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Surface Morphology of Cus Thin Films Observed by Atomic Force Microscopy

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شكل السطح الخارجي لغشاء رقيق من كبريتيد النحاس بواسطة مجهر القوة الذرية

أنور قاسم ، هو سون مين ، ليم كييان سيانق و سارافانان ناقالينقام

ملخص: لقد تم ترسيب أغشية رقيقة من كبريتيد النحاس على سطح زجاج مجهر باستعمال حامض الثارثارك في حوض ترسيب كيميائي. تهدف هذه الورقة لدراسة أثر زمن الترسيب السطحي على الشكل الخارجي للغشاء الرقيق. لقد تمت دراسة هيئة السطح الخارجي للأغشية الرقيقة بواسطة مجهر القوة الذرية. إن الأغشية التي تكونت في أقصر مدة تميزت بشكل خارجي متناسق وكانت خالية من الشقوق ولها شكل خارجي كثيف يغطي كل السطح. أما الأغشية التي تكونت نتيجة لزمن ترسيب تجاوز الستون دقيقة أعطت أغشية لم تتمكن من تغطية كل السطح. لذا وجد أن سمك الغشاء الخارجي وشكله يعتمدان بشكل أساسي على زمن الترسيب.

ABSTRACT: CuS thin films were deposited onto microscope glass substrates using the chemical bath deposition method in the presence of tartaric acid as a complexing agent. The objective of this paper was to study the influence of the deposition time on the morphology of thin films. The surface morphology of the thin films was investigated using atomic force microscopy. The thin films deposited for the shortest time were found to be uniform, without cracks and with a dense surface morphology covering the entire substrate surface area. However, the films prepared for 60 min and above indicated incomplete coverage of the material over the substrate surface. The surface roughness and film thickness values that were observed depended mainly on the deposition time.

KEYWORDS: Surface roughness; Film thickness; Thin films; Copper sulphide; Chemical bath deposition method.

1. Introduction

Copper sulphide thin films have been used in photo thermal conversion, solar cells, electro conductive electrodes and microwave shielding coatings. The copper sulphide thin films have been deposited using various methods such as spray pyrolysis (Nascu *et al.* 1997), successive ion layer adsorption and reaction method (Zhuge *et al.* 2009), photochemical deposition (Podder *et al.* 2005), electrodeposition (Anuar *et al.* 2002) and chemical bath deposition (Gadave and Lokhande, 1993). The chemical bath

deposition method is considered to be a cheap method to produce various chalcogenide thin films such as As_2S_3 (Mane *et al.* 2004), MnS_2 (Anuar *et al.* 2010a), In_2S_3 (Asenjo *et al.* 2010), FeS (Anuar *et al.* 2010b), CdSe (Gopakumar *et al.* 2010), PbS (Seghaier *et al.* 2006), SnS (Guneri *et al.* 2010), $Cd_{0.5}Zn_{0.5}Se$ (Kale *et al.* 2007) and $CuBiS_2$ (Sonawane *et al.* 2004) thin films. The chemical bath deposition method is based on the controlled precipitation from solution of a compound on to a suitable substrate. The substrate is immersed either in an alkaline or acidic solution containing the metal ion, chalcogenide source and complexing agent (such as ammonia, ammonium sulphate, sodium citrate, triethanolamine, disodium ethylenediaminetetraacetate and sodium tartrate).

The present work reports the preparation and physical characterization of CuS thin films onto microscope glass substrates using the chemical bath deposition method. The chemical bath contains copper sulfate and thiourea which provide Cu^{2+} and S^{2-} ions, respectively.

It is the first time we report the influence of deposition time ranging from 30 to 180 min on the CuS thin film in the presence of tartaric acid solution. The thin films were analyzed using atomic force microscopy.

