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Scanning tunnelling microscopy studies of nucleation and growth of silver films

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Different stages of nucleation and growth of silver films grown on gold-coated mica by vacuum evaporation have been studied by using scanning tunnelling microscopy. These studies reveal a complete picture of the sequence of events from initial island formation to a fairly smooth film surface. The surface roughness pattern matches the growth process. The angle of contact of the cap-shaped silver islands formed during the initial stages of growth was found to be about 12°, confirming three-dimensional island type of growth.

1. Introduction

To understand the nucleation and growth of thin films and the dependence of growth mechanisms on deposition parameters, electron microscopy techniques have been extensively used [1]. Based on these observations [2], four stages of the thin-film growth process have been identified: (i) nucleation and island structure, (ii) coalescence of islands, (iii) channel formation, and (iv) formation of continuous film. When the thin-film growth is influenced mainly by surface diffusion of adatoms on the substrate, rather than by direct impingement from the vapour phase, nuclei formed at the initial nucleation centres grow as three-dimensional islands. These islands, as they grow vertically and laterally, touch each other, merge together to form larger islands, and, at the same time, expose fresh surface for secondary nucleation. A secondary nucleus grows until it touches a neighbour and coalesces with it. As the islands grow, large shape changes occur in the immediate vicinity of the islands. Consequently, the islands become elongated and join to form a continuous network structure in which the deposited material is separated by irregular regions [1].

With the advent of the scanning tunnelling microscope (STM)[3], there is renewed interest in such studies because it allows direct imaging of the surface structure of as-deposited thin films down to atomic resolution, without further sample preparation. Additionally, STM has high lateral and vertical resolution for both periodic and non-periodic surfaces, and thus has the potential to reveal three-dimensional images of the morphology of surfaces with associated steps, facets, grain boundaries and dislocations. It also allows us to make measurements of the contact angle between the substrate and the islands formed during the initial stages of nucleation. A few STM studies [4–7] have recently been devoted to the characterization of film post-nucleation growth. Surface roughness studies of sputtered thin films of Fe_3O_4 [8] and gold [9, 10] have been made by comparing STM and TEM observations. Although STM studies on the very early stages of nucleation of metal overlayers on semiconductor surfaces have been performed by several groups under ultra-high-vacuum and *in situ* conditions [11], a study of the complete film-growth process up to the formation of a uniformly smooth film surface, has not been attempted. In this paper we report STM studies on the nucleation and growth mechanism of silver thin film on gold-coated mica deposited by vacuum evaporation, which reveal direct pictorial evidence of how an island type of growth takes place, starting from island formation to development of a smooth continuous film.

The contact angle, (θ), between the condensate material and the substrate, is dependent on the surface energies between condensate and vapour, between substrate and vapour, and between substrate and condensate. When $\theta = 0°$, complete wetting of the surface occurs. When $\theta = 180°$, there is no wetting and conditions do not favour a thin-film growth. When θ lies between 50° and 105°, clusters will form with low activation energy at steps rather than on the flat surfaces [1]. Experimental measurement of θ is reported here for the first time, which can be correlated to the observed growth mode.

2. Experimental procedure

Thin films of silver were deposited on mica by vacuum evaporation at a base pressure of 2×10^{-6} torr (1 torr = 133.322 Pa). Using a quartz crystal thickness monitor, the rate of deposition was maintained at $0.35\ \mathrm{nm\,s^{-1}}$. Films were deposited for different times on to substrates maintained at room temperature. The thicknesses of the deposited films were measured by a Form Talysurf (Taylor and Hobson). The as-deposited films were transferred to the STM sample holder as soon as they were removed from the evaporation unit.

