Scanning tunneling microscopy of surface microstructure on rough surfaces

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An important feature of the scanning tunneling microscope (STM) is its ability to image nonperiodic or disordered surfaces with atomic or near-atomic lateral and vertical resolution. Many physical and chemical properties of surfaces and interfaces are sensitive to, and in some cases determined by, random roughness or surface disorder, although our understanding is hampered by the lack of suitable techniques for investigating atomic-scale features. We present STM results for microcrystalline Ag and nanocrystalline silicon surfaces which demonstrate the unique topographic data obtainable using the STM. For comparison, the STM studies are complemented by data obtained using conventional techniques. Furthermore, the ability of the STM to investigate the influence of growth conditions on surface morphology, such as ion bombardment, adsorption, and condensation temperature, is discussed.

1. Introduction

Surface disorder and random roughness can play a determining role in many physical and chemical properties of surfaces and interfaces. Despite the importance of these phenomena in both fundamental and technological areas of research, our understanding of atomic- and near-atomic-scale topographies for nonideal surfaces is at best phenomenological.

For single-crystal surfaces, small perturbations in surface order can be assessed from the quality of diffraction patterns and diffuse scattering using low-energy electron diffraction (LEED) or reflection high-energy electron diffraction (RHEED). For example, the critical role of atomic steps at Si-SiO_2 interfaces used for MOSFET devices has been demonstrated using spot profile analysis of LEED (SPA–LEED) [1].

For polycrystalline, amorphous, or inhomogeneous surfaces, the experimental methods available with sufficiently high lateral resolution *and* vertical sensitivity are limited.

Scanning electron microscopy (SEM) is useful only for studying relatively large topographical structures with a typical resolution of $\gtrsim 100$ Å. Transmission electron microscopy (TEM) of thin (~ 100 Å) films has a lateral resolution of ≥ 2 Å, but it is not a surface topographic probe; however, TEM is extremely useful for investigations of morphology and microstructure. Replica-TEM analysis of thin replica films shadowed with heavy metals yields information on the surface topography. Unfortunately, the experimental difficulties and uncertainties associated with the replication process severely limit the utility of replica-TEM in the investigation of nm-scale features.

The purpose of this paper is to demonstrate the capabilities of scanning tunneling microscopy (STM) for studying random roughness at surfaces. We have investigated microcrystalline and nanocrystalline surfaces (Ag, Au, Si, Fe-Ni, etc.) which have characteristic grain-boundary microstructure accessible to analysis using conventional techniques. The correlation of STM results with LEED for single-crystal surfaces has been an important ingredient in establishing the success of STM [2]. Likewise, it is useful to correlate STM observations with direct lattice images from TEM, replica-TEM, X-ray diffraction (XRD), and additional methods to realize the potential (and drawbacks) of STM applied to randomness and disorder.

In the following two sections, STM data for two systems are reviewed. First, thin-film silicon surfaces comprising nanometer-sized crystallites prepared by plasma-chemical deposition [3] are discussed. Here, we correlate STM pictures with direct TEM lattice images, replica-TEM, XRD, and additional data. Further, we demonstrate the influence of growth conditions (simultaneous ion bombardment) on surface topography. Next, the influence of condensation temperature, annealing, and adsorption of organic molecules (pyridine) on the surface topography of silver films is discussed.

Our motivation for the latter system can be ascribed to the current interest in surface-enhanced Raman scattering (SERS) of molecules adsorbed on coldly condensed Ag films where atomic- or near-atomic-scale roughness is a necessary prerequisite for the enhancement effect [4, 5]. The former system serves well to illustrate STM's potential for elucidating thin-film growth processes and conditions in combination with established methods.

2. Nanocrystalline silicon

Nanocrystalline silicon (nc-Si) is a model randomly rough surface. The crystallite size can be conveniently selected by appropriate choice of the plasma-deposition parameters from a lower limit of ~30 Å to ~200 Å [6]. Furthermore, the surface exhibits a unique passivation to oxygen adsorption, as revealed by X-ray photoemission [7], which makes possible STM studies of atomically clean nc-Si surfaces. The properties and preparation method are reviewed in [3] and details of the STM experiments are given in [8, 9].

