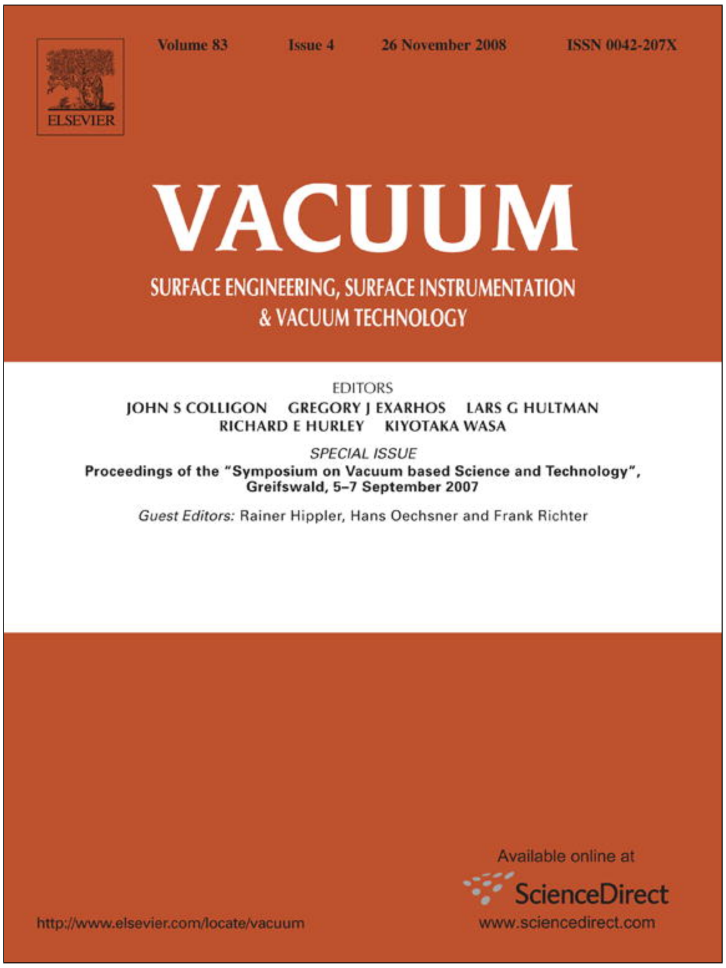

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Surface morphology and composition of films grown by size-selected Cu nanoclusters

Abhijit Majumdar [a,*], Marina Ganeva [a], Daniel Köpp [a], Debasish Datta [b], Puneet Mishra [b], Satyaranjan Bhattacharayya [b], Debabrata Ghose [b], Rainer Hippler [a]

[a] Institut für Physik, Ernst-Moritz-Arndt-Universität Greifswald, Felix-Hausdorff-Strasse 6, 17489 Greifswald, Germany
[b] Surface Physics Division, Saha Institute of Nuclear Physics, 1/AF Bidhan Nagar, Kolkata 700 064, India

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A B S T R A C T

We report the investigation of morphology and composition of copper nanocluster films deposited on Si substrates. The nanoclusters are formed in an aggregation tube at room temperature and magnetron sputtering source is used to get negatively charged Cu-clusters' beam which is subsequently mass-filtered to get size-selected cluster on the substrates as soft-landing process of deposition. For composition of the films, X-ray photoelectron spectroscopy (XPS) technique is used. For morphological changes of the films both scanning electron microscopy (SEM) and atomic force microscopy (AFM) analyses are carried out. Additionally, Energy Dispersive X-ray (EDX) spectra support the compositional and structural informations of the film. The analysis of Cu nanoclusters' films reveals that initial nucleation of Cu clusters takes place in the form of isolated islands and the arrival of subsequent Cu clusters onto Si substrates has preferential aggregation around the preceding clusters forming a mound structure.

1. Introduction

One of the recent trends of nanomaterials' research is the fabrication of thin films composed of nanometer size particles or clusters. Although the main purpose of such a research is aimed at its applications, the fundamental understanding of various aspects of thin film formation and its properties is of great importance. For example, substrate plays an important role in such films formation. The morphology of such films is another crucial factor to use the films in applications of nanomaterials. The production of nanocluster films using the plasma sputtering in the form of magnetron sputtering in combination of gas condensation techniques is being considered nowadays as one of the most controlled methods for such films formation [1]. Nanocluster films are also of strong interest to catalysis studies due to large surface to volume ratio that corresponds to the porous structure of films fabricated by soft landing nanoclusters onto a substrate. The formation of nanoparticles exhibits interesting magnetic, electronic and/or optoelectronic properties [2,3].

