RMS roughness is observed to increase from 0.529 nm for 5 nm film to 0.765 nm for 30 nm thickness film of Al_2O_3. The extremely low surface roughness is attributed to the amorphous structure of the Al_2O_3 ALD film and the surface chemistry that proceeds to completion with every reactant exposure. The sequential, self limiting surface chemistry removes the randomness that would be present during regular CVD.

4. Conclusions

The present work aimed at differentiating materials on the specimen using surface properties. In addition to topography images, materials were distinguished based on their friction properties and work function. Lateral Force Microscopy technique was used to determine surface composition based on the principle that lateral deflection experienced by tip was different when it scanned different materials. Rougher materials offered greater opposition to tip causing higher lateral twist than the smoother materials, thereby providing a way to distinguish various materials. This technique is advantageous in way that it could easily distinguish between different materials which had relatively no topographical variations.

Kelvin Probe Force Microscopy technique helped in surface composition determination based on surface potential and workfunction. Though the calculated workfunction values do not match with the reported values in literature, the difference in workfunction values is comparable with that of reported values. Thus, with prior knowledge of the sample and by knowing the difference in workfunction values, the two materials on the sample can be distinguished.

Thus, apart from height imaging, material differentiation can be accomplished based on frictional properties and work function or surface potential.

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