Figure 1 shows an STM graph of an ~(500-Å)^2 area typical of the surface topography of nc-Si deposited at 260°C under a floating potential (no energetic ion bombardment during film growth). The crystallite size determined from XRD data [6] for similarly prepared films is ~100 Å. Direct lattice images of the (111) planes of nc-Si indicate that the grain boundaries contain essentially no amorphous network and can be described in terms of low-angle boundaries [3, 10].

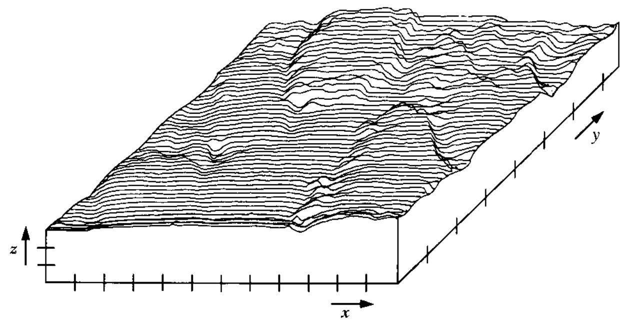

Figure 1

STM graph of nc-Si deposited at T = 260°C under a floating potential by plasma deposition. Divisions on axes correspond to 50 Å. A W-tip operated at V_t = +0.5 V, i = 10 nA [9]. © Elsevier Science Publishers B. V. (North-Holland Physics Publishing Division), 1985; reprinted with permission.

In Figure 1, relatively simple boundaries are clearly resolved separating flat areas ~100 Å in size. On the basis of their similarity in size to the crystallite size determined using XRD and the structures of the boundary regions to TEM micrographs [3, 6] of similarly prepared films, we interpret the features observed by STM to be individual nanocrystallites [8, 9]. The surface topography of the films used for STM investigations was studied using carbon-replica TEM, where the determined autocorrelation length, σ, of 200 Å and rms height, δ, of 12 Å [11] are consistent with the general features observed in a series of STM graphs similar to those of Figure 1.

Figures 2 and **3** illustrate the ability of STM to reproduce the surface topography faithfully. The time lapse between recording Figures 2 and 3 was ~30 minutes. A lateral drift of ~3 Å/min resulted in a shift of the image window; however, the features observed in the overlapping region are faithfully reproduced. It is particularly important to demonstrate such reproducibility for randomly rough surfaces in order to discriminate true surface disorder from possible instabilities in the tunnel junction, and to establish that distortions due to drifts are of insignificant importance.

Surface topography is sensitive to thin-film growth conditions. Simultaneous ion bombardment during growth gives rise to various changes in the physical and chemical properties of nc-Si. Ion bombardment results in compressive stresses of up to ~40 kbar and a decrease in the crystallite size [6]. At a critical size of ~30 Å, and under high negative bias potentials, nc-Si exhibits a phase transition to the amorphous state (a-Si) [12].

Figure 4 shows an STM graph (with higher vertical sensitivity than those of Figures 1–3) of nc-Si prepared at T = 260°C under −100 V bias. The changes in surface topography compared with Figures 1–3 are obvious. The

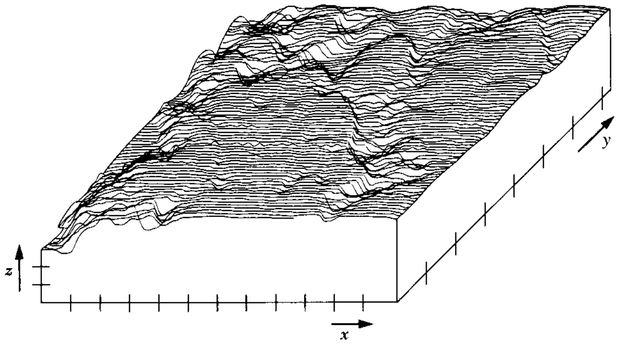

Figure 2

STM graph of nc-Si deposited at $T = 260°C$ under a floating potential by plasma deposition. Divisions on axes correspond to 50 Å. A W-tip operated at $V_t = +0.5$ V, $i = 10$ nA [9]. © Elsevier Science Publishers B. V. (North-Holland Physics Publishing Division), 1985; reprinted with permission.