2. Materials and methods

Microscope glass slides were used as the substrate during the deposition process. The substrates were first cleaned in ethanol then ultrasonically washed with distilled water. Finally, substrates were dried in an oven at 90 °C. Copper sulfate, thiourea, tartaric acid and hydrochloric acid of analytical reagent grade were used as received. Deionized water (Alpha-Q Millipore) with a resistivity of 18.4 MΩcm was used as the solvent. Aqueous solutions of copper sulfate, thiourea and tartaric acid were separately prepared before the experiment. 20 mL of copper sulfate (0.125 M) and 20 mL of tartaric acid (0.125 M) were mixed in a beaker. During the deposition process, the tartaric acid served as a complexing agent to chelate with Cu^{2+} to obtain complex solution. Then, 20 mL of thiourea (0.125 M) was added and the pH of the solution was adjusted to pH 1.5 by addition of hydrochloric acid using the pH meter. The substrates were immersed vertically into the solution. Then, the deposition was conducted at 80 °C. The beaker was not stirred during the thin films deposition. After completion of film deposition (30 - 180 min), the deposited films were washed with distilled water and dried in air for further characterization.

The surface morphology, thickness and surface roughness were examined by recording atomic force microscopy images with a Q-Scope 250 in contact mode with a commercial Si_3N_4 cantilever. Values of root mean square (RMS) roughness were calculated from the height values in the atomic force microscopy images using the commercial software.

3. Results and discussion

Atomic force microcopy (AFM) has been proved to be a unique, convenient and versatile technique to analyze surface morphology, film thickness and grain size. The three-dimensional and two-dimensional AFM images of copper sulfide thin films deposited at different deposition times in an area of 20µm x 20 µm were as shown in Figure 1(a), 2(a), 3(a), 4(a), 5(a), 6(a) and Figure 1(b), 2(b), 3(b), 4(b), 5(b), 6(b), respectively. Significantly, the microstructures of the thin films changed depending on the deposition time. It can be observed that there are many pinholes on the copper sulphide thin films deposited for 60 min and above. The AFM images indicate these samples were found to cover the surface of the substrate incompletely. The reduction of the deposition time is an effective method to diminish the pinholes on the copper sulphide thin films.