Our STM consists of a double tube scan head (UHV-635 of RHK Technology Inc.) with an

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"inchworm" motor for positioning the tip over the sample without any crashing. The films were mounted on to the sample-holding stub using silver paste for electrical contact between the thin-film surface and the stub. It was dried in a vacuum desiccator for 48 h to avoid any possible drift during scanning due to adhesive shrinkage. The STM images were taken by scanning the films in air using an electrochemically etched tungsten tip [12] as probe. The quality of the tip was confirmed by obtaining atomically resolved images of the (0 0 0 1) surface of a graphite single crystal. Films were scanned in the constant current (topographic) mode with the tunnelling current fixed at 1.2 nA at a biasing voltage of 200 mV. Several scans ranging from 10 nm × 10 nm to 1 μm × 1 μm were recorded for each film. The surface roughness R_s, of each of these films was calculated as the average of the arithmetic mean of the magnitude of departures from the mean value of a line profile. The final value of R_s is the average of R_s values calculated by taking line profiles in different directions.

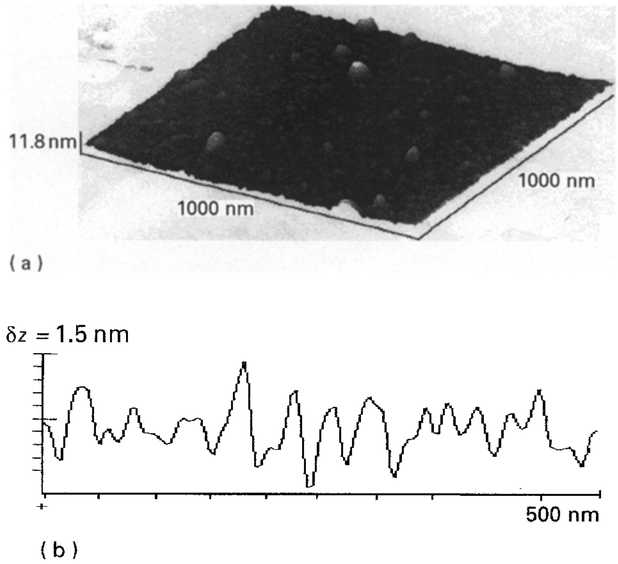

Figure 1(a) STM image of a 5 nm silver thin film on gold-coated mica substrate. The image shows silver islands of varying sizes and heights nucleated in the initial stages of film growth. (b) A line profile along the dark line drawn in (a), showing a height variation of less than 2 nm.

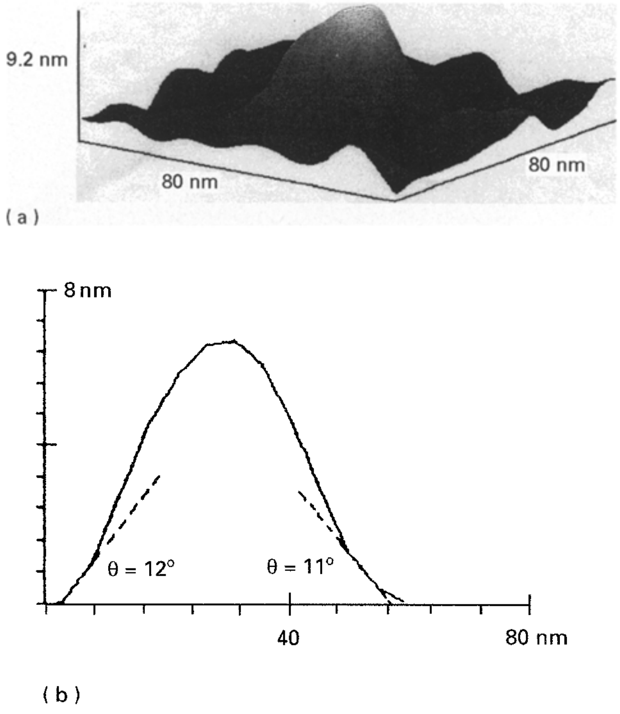

Figure 2(a) STM image of a single silver island in three dimensions. (b) A line profile across the island showing the angle of contact.

3. Results and discussion

Silver films of thickness less than 10 nm grown on a cleaved mica substrate did not show any electrical continuity (being discontinuous) and thus their observation by STM was not possible. Therefore, nucleation of silver films deposited on gold-coated mica was studied. The underlying gold film gives a continuous electrical contact for tunnelling to take place. The STM of these films revealed the formation of silver islands of height 5–12 nm and covering an area ranging from 1–10 nm^2, as shown in Fig. 1a. The gold coating on the mica substrate was done by d.c. sputtering at high pressure (~ 0.1 torr) which results in a fine-grained polycrystalline deposit with a surface roughness of less than 2 nm, as depicted by a line scan profile (Fig. 1b), taken along the dark line of Fig. 1a. The three-dimensional island formation at small thicknesses is an indication of a large nucleation barrier.