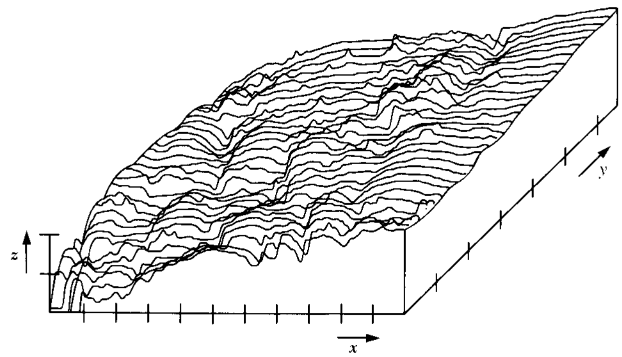

Figure 4

STM graph of nc-Si deposited at $T = 260°C$ under -100 V bias (simultaneous ion bombardment) by plasma deposition. Divisions on axes correspond to 50 Å. A W-tip operated at $V_t = +0.5$ V, $i = 10$ nA [8]; reprinted with permission.

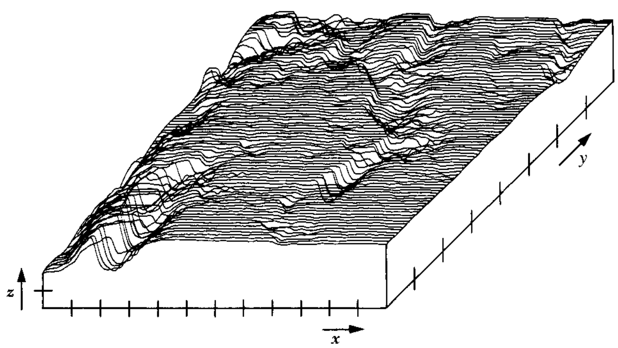

Figure 3

STM graph of nc-Si deposited at $T = 260°C$ under a floating potential by plasma deposition. Divisions on axes correspond to 50 Å A W-tip operated at $V_t = +0.5$ V, $i = 10$ nA. This figure shows the same area as Figure 2 after approximately 30 min. Note offset in image window arising from 3 Å/min drift [9]. © Elsevier Science Publishers B. V. (North-Holland Physics Publishing Division), 1985; reprinted with permission.

granular structure observed has a grain size of 30–60 Å [9] in agreement with the crystallite dimension of ~30 Å determined from XRD data [6]. It is well known that ion bombardment during film growth is responsible for a variety of topographical changes. Effects such as sputtering, enhanced surface diffusion, and implantation contribute to morphological changes [13]. The overall rounding and increase in minor secondary roughness are the results of these and related processes such as finite crystallite size [12]. Recently, the surface morphology of oxidized and ion-etched silicon was investigated by STM [14]. An increased roughening was observed and hillocks similar to the structure of nc-Si deposited under simultaneous ion bombardment were observed.

3. Coldly and warmly condensed Ag films

Several attempts have been made to investigate the roughness of Ag films condensed at low temperature owing to its importance in surface-enhanced Raman scattering (SERS) [4, 5]. The various models for the surface structure of coldly condensed SERS active Ag films are based on indirect observations: photoemission of adsorbed xenon (PAX) [4, 15], thermal desorption (TDS) [4, 16], and optical absorption [17]. Direct observations by microscopic methods with limited resolution have also been reported [17]. However, most studies have shown that the SERS relevant structural features lie in the nanometer-to-subnanometer range [4, 5, 15, 16]. Until recently, suitable surface techniques were not available to obtain real-space topographies of surfaces with the resolution required. Three types of thick (>100-nm) Ag deposits were studied:

1. Films condensed at 100 K with pyridine adsorbed at the condensation temperature.
2. Films condensed at 100 K.
3. Films condensed at 300 K.