In the present work, we investigate the chemical properties (bond structure) and the surface morphology of the Cu nanoclusters that are produced in the form of negatively charged copper clusters in a source operated at room temperature and this low energy cluster beam is deposited on Si substrates to get soft landing films composed of mass selected clusters. There are a few reports on Cu nanocluster deposition [4–6]. In these studies, the scaling aspects are mainly dealt. In our studies we showed that Cu nanoclusters deposition in early stage is dominated by the nucleation of fractal structures that subsequently spread out to form a continuous film in the existing models of DDA (deposition diffusion aggregation) and DLA (diffusion limited aggregation) concepts of nanocluster thin film formation.

2. Experimental

Cu nanoclusters were deposited using DC magnetron sputtering technique of a commercially available NC 200 nanocluster source (Oxford Applied Research [3,7]). The base pressure in the deposition chamber was $\approx 7 \times 10^{-8}$ mbar. During magnetron sputtering with Ar gas the pressure was $\approx 3 \times 10^{-3}$ mbar. The discharge power during sputtering was 130 W (325 V, plasma current 0.4 A). The Ar flow rate is regulated by means of a mass flow controller (MKS Instruments) at a constant flow of 40 sccm (standard cubic centimeter). Clusters were formed by the attachment of free sputtered atoms and by coagulation processes inside the chilled water cooled aggregation tube. The energetic negatively charged clusters ions were passed through a mass filter (QMF 200) to obtain size-selected copper nanoclusters. In the present experiment, a cluster mass of 113,000 amu is selected. The number of Cu atoms in a cluster is found to be 1750 and the corresponding size

* Corresponding author.
E-mail address: majumdar@physik.uni-greifswald.de (A. Majumdar).

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(diameter) of a cluster obtained from the quadrupole filter is 3.4 nm (with Wigner–Seitz radius of Cu atoms 0.141 nm).

Cu nanocluster was produced in the source using the mass filter attached with the system. After the films were prepared X-ray photoelectron spectroscopy was carried out with the as-deposited Cu nanocluster films. X-ray photoelectron spectroscopy (XPS) measurements of the Cu nanoclusters were performed on a VG Microtech (CLAM2: Multi-technique 100 mm hemispherical electron analyser) X-ray photoelectron spectroscope, using Mg Kα radiation (photon energy 1253 eV) as the excitation source and the binding energy (BE) of Au (Au $4f_{7/2}$: 84.00 eV) as the reference. The XPS spectra were collected in a constant analyser energy mode, at a chamber pressure of 10^{-8} mbar and pass energy of 23.5 eV at 0.125 eV/step. After the XPS analysis the Cu nanocluster films were examined by SEM with EDX (FEG ICON) facility. The SEM was employed for this investigation in a number of tilt angles to the sample surface to get an idea about the heights of the morphological features. The EDX spectra were taken both in the region and in the spot modes for 100 s in each case. The samples were then investigated by AFM (NanoScope IV, Veeco Instr., USA) in the tapping mode under ambient condition using Si tip with nominal radius of curvature 12 nm having resonance frequency 428 kHz. The images thus obtained were flattened using the software provided by this AFM.

3. Results and discussions

Quantitative analyses as well as chemical synthesis of the Cu nanoclusters' film have been done by XPS and the measurement gives the percentage amount of copper (including Cu $2p_{3/2}$, Cu $2p_{1/2}$, Cu $3p_{3/2}$, and Cu $3p_{1/2}$) as well as silicon and oxygen. Fig. 1 shows the full scale spectrum of the Cu nanocluster film. Cu 2p, Cu 3p, Si 2p, Si 2s and O 1s bonds have been observed in the XPS analysis. The detail analysis of the peaks Si 2p and O 1s is not discussed here. Si 2s peak is not discussed here, since the atomic scattering factor (ASF) is very less in case of Si 2s to perform quantitative peak analysis by spectral deconvolution method. Large amount of oxygen is appeared due to contamination of the air [8]. A clear image of the possible chemical bonds of copper can be deduced from a deconvolution of the individual Cu 2p and Cu 3p lines into Gaussian line shapes [8].