When the shape of a silver island (Fig. 2a) was examined by scanning its profile, it was observed to be cap-shaped (Fig. 2b) in most cases, the height ranging from 5–11 nm. This gives an estimate (~ 10^2–10^3 nm^3) of the volume of the islands which are formed on the surface. The contact angle between the silver caps and the substrate, θ, lies in the range 10°–15°.

As the islands grow in size, they touch each other and, at around 30 nm thickness, a perfectly conducting film is obtained in virgin mica substrate. The STM image of 30 nm film shown in Fig. 3a, indicates that the silver has grown in the form of islands with an average grain diameter of 18 nm and a density of about 5×10^{11} islands/cm^2. The coarse-grained film is another indication of a large nucleation barrier for silver condensation on mica at room temperature. This is also the reason why it is not possible to obtain an electrically continuous film up to a thickness of 30 nm. As the film grows, the island size further increases, and there is coalescence of neighbouring islands to form large single grains. During coalescence, as the surface area is reduced, gaps occur between the newly formed grains. This is seen in Fig. 3b which is a 100 nm × 100 nm scan of 50 nm thick film.

As the islands grow larger, shape changes occur near the regions in the immediate vicinity of the junctions of the islands. Consequently, the islands become elongated and join to form a continuous network structure with ginger-like formation. This leads to some regions of lower thickness, which may be as much as 15 nm deep as shown in Fig. 3c. Just as the