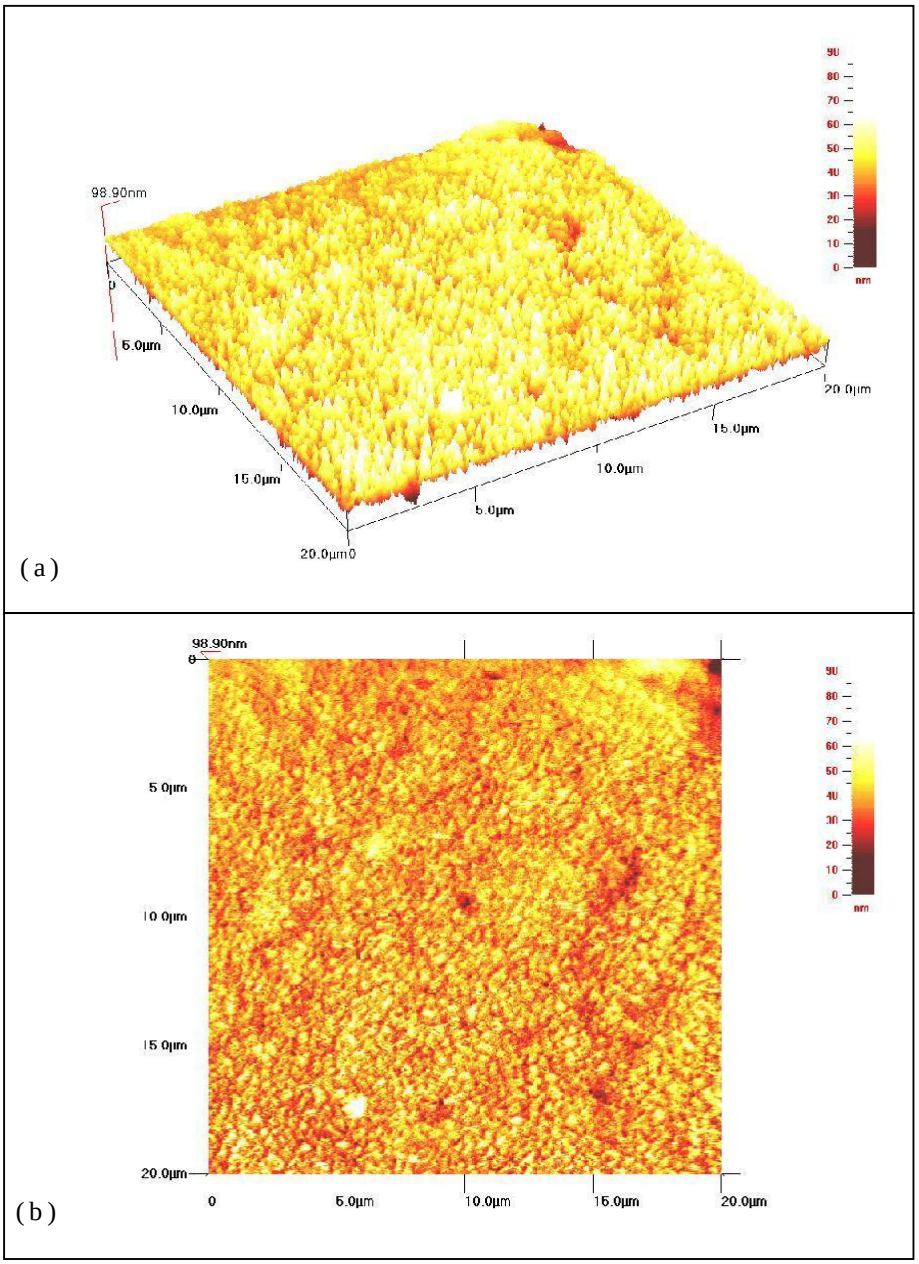

Figure 1. 3-dimesional (Figure 1a) and 2-dimensional (Figure 1b) AFM image of CuS thin films deposited for 30 min.

As the deposition time decreases to 30 min, the surface morphology of the thin films becomes more homogeneous. From the AFM image, it is found that these thin films (Figure 1a, 1b) are uniform, without cracks, with dense surface morphology and covering the entire substrate surface area.

