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The Influence of Agglomeration and Porosity on the Annealing of PbPc and CuPc Thin Films

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ABSTRACT: The thin film of Lead Phthalocyanine (PbPc) and Copper Phthalocyanine (CuPc) on glass are prepared by Vacuum deposition method. Deposition of PbPc and CuPc on pre-cleaned glass substrates under the pressure of 10^{-6} Torr are achieved by slowly varying the current. The rate of evaporation is properly controlled and maintained constant during all the evaporations. The thicknesses of the films are 150 nm, 300 nm and 450 nm on glass substrate. The thickness of sample 450 nm annealed at 323 K and 373 K temperature. SEM and AFM are the best tools to investigate the surface smoothness and to find the grain size of the particles. AFM has been used to see the effect of the different thickness on the surface morphology of the PbPc and CuPc thin films.

Keywords: Phthalocyanine, surface morphology, Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM).

1. INTRODUCTION

The search for materials suitable for low cost, versatile electronic devices has stimulated interest in organic thin film transistors[OTFTs] and sensors has led in recent years to an extensive investigation of a range of metal substituted phthalocyanines [1,2]. Application of OTFTs as chemical sensors has shown promise in the development of electronic noses and in nerve agent detection [3-5]. A key issue regarding the widespread production of OTFTs is the long term stability and device integrity in ambient operating conditions [6,7]. Among the small molecule based OTFTs, pentacene OTFTs have received significant attention regarding instability to ambient components such as oxygen and humidity [8-12]. Several mechanisms have been proposed to explain this instability in pentacene OTFTs, including water adsorption in grain boundaries [10,11] and oxygen generated impurities[13].

Phthalocyanines have potential applications in optical logic display devices, electro photography, security printing, gas detectors [14], solar cells [15, 16], sensitisers and colour filters [17]. These materials are generally p-type semiconductors and have the advantage of being sufficiently stable towards chemicals and heat. They can be easily sublimed, resulting in high purity thin films without decomposition. The physicochemical properties can be altered by changing the metal ion. Film properties of this prototype organic semiconductor are dependent on the evaporation rate, substrate temperature and post-evaporation annealing [17, 18]. Photovoltaic devices made from organic pigments have reached power conversion efficiency of a few percent [19, 20] that is much lower than those of their inorganic combinations.

This paper deals with the surface characteristics of lead phthalocyanine (PbPc) and copper phthalocyanine thin films prepared by vacuum evaporation technique. We have studied the temperature dependent of surface morphology of CuPc and PbPc thin film. Information on the surface characteristics of CuPc and PbPc thin films can be obtained by Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM).

2. EXPERIMENTS

The powder of PbPc (80% dye, Sigma Aldrich company, Bangalore, India) is kept in a molybdenum boat (100 A current rating) heated with high current controlled by a transformer. The transformer is capable of supplying 150 amps at 20 volts which is used to provide the accessory current for heating the molybdenum source. It is used for the evaporation process. Prior to evaporation, the evaporant material is carefully degassed at lower temperature for about 45 minutes with the closed shutter. Thin films of PbPc are deposited at room temperature on pre-cleaned glass substrates under the pressure of 10^{-6} Torr using a (12 A 4D Hind Hivac, India) coating unit. The rate of evaporation is properly controlled and maintained constant during all the evaporations. Rotary drive is employed to maintain uniformity in film thickness. The thicknesses of the films are 150 nm, 300 nm and 450 nm. The thickness of the films is measured by Quartz crystal monitor. This procedure is used for preparing PbPc and CuPc thin film on pre-cleaned glass substrate. The adhesion of the films to the substrate seems to be extremely good. The samples prepared in a similar environment were used for studying their various properties. The surface characteristics of CuPc and PbPc thin films were examined by Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM).

3. RESULTS AND DISCUSSION

3.1. SEM Analysis

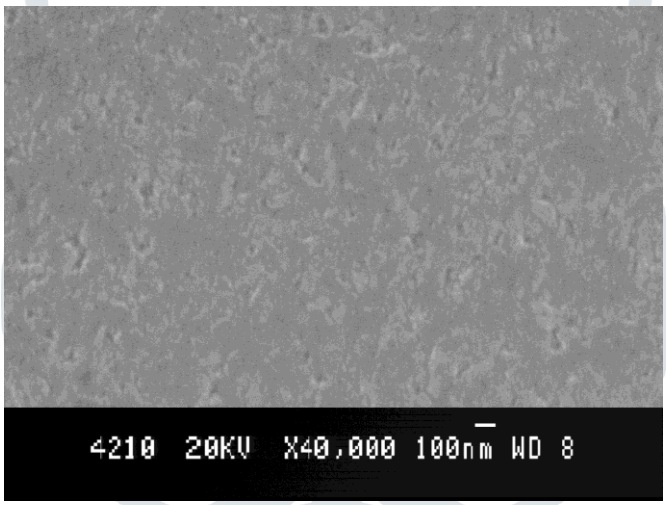
The SEM provide the investigator with a highly magnified image of the surface of a material that is very similar to what we would expect if one could actually see the surface visually. SEM is one of the best tools to investigate the surface smoothness and to find the grain size of the particles. From the image it is evident that the surface of the films is smooth and grain size is less than a micrometer.

3.1.1. Effect of thickness

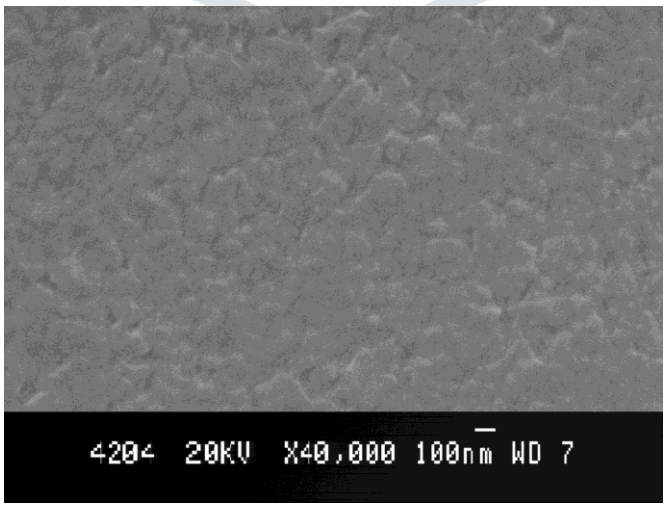
Figures 1(a, b and c) and 2 (a, b and c) shows surface topography of the SEM photographs of PbPc and CuPc films of thicknesses 150 nm, 300 nm and 450 nm. The SEM image of lower thicknesses shows very fine particles and disordered phases in PbPc [21, 22] and in CuPc mainly consists of integer CuPc molecules [23]. Along with these fine particles, rods like structures are seen in the case of film with higher thickness 450 nm of PbPc and capsule like structures in CuPc.

From the SEM image of the films, it is clear that the grain size of the films increase with increase in the thickness. The surfaces of the films are rough. There are powder agglomerations that were confirmed by EDAX analysis. The area fraction of the powder agglomeration on the film increases as the film content increases.

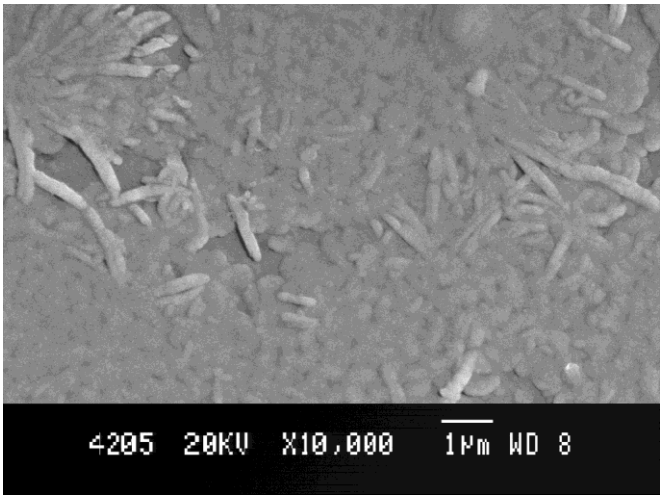
The agglomerations of film powder make the film structure porous. The higher the film content, the more numerous are the agglomerations and the higher is the porosity. The porosity and the amount of material on the film are responsible for the increase in film thickness with increasing material content. CuPc film has a smoother morphology than that of PbPc on glass surface. In a typical SEM planar view of the PbPc and CuPc films deposited on glass, it can be seen that the film was made of homogeneous small crystal grains with an average diameter of 20–60 nm. This value was in good agreement with the crystallite sizes calculated from the XRD measurements. Since charge mobility is higher in crystalline materials than in amorphous ones [24].