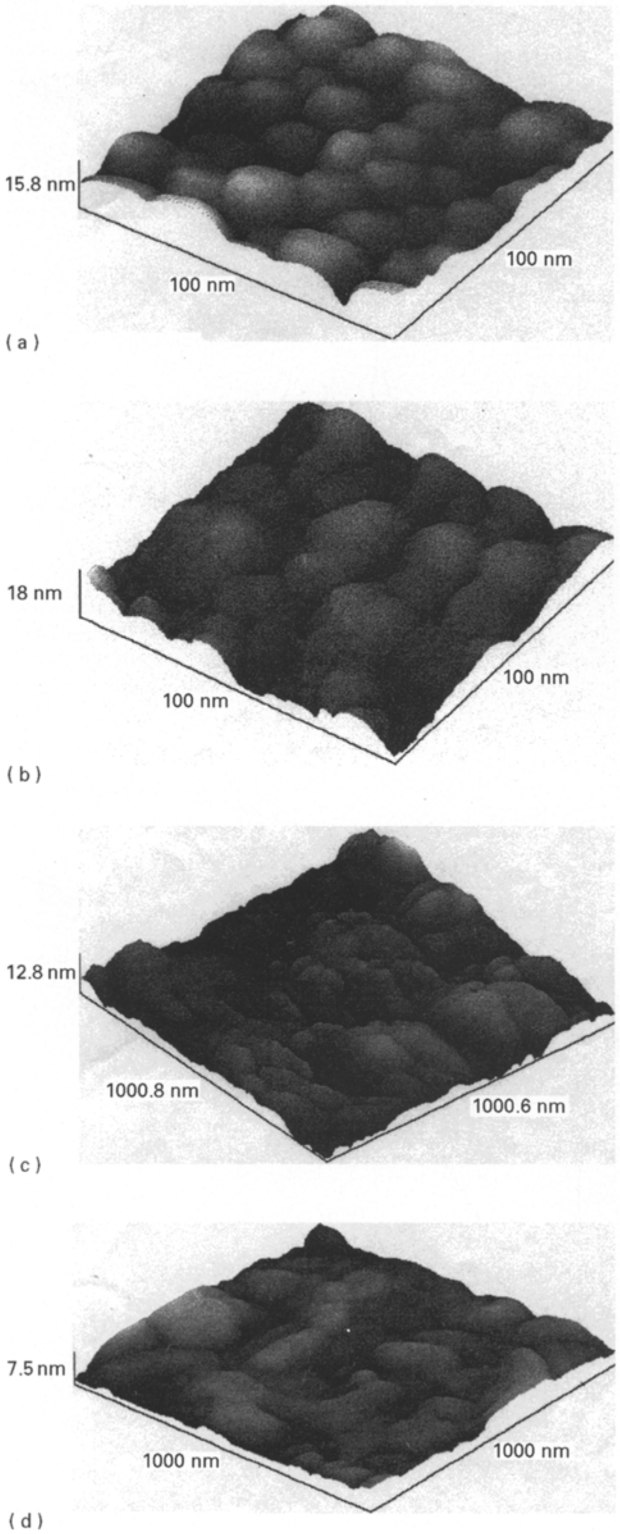

Figure 3 Different growth stages of silver film on mica, depicted by STM images of films of thickness (a) 30, (b) 50, (c) 100, and (d) 200 nm.

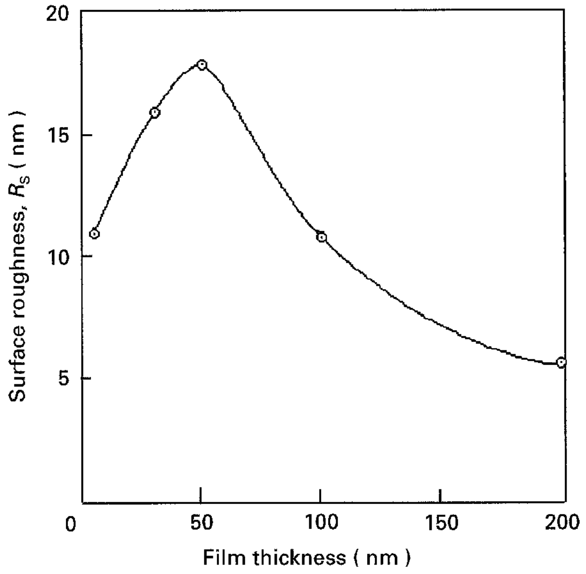

Figure 4 Surface roughness as a function of film thickness of silver on mica as measured by STM.

tentacles of ginger grow along the plane on further increase in thickness, the deposited material tends to cover the surface uniformly, reducing the average surface roughness to around 6 nm as seen over an area 1 μm × 1 μm. The micrograph in Fig. 3d shows the formation of a continuous film without any pores at a thickness of 200 nm.

The exposure of the film surface to air for STM imaging might have changed its surface chemistry due to adsorption of gases. However, this change and its effect on the tunnelling current are expected to be uniform all over the film surface. Thus, the topographic data collected by operating STM in a constant current mode will still represent the true surface profile.

The surface roughness, R_s, of these films of different thicknesses was measured by using the STM (Fig. 4). R_s increases initially with increasing film thickness with a maximum of 18 nm at a film thickness of around 50 nm, and then decreases continuously to 6 nm for 200 nm thick film. Owing to the initial formation of three-dimensional islands which grow in height more than in area because of a large nucleation barrier, R_s is of the order of the film thickness. As coalescence of islands takes place, fresh areas are exposed and there is a sharp increase in R_s. Once the substrate area is covered, R_s decreases continuously with increasing film thickness.

Conductivity measurements of silver films show metallic behaviour in all films thicker than 30 nm. The exact film thickness at which a continuous film formation commences, as well as the nature of the growth mode, are dependent upon the size of the nucleation barrier which, in turn, is dependent upon the nature of the film and substrate materials, substrate temperature, and deposition rate [1]. A more detailed STM study is underway to analyse quantitatively the effect of these deposition parameters on the film nucleation and growth.

4. Conclusions

Scanning tunnelling microscopy has provided a very detailed and quantitative description of the three-dimensional nucleation and growth stages of silver films deposited on virgin and gold-coated mica. In addition to verifying the qualitative results obtained by electron microscopy, direct measurements of surface roughness and contact angle have been obtained for the first time. These data should be of considerable interest for refining nucleation theories.

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