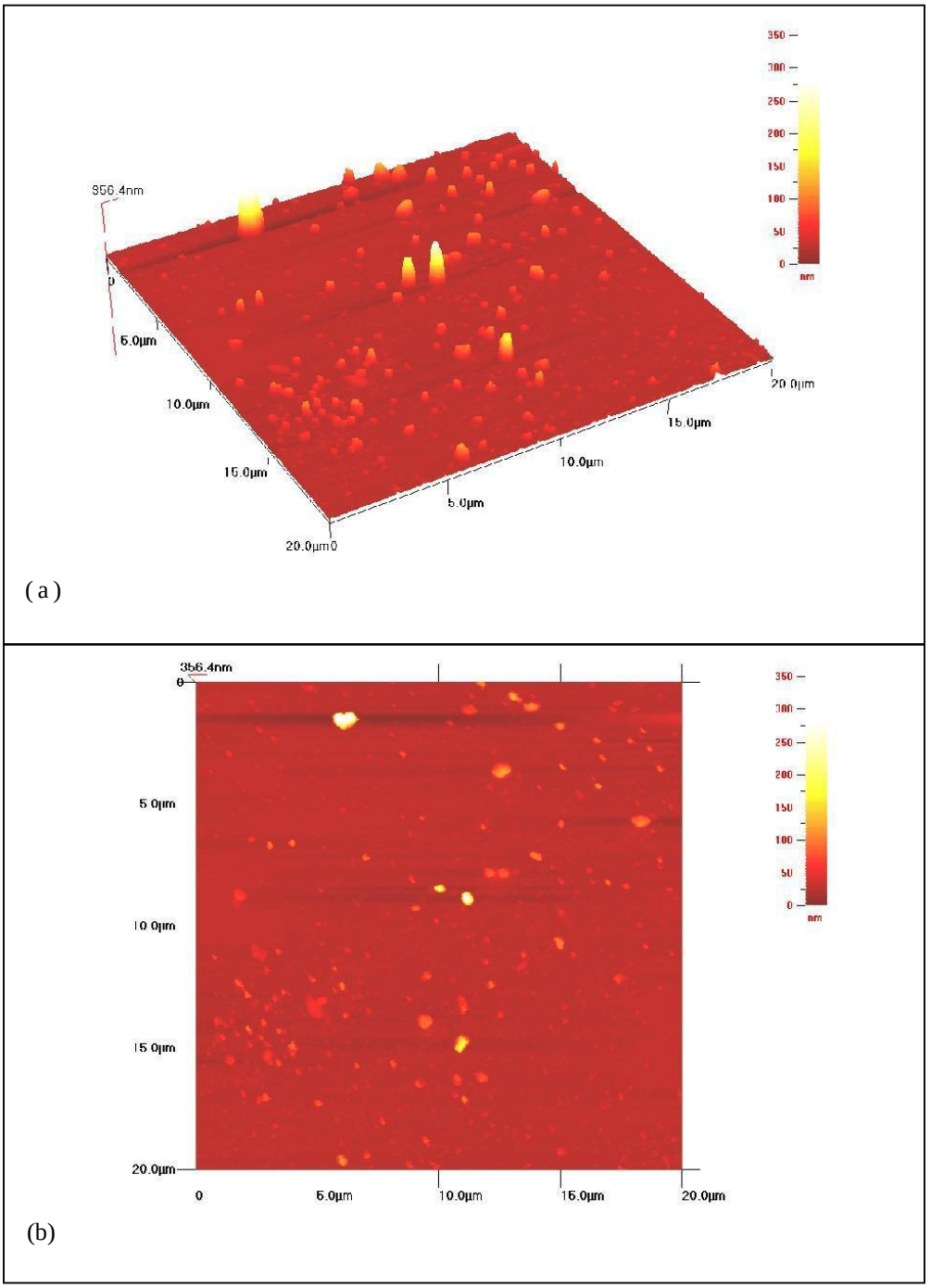

Figure 2. 3-dimesional (Figure 2a) and 2-dimensional (Figure 2b) AFM image of CuS thin films deposited for 60 min.