(a) 150 nm

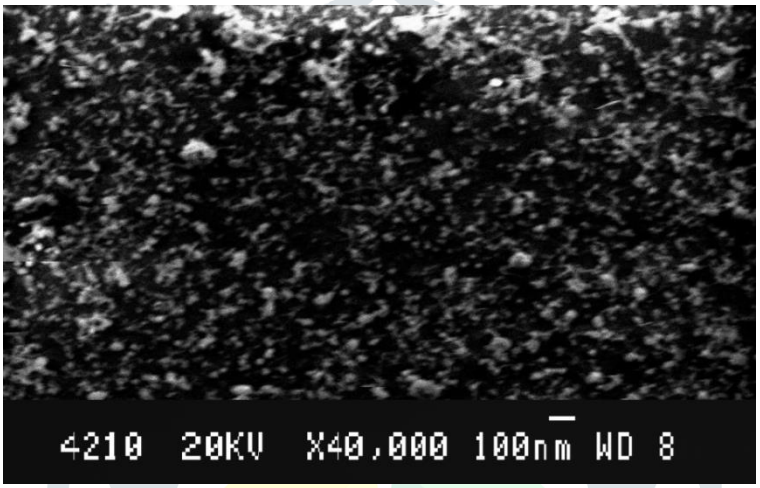


(b) 300 nm

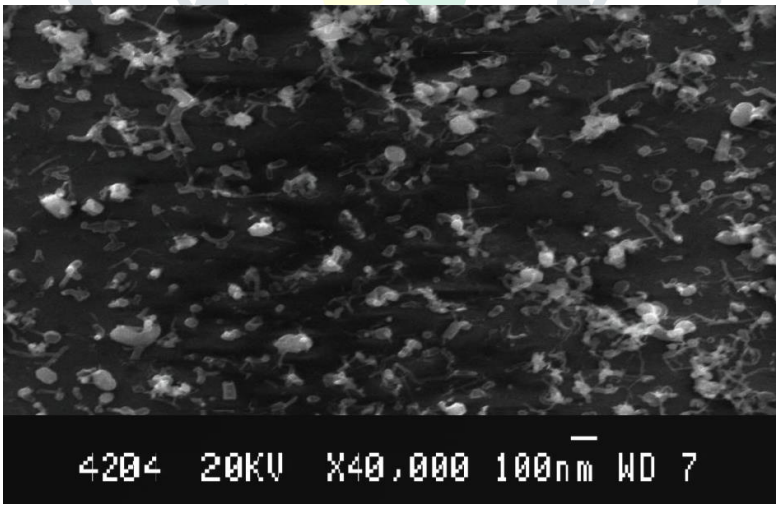


(c) 450 nm

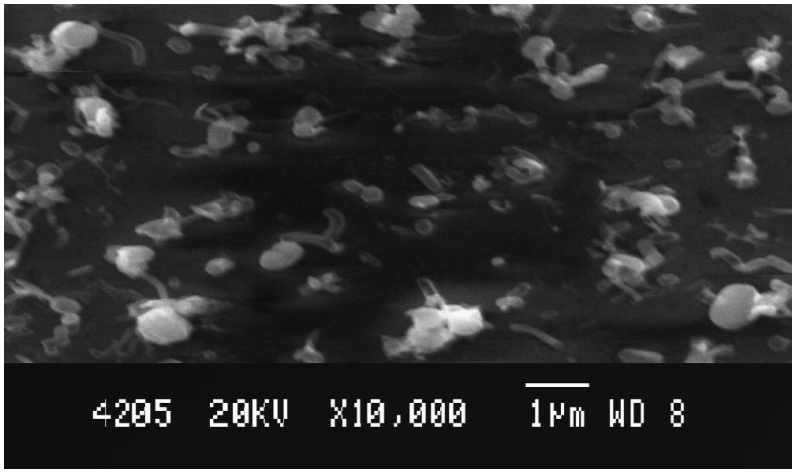
Figure 1 SEM images of PbPc films for thicknesses



(a) 150 nm



(b) 300 nm



(c) 450 nm

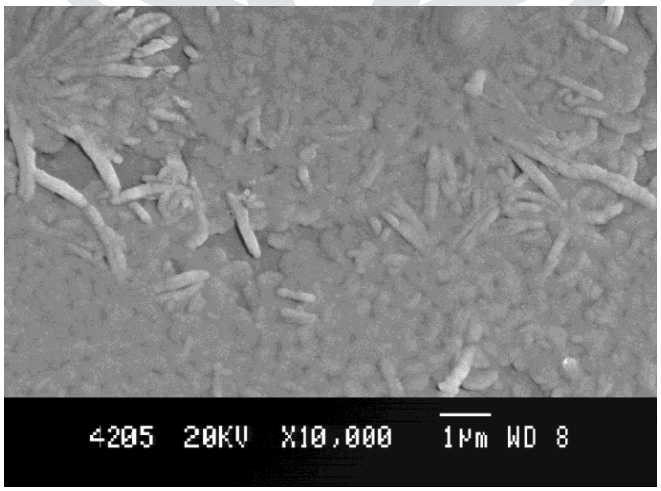
Figure 2 SEM images of CuPc films for thicknesses

3.1.2 Effect of temperature

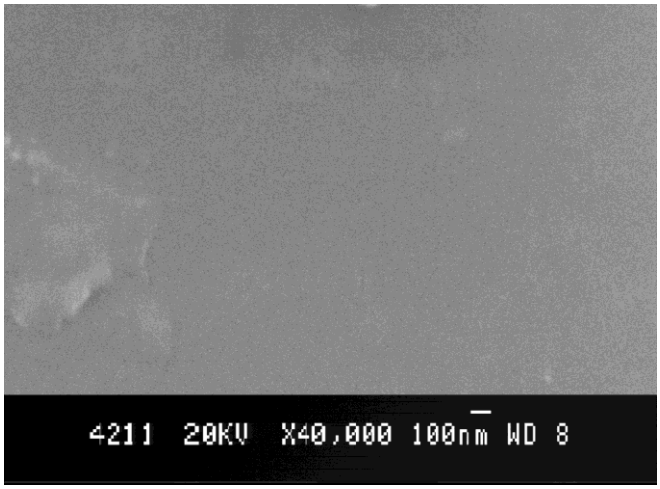
Figures 3(a, b and c) and 4 (a, b and c) shows the SEM images of PbPc and CuPc films of thickness 450 nm at different annealed temperatures. The film at 303 K shows a mixture of fine particles and rod like structures. As the temperature increases the smoothness and uniformity of the film also increases.

In annealed films, the rod like (PbPc) crystal and capsule like (CuPc) crystals deform and become small particles as a result of the oxidation of phthalocyanine by adsorbed and /or diffuse in the bulk oxygen, therefore no larger rod like crystals and capsule like crystals were observed and small particle appeared, taking a different form from the fine particles observed for the film annealed at 373 K temperature. Therefore the formation of the fine particles may proceed as a result of the interaction between the absorbed oxygen and phthalocyanine. These absorbed tendencies imply that the surface of phthalocyanine particles is oxidized by annealing at 373 K and the crystal growth is depressed by the formation of lead oxide on the surface. For more the rod like crystal in PbPc and capsule like crystals in CuPc deform and become small particles.

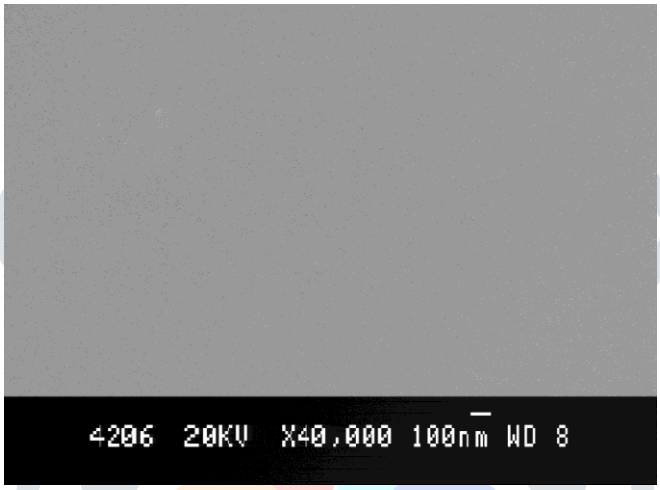
The topography of the film of thickness 450 nm is shown in figures. It is apparent that the deposited films formed on glass consist of fine particles and disordered phases that exist between the interparticles. At a higher magnification, it appears that the degree of crystallinity of the fine particles was poor in the deposited films. The surface of the material films is rough. These are powder agglomerations that were confirmed as MPc. The area fraction of the powder agglomeration on the films increases as the MPc. The area agglomerations of PbPc Powder make the film structure porous [25]. The higher the PbPc content, the more numerous are the agglomeration and the higher is the porosity. The porosity and the amount of PbPc on the films are responsible for the increase in film thickness with increasing PbPc content.