The deconvoluted XPS spectra of Cu 2p and Cu 3p are shown in Figs. 2 and 3. The best Gaussian fits to the XPS lines resulted in two different peaks for the Cu 2p line and two peaks for the Cu 3p line. Fig. 2 exhibits the peaks at 932.36 eV and 952.20 eV, which have been attributed to the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ bonds, respectively. Similarly, from Fig. 3, the deconvoluted Cu 3p spectrum shows two peaks at 75.20 eV and 77.35 eV which have been assigned to Cu $3p_{3/2}$ and Cu $3p_{1/2}$ bonds, respectively [9]. Table 1 shows the peak position and the corresponding amount (%) of copper, oxygen, metal oxide, silicon, and silicon oxide in the deposited Cu nanocluster film. It has been found that copper is 13%, oxygen (total) 41%, metal oxide (CuO, oxygen bound to Cu) 11%, Si 26% and SiO (oxygen bound to Si) 9% in the deposited Cu nanocluster film. The approximated error bar of the calculated percentage amount of the chemical composition is about ±2%; depends on the XPS peak fitting parameters. Large amount of oxygen is adsorbed at the surface of the Si wafer and rest of oxygen is bound to Cu as well as to Si. Since it is ex situ measurement and the deposited Cu nanocluster film is oxidized due to air contamination.

Figs. 4–6, show the morphological behavior of Cu nanoclusters' films deposited on Si (100) substrates. Along with the

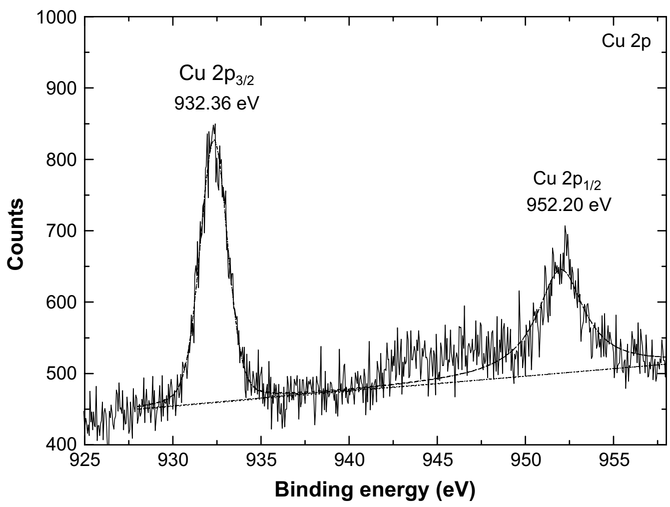


Fig. 2. Typical Cu 2p, XPS spectra of Cu nanoclusters' film deposited on Si substrate.

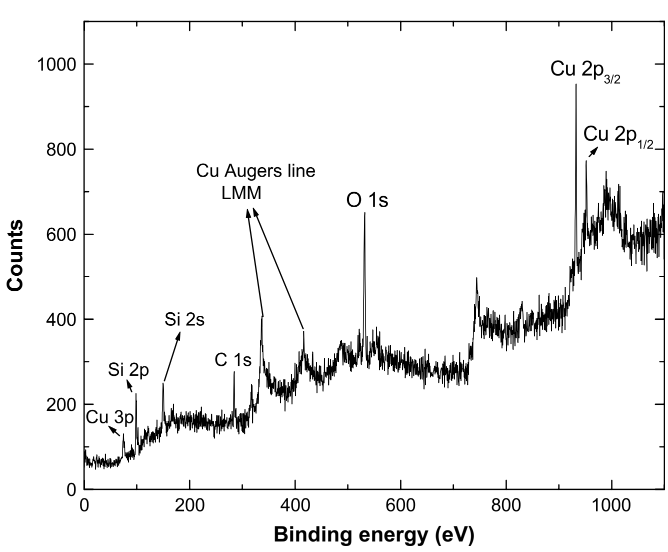


Fig. 1. Full scale spectrum of the Cu nanoclusters' film deposited on Si (100) substrate.