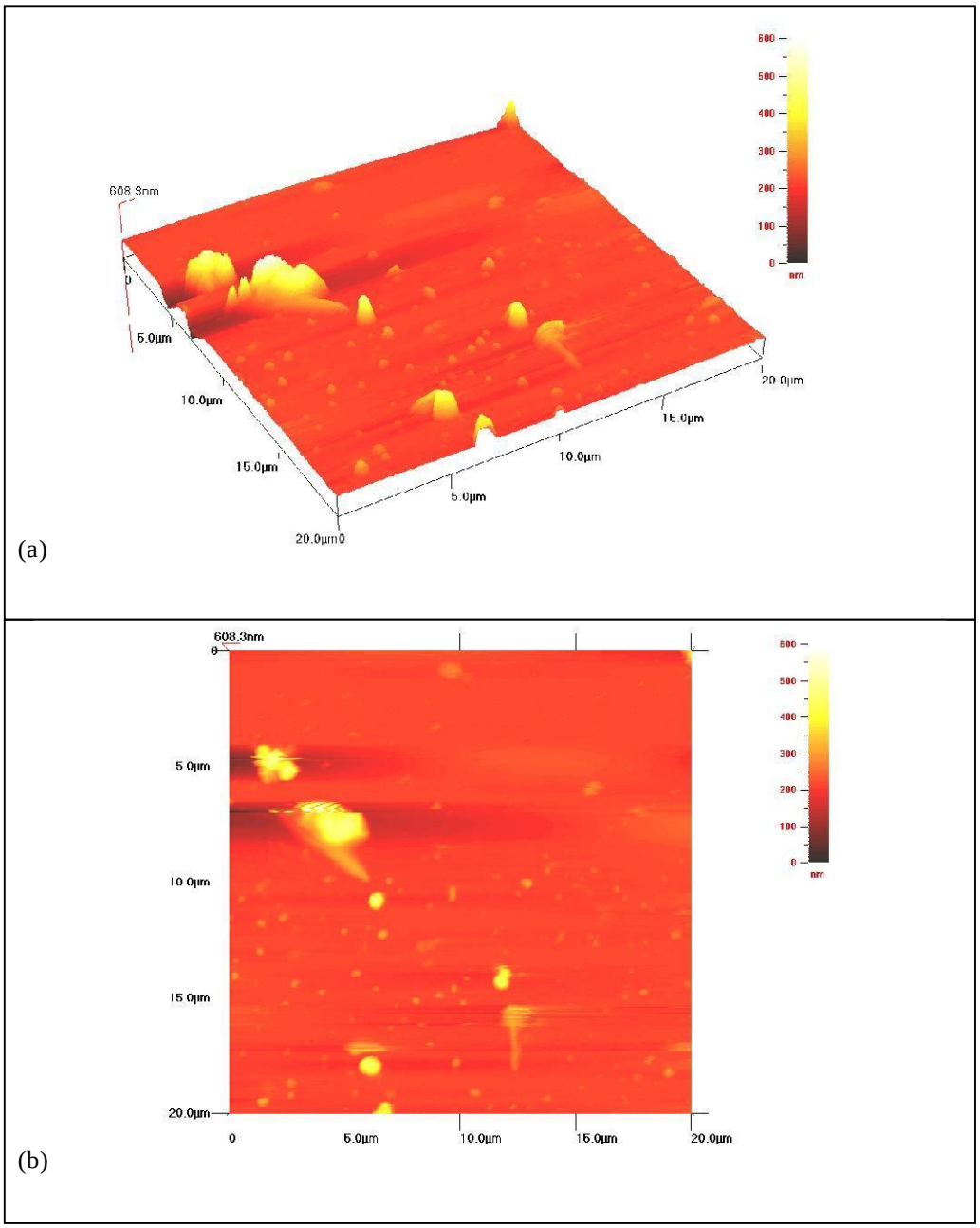

Figure 3. 3-dimensional (Figure 3a) and 2-dimensional (Figure 3b) AFM image of CuS thin films deposited for 90 min.

These films also indicate that grains are very small in size (0.5 µm) with no well-defined grain boundaries. For the films deposited for a longer deposition time, the grain size increased compared to the sample deposited for 30 min and indicates an agglomerated morphology. It is observed that the film formation is

irregular and the sizes of the grains are dissimilar to each other (0.6-2 μm), indicating the non-uniformity in the grains produced at these deposition times. Based on the AFM image analysis, the films deposited for the longest deposition time (180 min) show less particles compared to other films.

Table 1 shows the dependence of the thickness of the copper sulfide thin films on the deposition time. The deposition time was varied from 30 to 180 minutes to obtain copper sulfide thin films with different thicknesses (65.6 to 608.9 nm). Based on Table 1, we can conclude that thicker films are formed for the films prepared for 60 min.

Table 1. Thickness variation versus deposition time of the copper sulphide thin films.

Thickness (nm)	Time
98.9	30
608.9	60
356.4	90
461.2	120
80.7	150
65.6	180

Root mean square (RMS) roughness defined as the standard deviation of the surface height profile from the average height, is the most commonly reported measurement of surface roughness (Jiang *et al.* 2005). The surface roughness values of 7.48 and 31.91 nm were observed for the films prepared for 30 and 60 min, respectively indicating that the surface roughness increases with increasing deposition time up to 60 min. According to the surface roughness (Table 2), the films deposited for 180 min have a smoother surface while the films prepared for 60 min have a rougher surface. We observed that the surface roughness depends on the deposition time. The surface roughness is unavoidable due to three-dimensional growth of the films.

Table 2. Surface roughness variation versus deposition time of the copper sulphide thin films.

RMS (nm)	Time
7.48 nm	30
31.91	60
12.38	90
31.18	120
2.90	150
2.41	180

4. Conclusions

Here, we showed the results of atomic force microscopy of the CuS thin films prepared using the chemical bath deposition technique. The influence of the deposition time on the morphological properties of thin films was investigated. The thin films deposited for the shortest time were found to be uniform, without cracks and with a dense surface morphology covering the entire substrate surface area. However, the films prepared for 60 min and above indicated incomplete coverage of material over the substrate surface. The surface roughness and film thickness values were found to depend mainly on the deposition time.