(a) 303 K

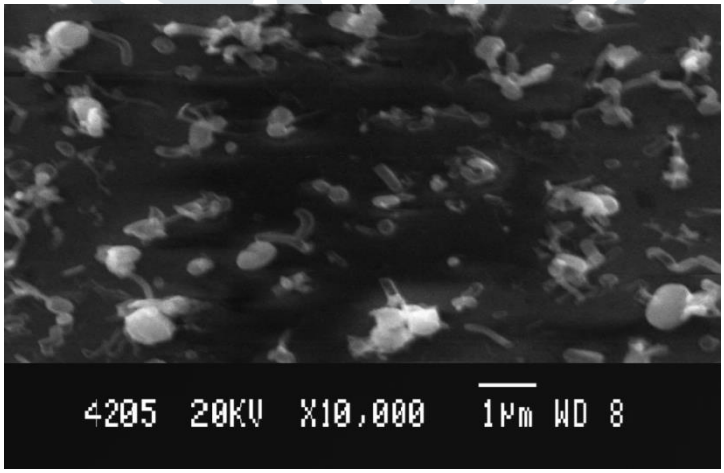


(b) 323 K

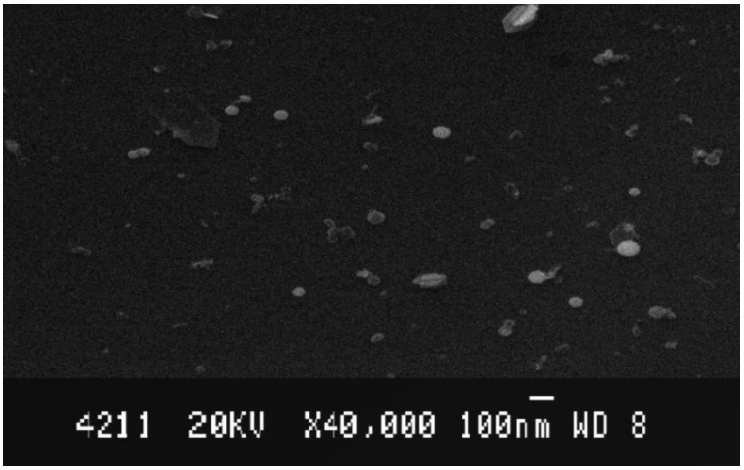


(c) 373 K

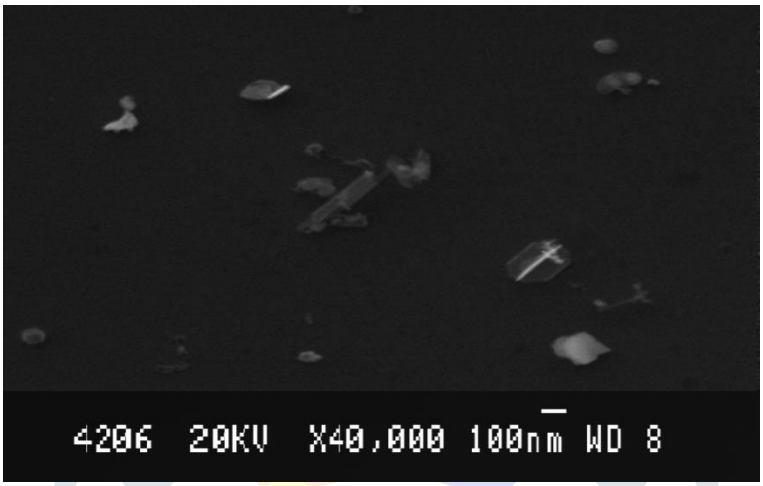
Figure 3 SEM images of PbPc films for thickness 450 nm at annealed



(a) 303 K



(b) 323 K



(c) 373 K

Figure 4 SEM images of CuPc films for thickness 450 nm at annealed

The structure of the annealed CuPc films evolves from the sample heated at 323 K and 373 K. SEM images point out the formation of capsule like crystallites on the film surface. The changes of structure and morphology are related to the treatment temperature, that is the higher the temperature, the more pronounced the changes. The thickness of the film increases after annealed at 373 K. Therefore, the heat is responsible for the increase in film thickness. Since the films expand, it is believed that the porosity is increased.

3.2 AFM Analysis of the Film

3.2.1 Effect of thickness

Interesting results have been obtained by means of AFM measurements. AFM has been used to see the effect of the different thickness on the surface morphology of the PbPc thin film. AFM is one of the best tools to investigate the surface smoothness and find the grain size of the particles.

The two dimensional and three dimensional AFM micrographs of PbPc and CuPc thin film of thickness 150 nm, 300 nm, 450 nm are shown in figures 5 to 7 and figures 8 to 10 respectively. The Figure 5 shows the alpha phase of PbPc film, which consists of small grain size about 12-28 nm. The AFM image indicates a smooth surface. The Figures 6 and 7 shows the beta phase films PbPc which consist of large grain size of about 16-50 nm and 24-62 nm respectively. The alpha phase film have smoother planar than the beta phase films [26]. The Figure 8 shows the alpha phase of CuPc film, which consists of small grain size about 12-26 nm. The Figures 9 shows the beta phase films CuPc which consist of large grain size of about 16-48 nm. The Figures 10 shows the gamma phase films of CuPc which consist of large grain size of about 22-61 nm [27]. The alpha phase film have smoother planar than the beta and gamma phase films [28].

In Figure 5 we can observe roughly cubic crystallites of 110×120 nm width of PbPc. The crystallite size is roughly constant. The surface area is about 1.2 μm^2 on a 1×1 μm^2 scanned area which is 20% more than a 1×1 μm^2 flat area. Figure 7 shows the well defined cylindrical crystallites of 120×200 nm width. The surface area is about 1.4 μm^2, which is 40% more than a 1×1 μm^2 scanned area. In Figure 8, we can observe roughly cubic crystallites of 80×100 nm width of CuPc. The crystallite size is roughly constant. The surface area is about 1.35 μm^2 on a 1×1 μm^2 scanned area which is 35% more than a 1×1 μm^2 flat area. Figure 10 shows the well defined cylindrical crystallites of 90×140 nm width. The surface area is about 1.5 μm^2, which is 50% more than a 1×1 μm^2 scanned area.