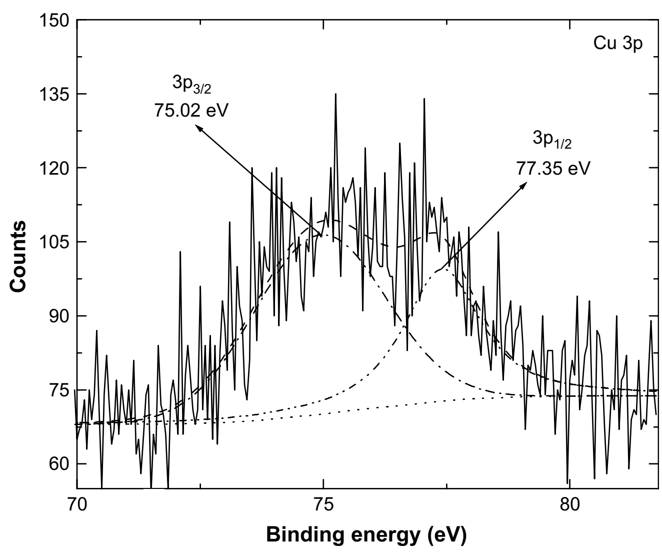


Fig. 3. Typical Cu 3p, XPS spectra of Cu nanoclusters' film deposited on Si substrate.

Table 1
Deconvoluted peak position and amount (%) of Cu (2p and 3p), O 1s and Si 2p obtained from XPS analysis

Peak	Peak position (eV)	Amount (%)
Cu $2p_{3/2}$	932.36	6
Cu $2p_{1/2}$	952.20	4
Cu $3p_{3/2}$	75.20	2
Cu $3p_{1/2}$	77.35	1
O 1s	531.95	41
Metal oxide (O bound to Cu)	530.35	11
Si	98.7	26
SiO (O bound to Si)	102.06	9

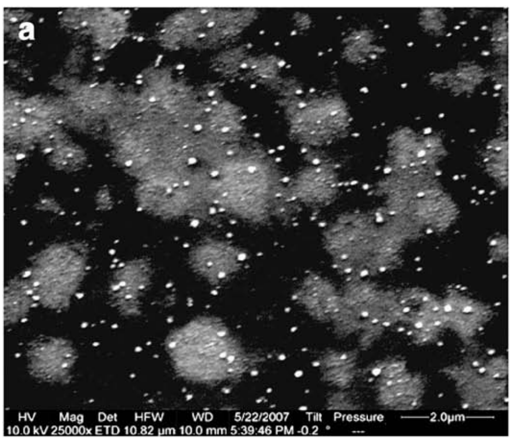
morphological studies, EDX spectra corresponding to the SEM images were taken at both region and spot modes. The SEM observation of Cu nanoclusters' films reveals that initial nucleation of Cu clusters takes place in the form of isolated island and the arrival of subsequent Cu clusters onto Si substrates has preferential aggregation around the preceding clusters forming a structure as seen in Fig. 4(a). The image of this figure shows that some parts are locally populated by Cu clusters (white contrast in the images), while the remaining (black region) portions are still Si rich. Some tiny clusters islands are also seen in the image. The morphology of these samples also shows irregular cluster islands with varied size distributions. The EDX spectra were taken from a white contrast region, where Cu rich clusters are presumably considered. The EDX pattern clearly shows only a stress signature of Cu has arrived at the region as shown in Fig. 4(a). During the deposition of Cu clusters there was a slight variation of thickness of the Cu film. However, Fig. 4(a) was taken on the perimeter of the deposited Cu film. Fig. 5(a) shows an image taken from the central part of the deposited film and here Cu islands are more prominent. This is also substantiated by the EDX spectra shown in Fig. 5(b), where Cu signal is more pronounced than that of the spectra in Fig. 6(b). However, this EDX spectrum was taken in the spot mode as indicated in Fig. 5(a) by an arrow. A closer observation shows that due to electron bombardment the cluster was deformed and took an elongated shape. In order to get more information from the SEM images we examined the Cu nanocluster film at tilt angles in the SEM observations. Fig. 6(a), shows such an image at relatively lower magnification. The morphology as seen in this image clearly shows a fractal kind of cluster evolution on Si substrate. When this image is magnified we observed the morphology as shown in Fig. 6(b), where Cu clusters are prominently seen on Si substrate. This image was taken at a tilt angle of 40°. From this image one can get some idea about the height of the clusters apart from the spatial dimension of the clusters so formed.

Atomic force microscopy (AFM) analysis of the Cu nanocluster films was carried out to investigate the morphology and to obtain information about the height of the Cu nanoclusters agglomerated on the Si substrate. Fig. 7(a) and (b) shows the morphology of the film examined by AFM in tapping mode under ambient condition. Analysis of the AFM images shows that the average height of the islands are about 17 nm, where we found diameters of these islands are about 80 nm from SEM images (Fig. 6(b)). This means that the clusters have coagulated on the substrate surface.