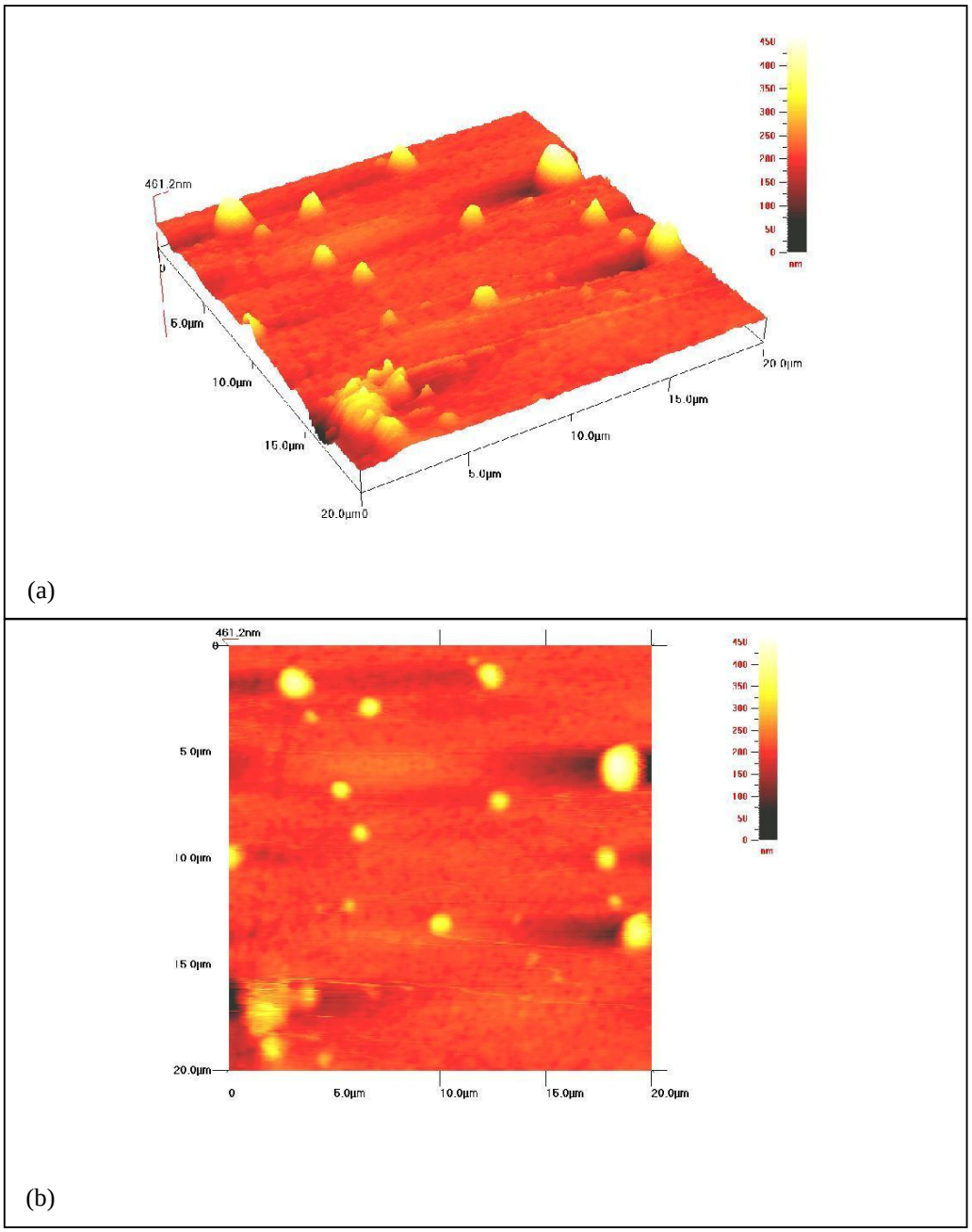

Figure 4. 3-dimensional (Figure 4a) and 2-dimensional (Figure 4b) AFM images of CuS thin films deposited for 120 min.