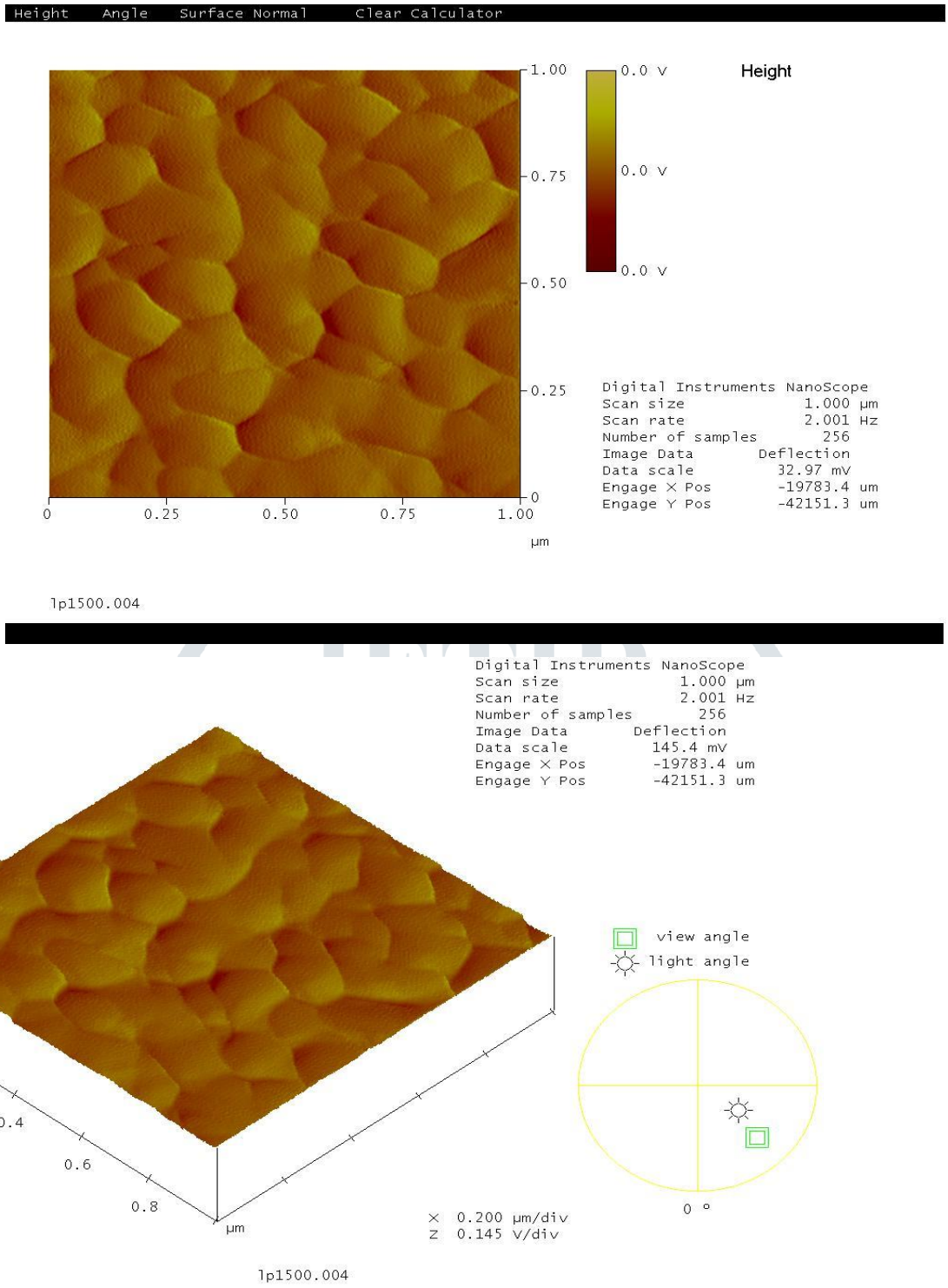


Figure 5 AFM micrographs of PbPc thin films of thickness 150 nm

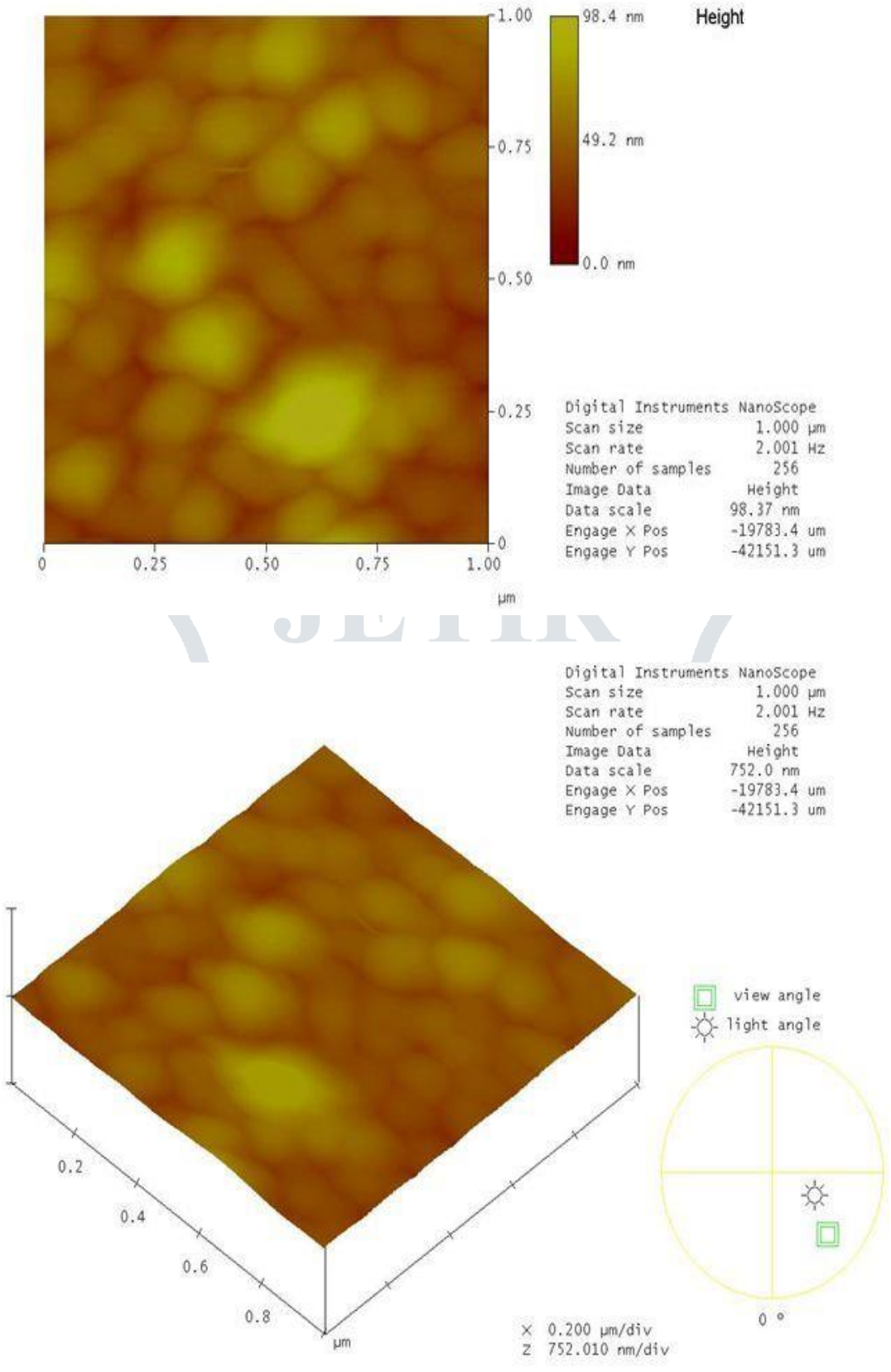


Figure 6 AFM micrographs of PbPc thin films of thickness 300 nm

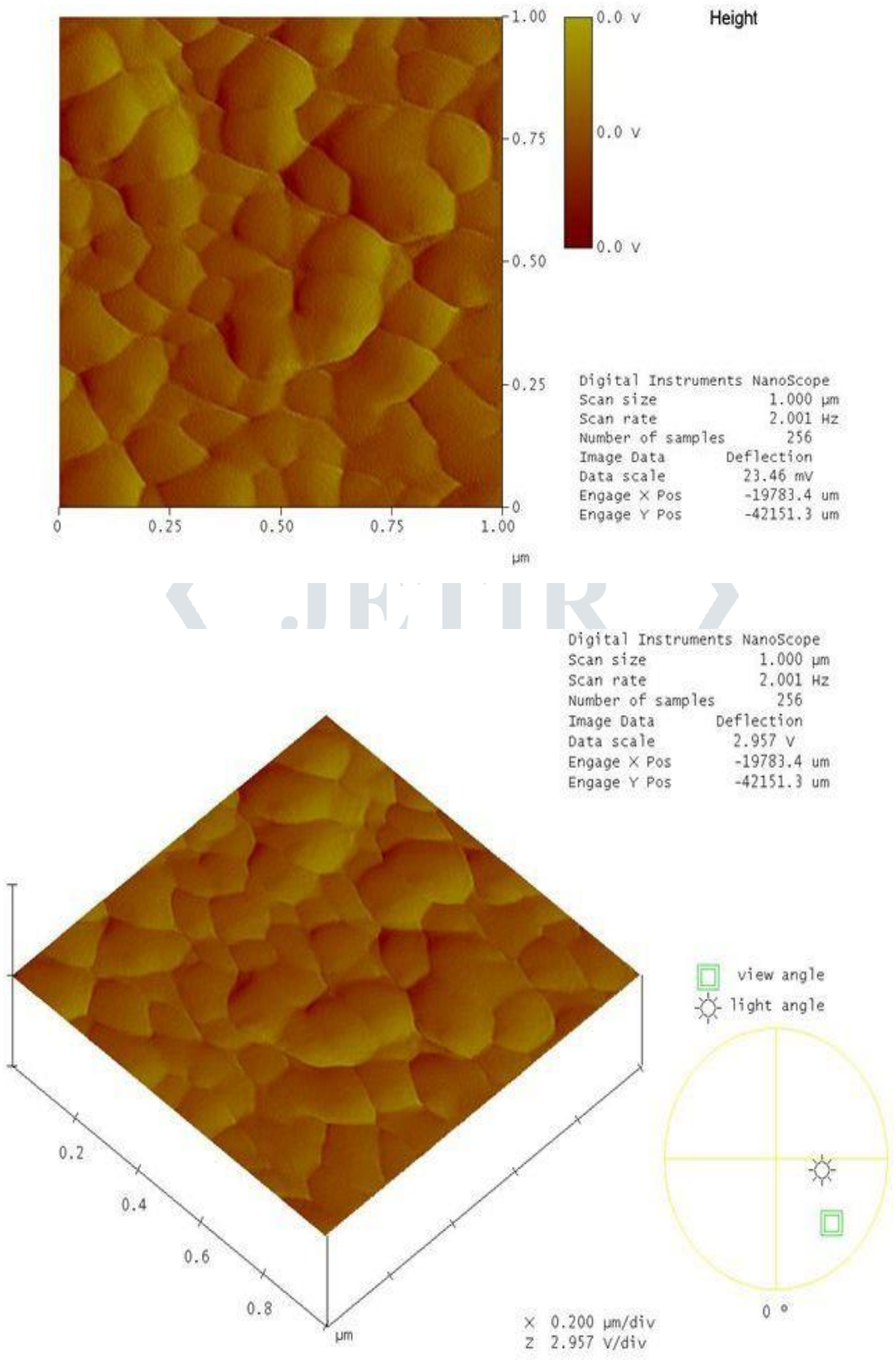


Figure 7 AFM micrographs of PbPc thin films of thickness 450 nm

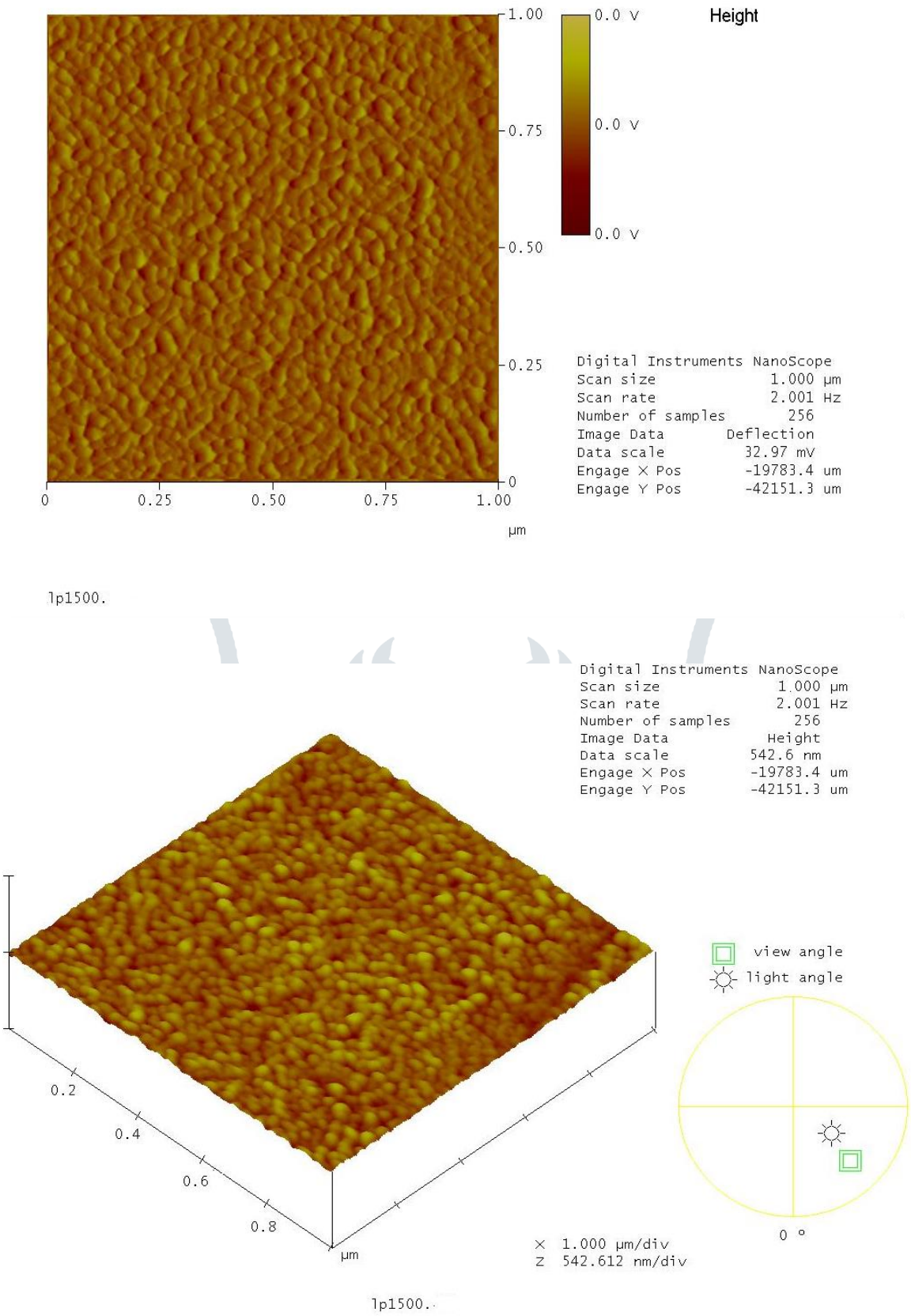


Figure 8 AFM micrographs of CuPc thin films of thickness 150 nm

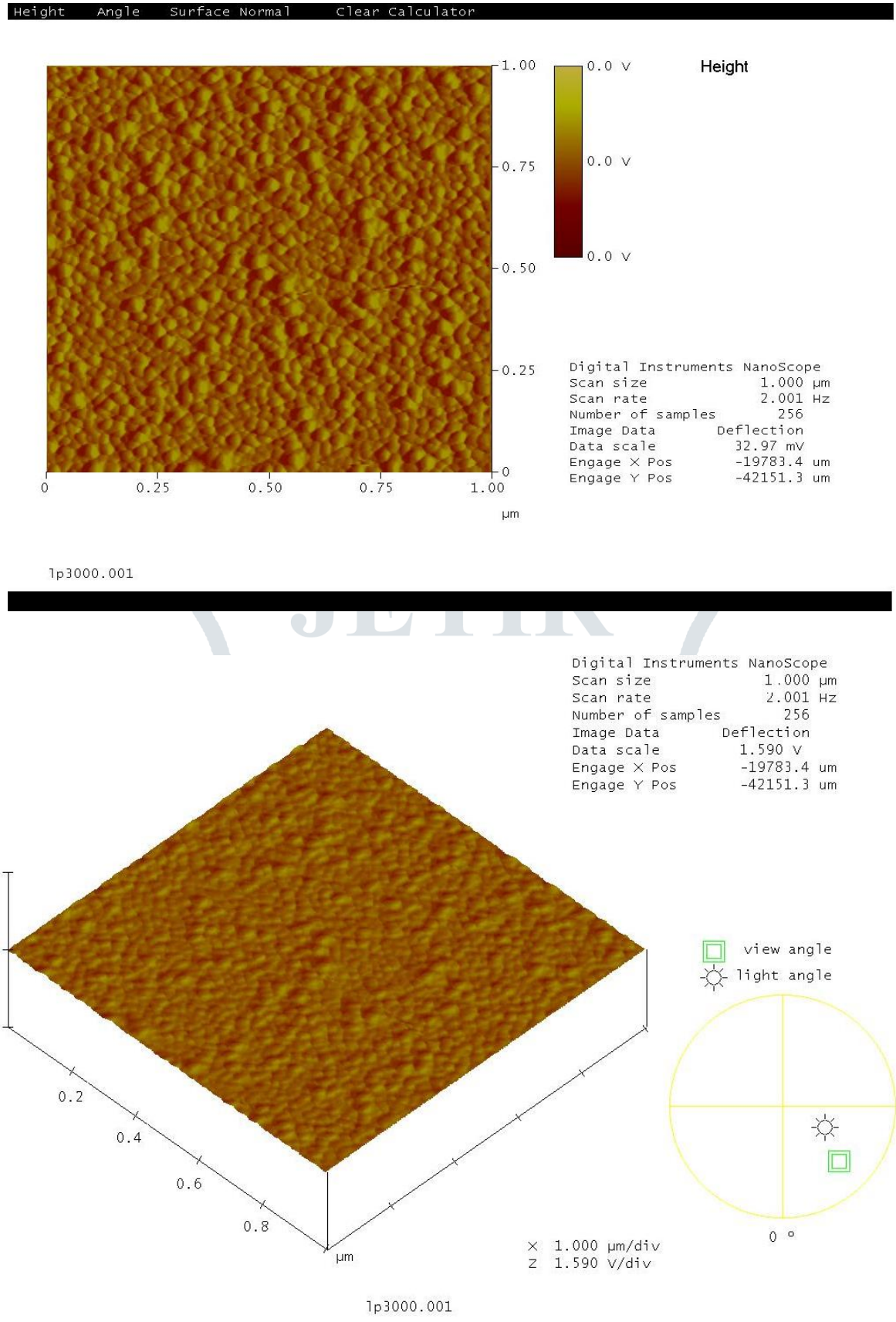


Figure 9 AFM micrographs of CuPc thin films of thickness 300 nm

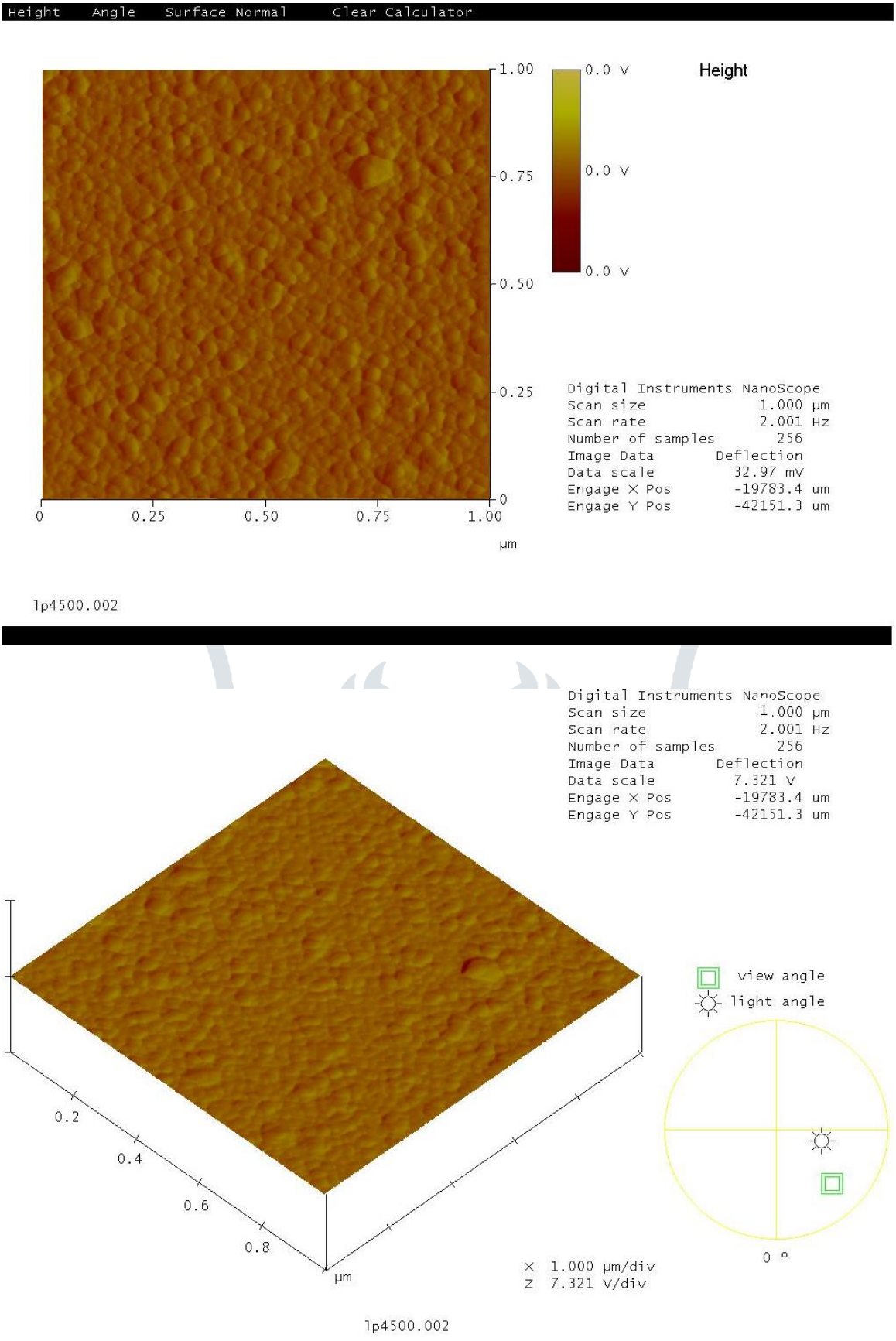


Figure 10 AFM micrographs of CuPc thin films of thickness 450 nm

We can observe well defined crystallites, some of them having slightly larger size than that in the deposited sample of both films. Moreover the surface is more 'disordered' with respect to that of the deposited films and the surface area increase because of the formation of the smaller crystallites [29]. The AFM micrograph of figure shows that the surfaces of the films consists of larger grain