Three physical phenomena arise [9] when clusters are deposited on a substrate. These are (i) deposition of clusters, (ii) diffusion of clusters on the surface and (iii) interaction of the deposited clusters. Initially, as nanoclusters arrive on a substrate, the surface coverage remains low. Subsequently, the already deposited clusters along with other clusters are diffused to form islands on the substrate. Careful observations of SEM as well as AFM images reveal that the character of cluster attachment to the Si surface is similar to that in the case of formation of fractal structures when solid particles attach to a surface and can move over it. This mechanism of joining of solid particles on a surface, in accordance with the DLA model (diffusion limited aggregation) [10–13] or DDA model (deposition diffusion aggregation) [14], accounts for diffusion motion of particles on the surface. This model developed under various conditions was analyzed [15] and can be applied to the present case. According to DLA model, a cluster is assembled by adding individual particles to it. A definite number of particles are introduced into the formation region initially and the particles coalesce when they collide with one another. This will initially result in the appearance of a larger number of smaller clusters, and subsequent collisions will lead to their aggregation. In the morphology represented by Figs. 4–6, joining of clusters takes place and these connected clusters form fractal structures, i.e., fractal clusters, as seen more prominently in Fig. 6(a).

4. Conclusion

We have investigated the morphological and chemical aspects of Cu nanocluster films deposited onto silicon substrate at room temperature. Cu 2p, Cu 3p, Si 2p, Si 2s and O 1s bonds have been observed in the XPS analysis. XPS analysis reveals that the Cu nanoclusters' film composed of 12.65% of Cu, 41.28% of oxygen, 10.50% of metal oxide, 26.43% of Si 2p and 9.13% of Si O. Moreover it is observed that, the Cu nanoclusters' film is highly oxidized. The morphology shows that clusters are diffused on the surface to form



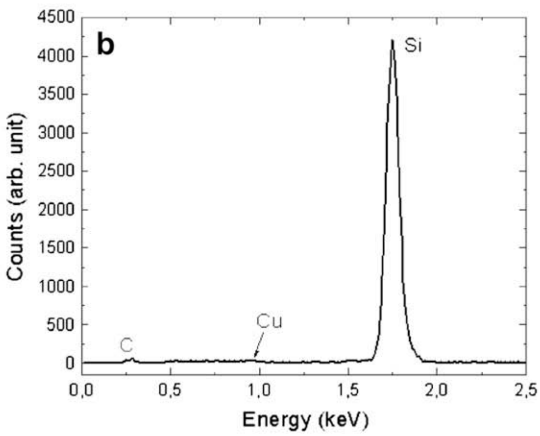


Fig. 4. Scanning electron micrograph of the size-selected (diameter = 3.4 nm) Cu nanoclusters' film deposited on Si substrate at relatively lower magnification and (b) its corresponding EDX pattern in the region mode.

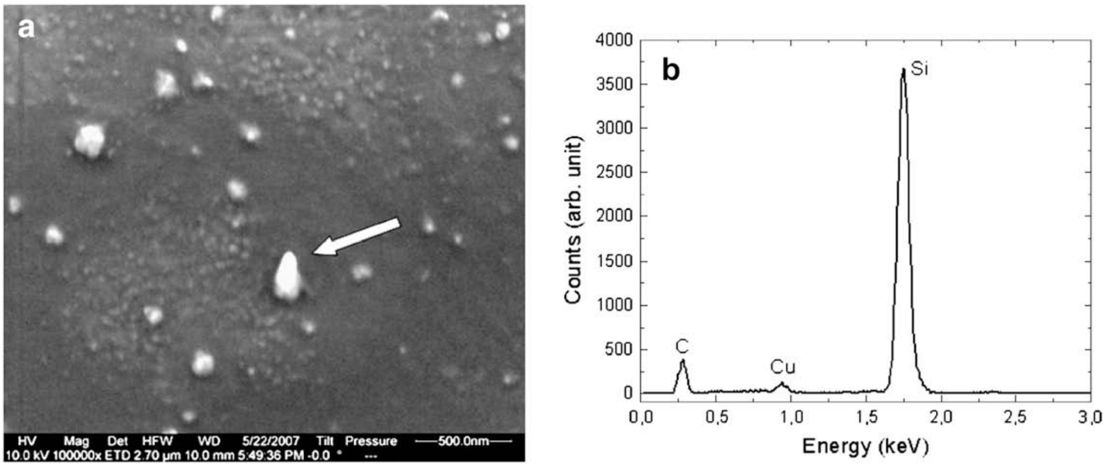


Fig. 5. Scanning electron micrograph of the size-selected (diameter = 3.4 nm) Cu nanoclusters' film deposited on Si substrate and (b) its corresponding EDX pattern in the spot mode. The spot is indicated by the arrow and it may be noted that the spot is melted due to electron bombardment (about 100 s) and the feature is elongated.