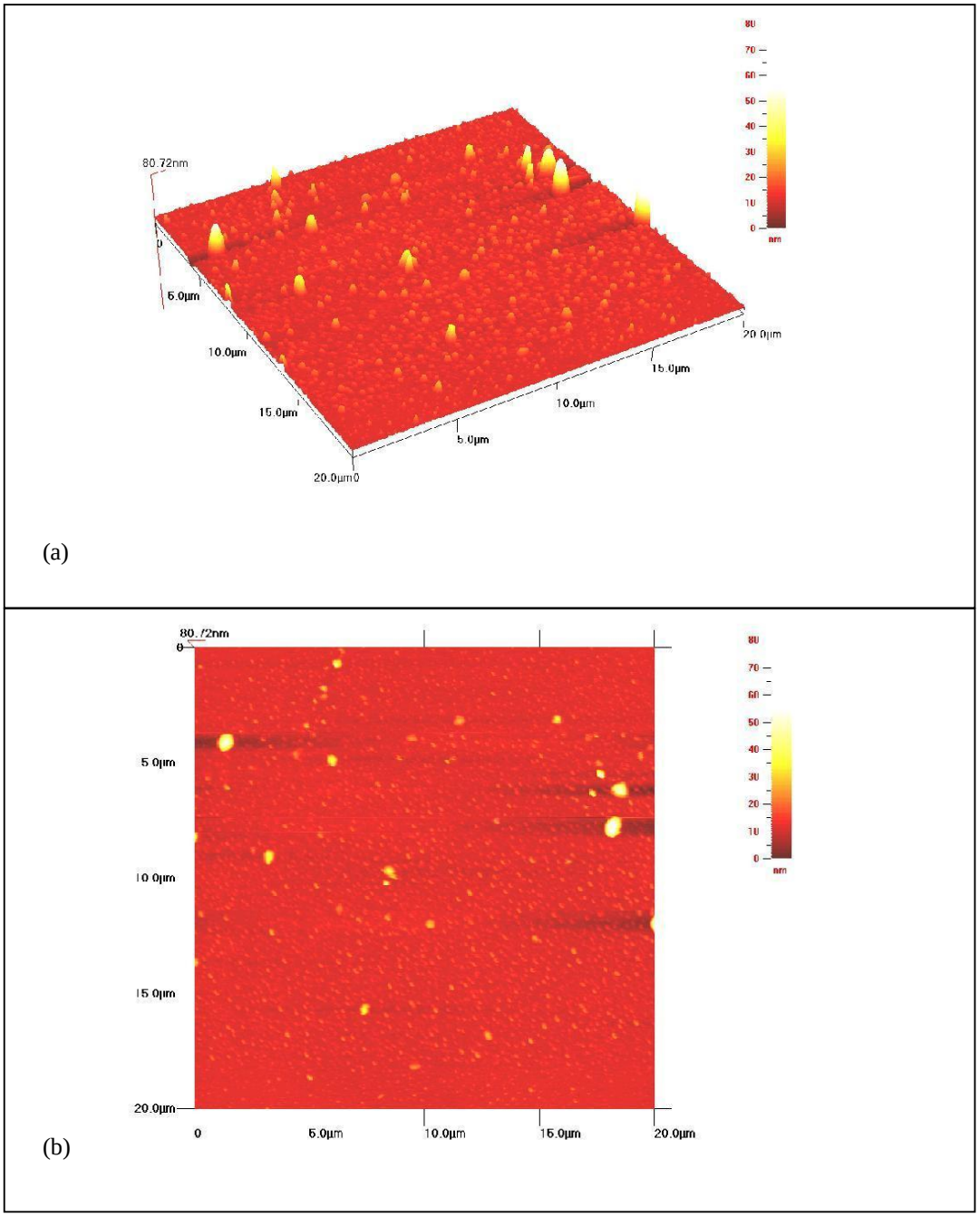

Figure 5. 3-dimensional (Figure 5a) and 2-dimensional (Figure 5b) AFM images of CuS thin films deposited for 150 min.