size and are homogeneously distributed. It is very clear that the grain size increases with increase in film thickness which was confirmed from the XRD analysis also. The roughness of the image surface also increases with increase in film thickness [30].

3.2.2 Effect of temperature

The AFM has been used to see the effect of the different annealing temperature on the surface morphology of the PbPc and CuPc thin films. The two dimensional and three dimensional AFM micrographs of PbPc thin film of thickness 450 nm annealed at 323 K and 373 K are shown in Figures 11 and 12. The Figure 11 shows the AFM picture of PbPc annealed at 323 K where we can observe well defined crystallites, some of them having slightly larger size than that in the deposited sample. Moreover the surface is more 'disordered' with respect to that of the deposited PbPc thin film and the surface area decreases because of the formation of the larger crystallites. The Figures 11 and 12 shows the beta phase films.

In Figure 7 the surface areas is about 1.4 μm^2 on a 1×1 μm^2 scanned area for 450 nm of PbPc. The sample of 450 nm annealed at 323 K is shown in Figure 11. It becomes compact and the surface area decreases to 1.3 μm^2 which is 7% less than a 1.4 μm^2 area. Similar behaviour has been observed for 373 K annealed sample. Figure 12 shows the surface area of about 1.2 μm^2, which is 15% less than a 1.4 μm^2 area of the figure 7. CuPc sample of 450 nm annealed at 323 K is shown in Figure 13. It becomes compact and the surface area decreases to 1.4 μm^2 which is 6.6% less than a 1.5 μm^2 area. Similar behaviour has been observed for 373 K annealed sample. Figure 14 shows the surface area of about 1.3 μm^2, which is 13% less than a 1.5 μm^2 area of the Figure 10. Surface images of CuPc thin films of thickness 450 nm before and after thermal annealing of 323 K and 373 K were shown in Figures. Before thermal annealing, there were well shapes on the surface in an AFM image. After thermal annealing, it was found that surfaces roughness decreased and lowered shapes at the surface were observed [27].