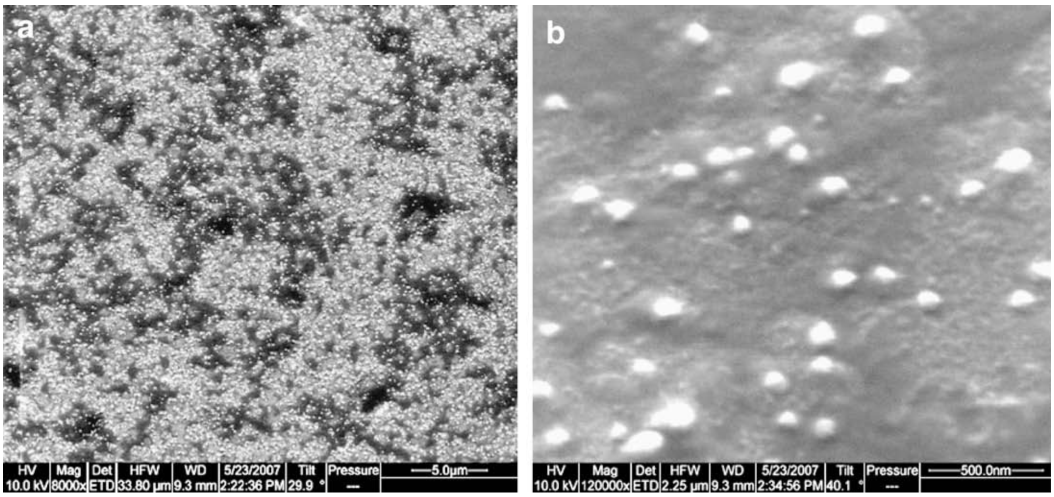


Fig. 6. Scanning electron micrograph of the size-selected (diameter = 3.4 nm) Cu nanoclusters' film deposited on Si substrate at tilt angle of 30° at a lower magnification. (b) SEM on the same region at higher magnification at a tilt angle of 40°.

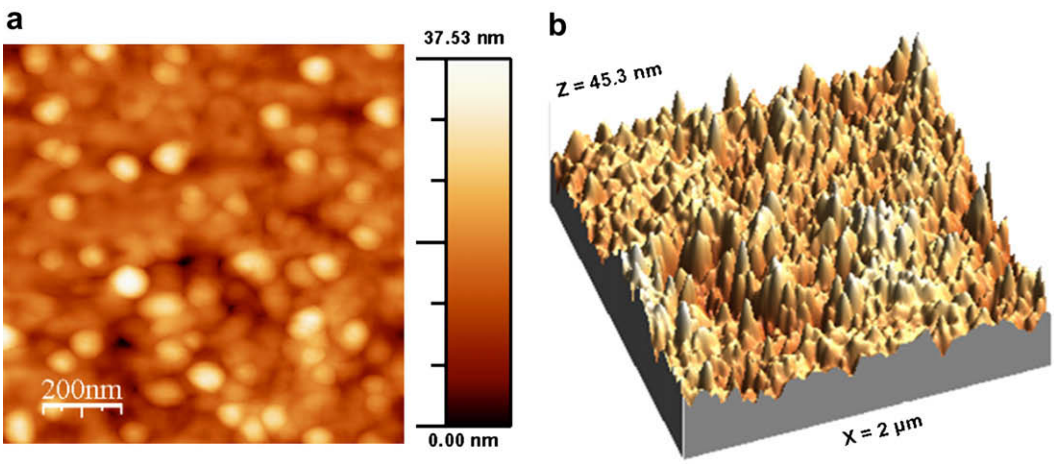


Fig. 7. Atomic force microscopy analysis of Cu nanocluster (diameter = 3.4 nm) deposited on Si substrate, showing (a) two-dimensional image with RMS roughness of 4.7 nm and average height of 15.2 nm and (b) three-dimensional image with RMS roughness of 5.4 nm and average height of 23.7 nm. These images ((a) and (b)) were taken from two regions of the deposited films.

fractal-like structure and the flattening takes place as a result of impact energy of the clusters.

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