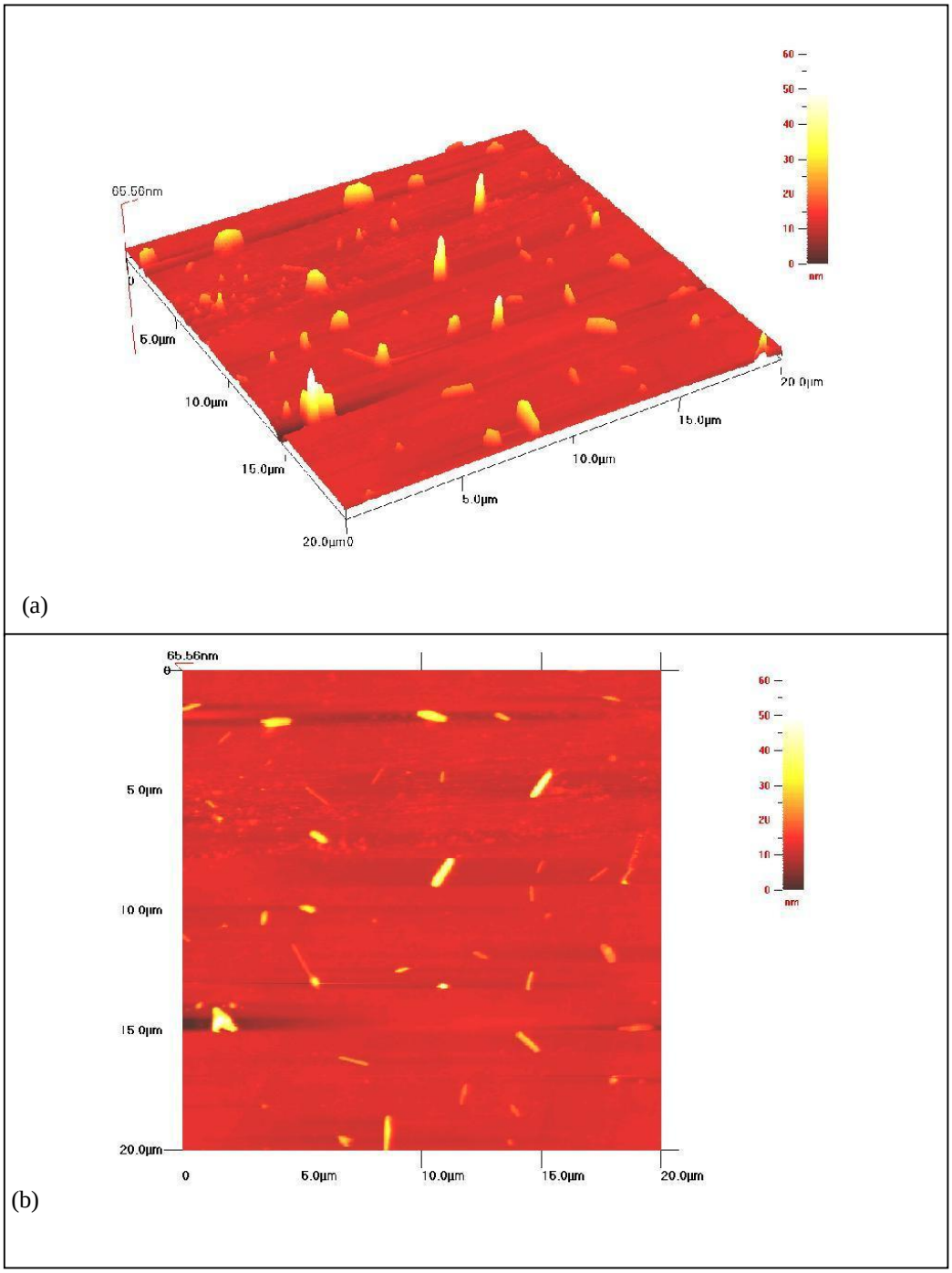

Figure 6. 3-dimensional (Figure 6a) and 2-dimensional (Figure 6b) AFM images of CuS thin films deposited for 180 min.

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6. References

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