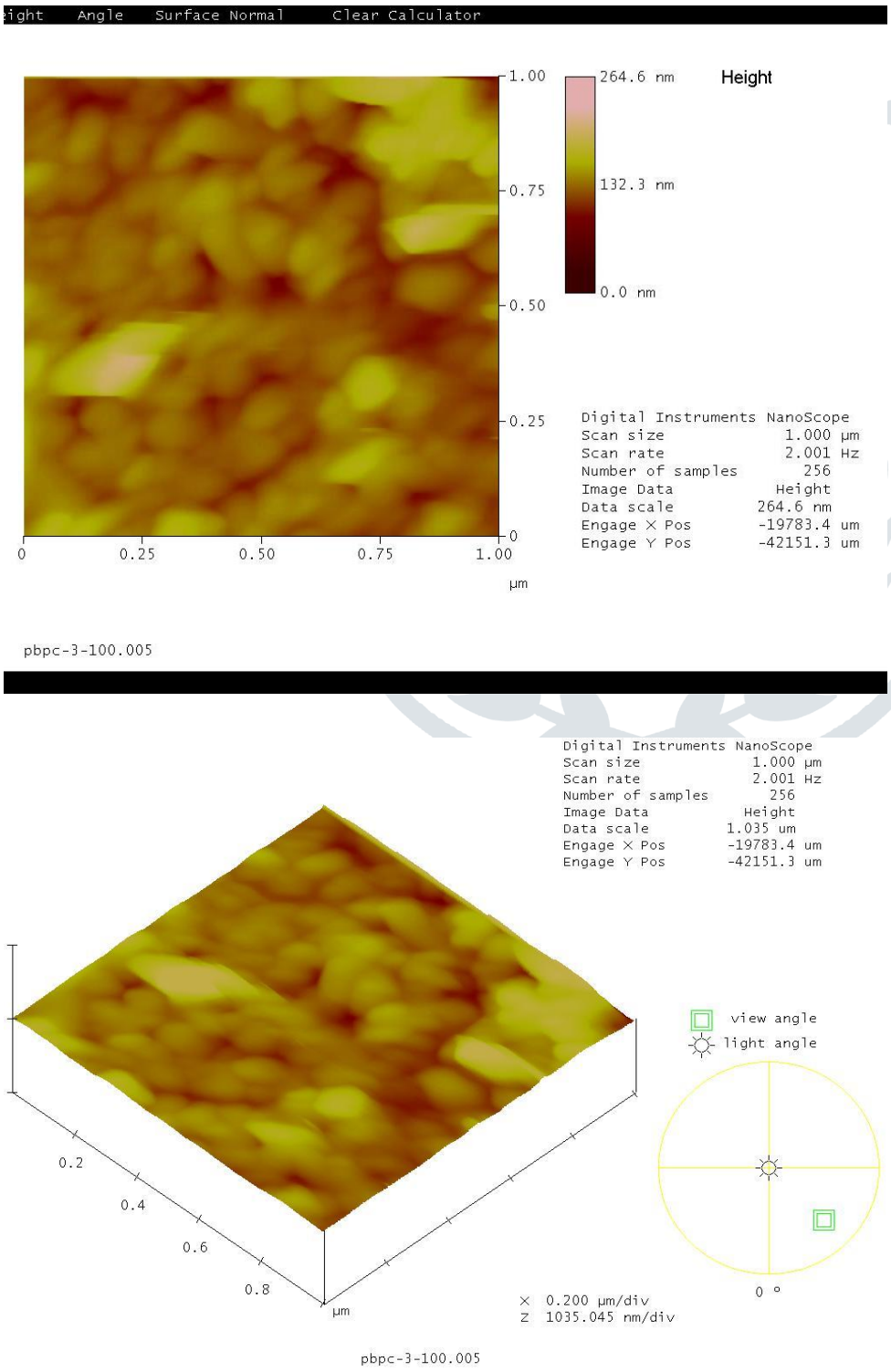
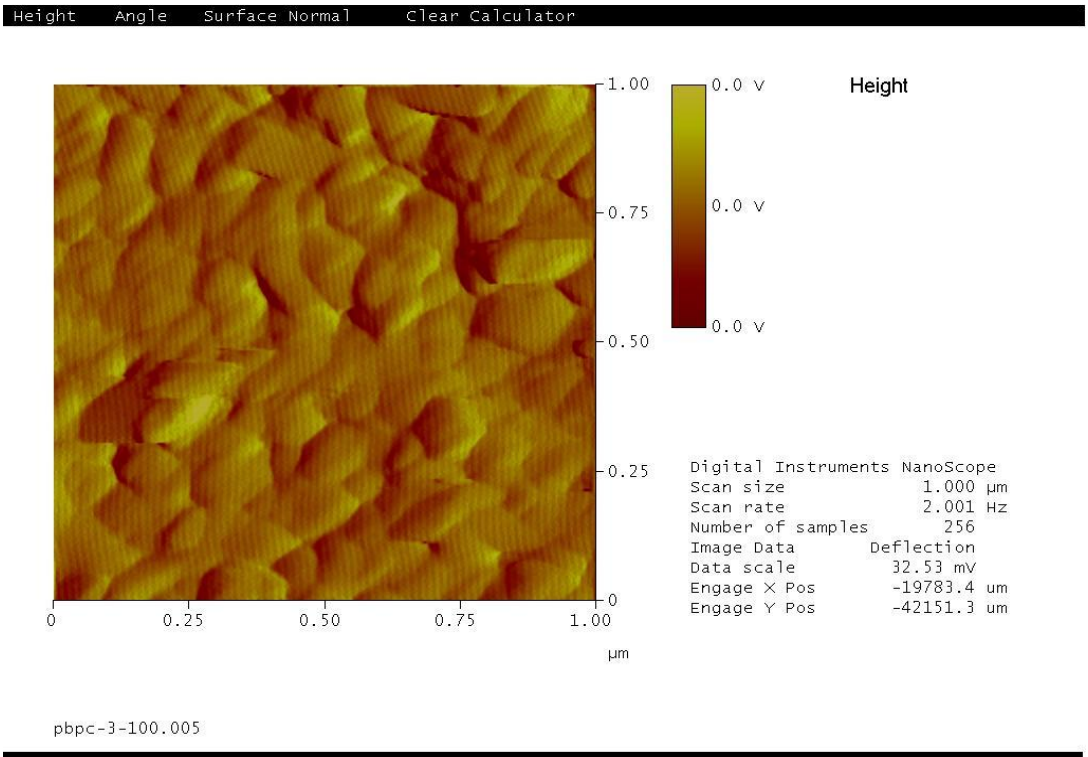


Figure 11 AFM micrographs of PbPc thin films of thickness 450 nm annealed at 323 K



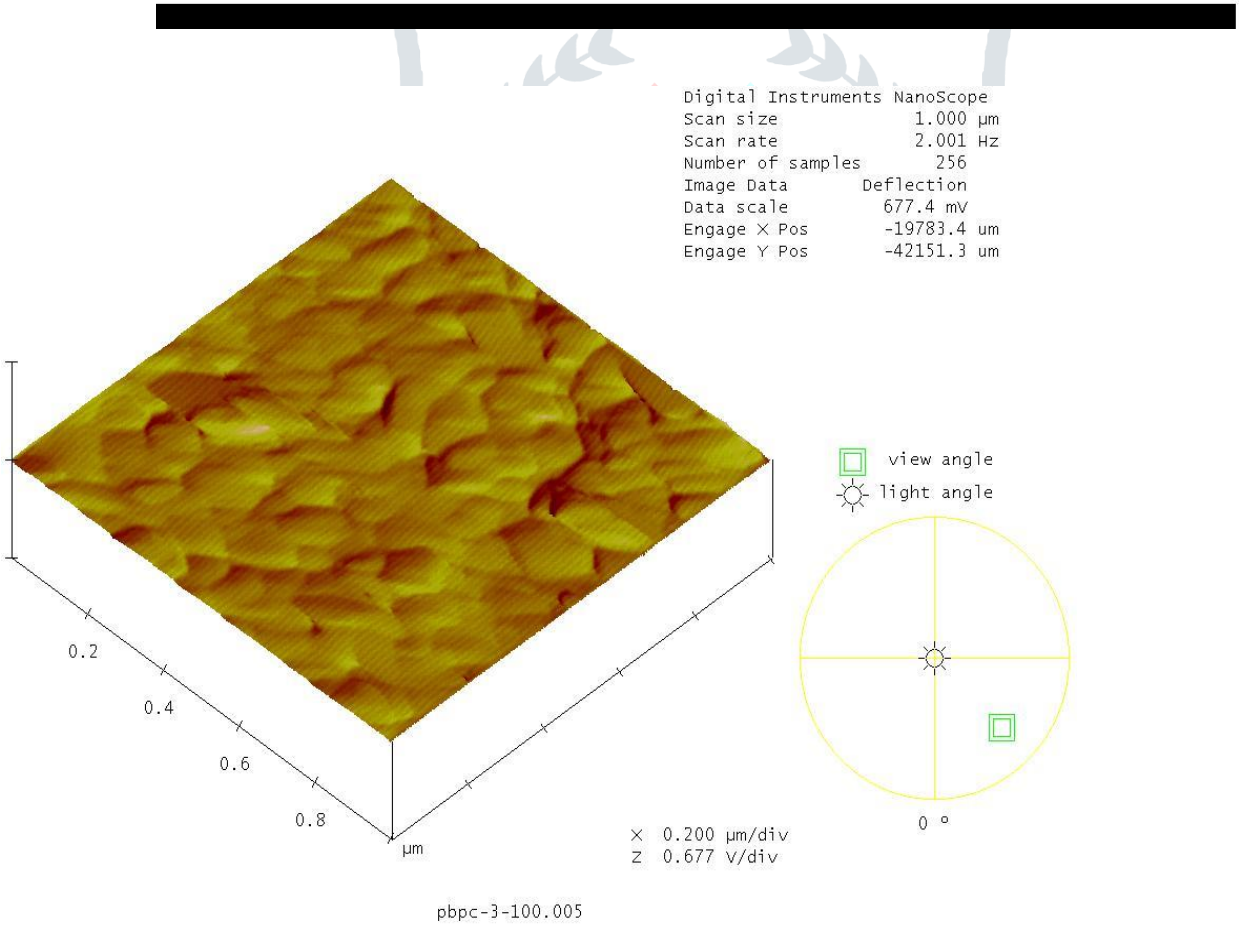


Figure 12 AFM micrographs of PbPc thin films of thickness 450 nm annealed at 373 K

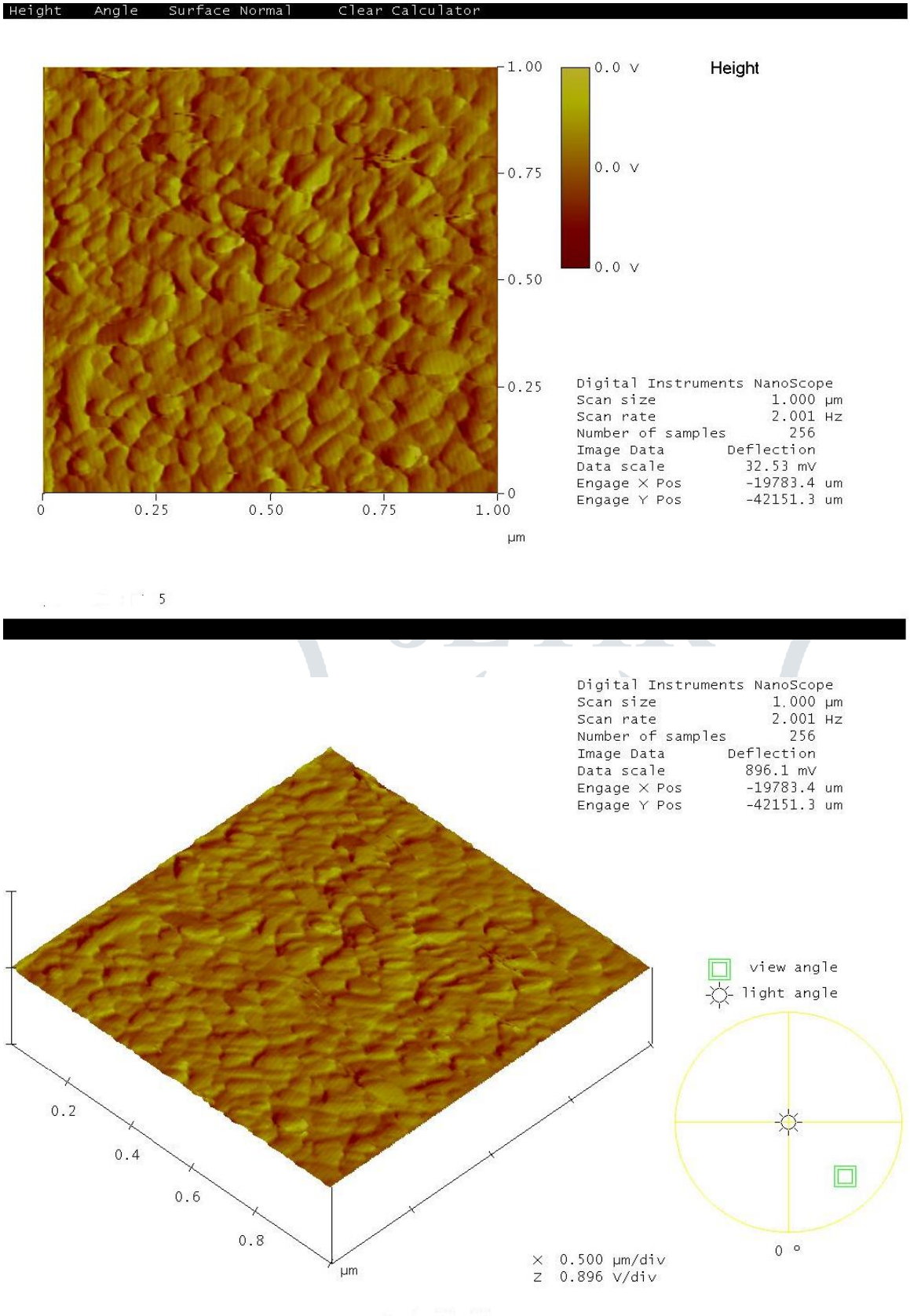


Figure 13 AFM micrographs of CuPc thin films of thickness 450 nm annealed at 323 K

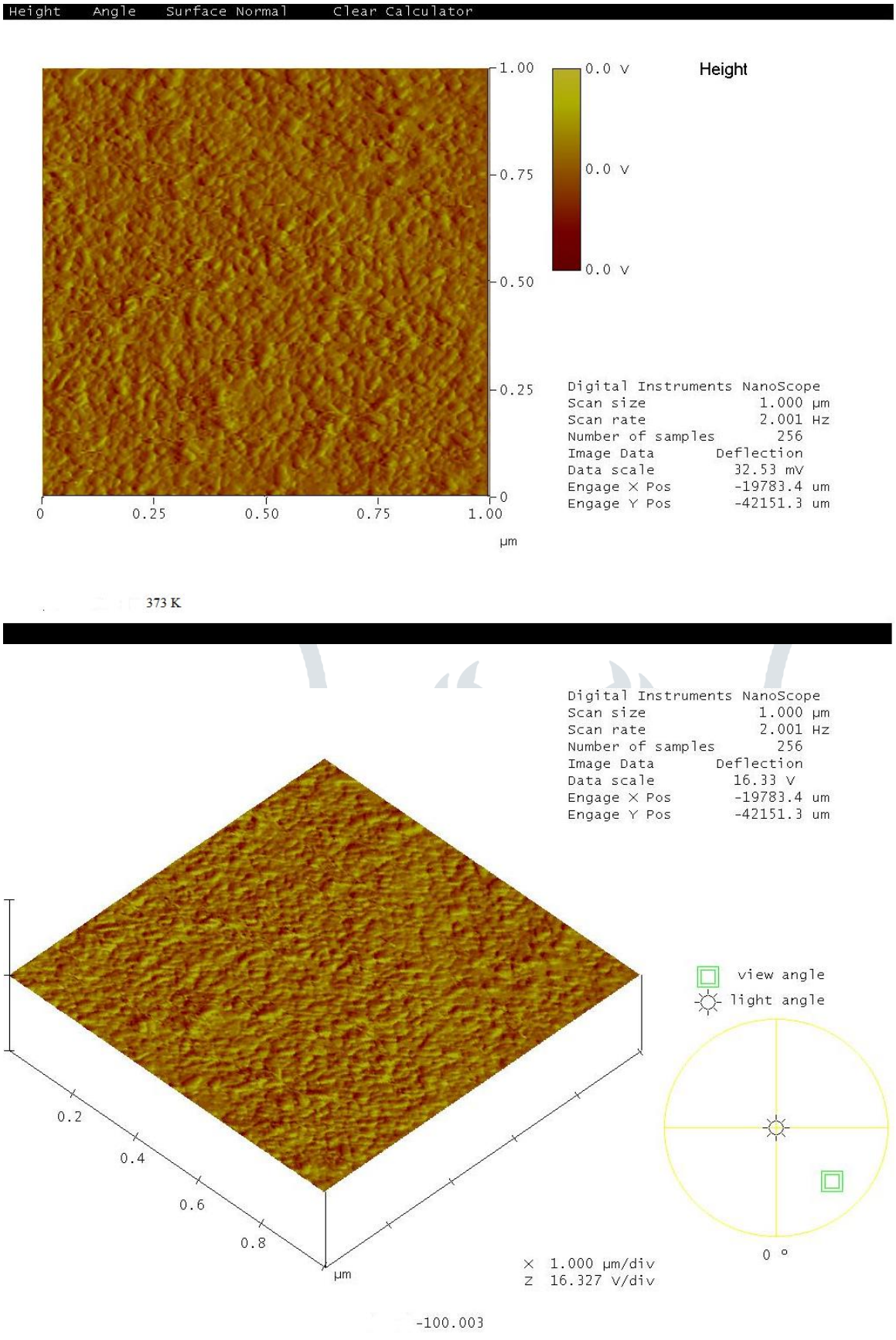


Figure 14 AFM micrographs of CuPc thin films of thickness 450 nm annealed at 373 K

The annealed AFM micrograph shows that the surfaces of the films consists of large holes, some hundreds of square nanometers wide and about 10,000 nm deep. In-between the holes, larger compact areas formed of little crystallites of 20 nm are observed [31].

The AFM image suggests that part of the film has evaporated after the annealing at 373 K. It is very clear that the grain size decreases with increase the annealing temperature. The annealed AFM image indicates a smooth surface. The roughness also decreases with increase in film annealing temperature [26, 29].

4. CONCLUSION

From the SEM image of the films, it is clear that the grain size of the films increase with increase in the thickness. As the temperature increases the smoothness and uniformity of the film also increases. The SEM analysis shows that with increasing thickness, rod like structures with fine particles are seen and with increasing annealed temperature, the surface becomes smooth and uniform.

The AFM analysis helps to study grain size and surface of the films. The crystallite size is roughly constant. The surface area is about 1.2 μm^2 on a 1×1 μm^2 scanned area which is 20% more than a 1×1 μm^2 flat area of PbPc film, the surface area of CuPc is 1.35 μm^2 on a 1×1 μm^2 scanned area which is 35% more than a 1×1 μm^2 flat area.

The surface is more 'disordered' with respect to that of the deposited films and the surface area decrease because of the formation of the smaller crystallites. Before thermal annealing, there were well shapes on the surface in an AFM image. After thermal annealing, it was found that surfaces roughness decreased and lowered shapes at the surface were observed. The annealed AFM image indicates a smooth surface. The roughness also decreases with increase in the film annealing temperature.

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