All samples were studied at room temperature (post-annealed).

The structural zone model for vacuum-deposited films [18] gives an insight into the dependence of microstructural characteristics on the substrate temperature T in terms of its ratio τ to the condensate melting temperature $T_m (\tau = T/T_m)$. At $T = 90$ K, ($\tau \approx 0.1$) adatom diffusion is insufficient to overcome shadowing effects resulting in a fine columnar microstructure. At $T = 300$ K, ($\tau \simeq 0.25$) adatom diffusion dominates and the density of boundaries between columns increases, accompanied by lower defect concentrations. The microstructure of the film is also

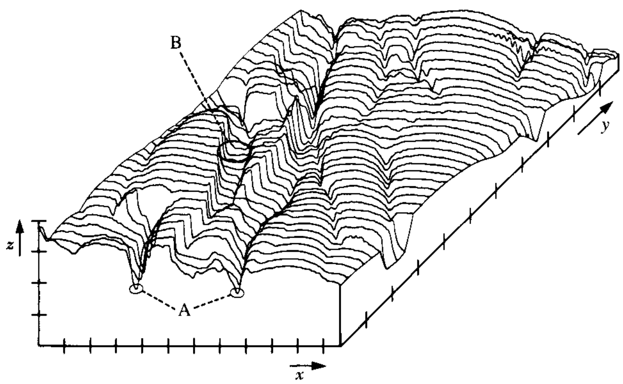

Figure 5

STM graph of a Type-I Ag film. Feature A corresponds to narrow trench sites where tip penetration limits topographic reproduction. Feature B corresponds to trench sites where the tip tunnels with the bottom of the trench (see also Figure 6). Divisions on axes correspond to 50 Å. A W-tip operated at $V_t = +350$ mV, $i = 10$ nA [10]. ©The American Physical Society, 1985; reprinted with permission.

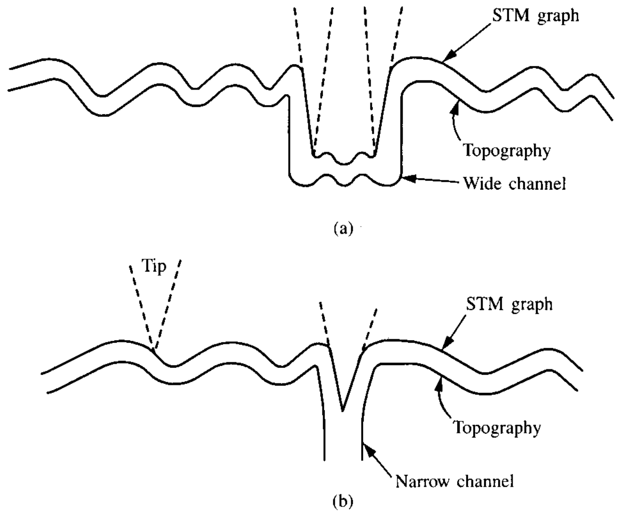

Figure 6

Schematic illustration of scanning the tunneling tip across a trench site for a wide trench (a) and a narrow trench (b) with respect to the tip dimensions. Both topography and the corresponding STM image are shown [10]. ©The American Physical Society, 1985; reprinted with permission.

determined by many additional effects such as internal stresses, defects, and the stabilization of phases by impurities. The films condensed at 90 K are post-annealed in UHV to room temperature. Here, post-annealing is expected to result in modification of the microstructure by adatom mobility. The influence of pyridine adsorption on coldly condensed films during annealing was investigated because of its reported role in preserving features characteristic of coldly condensed films at low temperature.

Our results show that pyridine preadsorption plays a key role in preserving features characteristic of cold films.

Details of sample preparation are reported elsewhere [19–21].

Type-I films **Figure 5** shows a typical STM picture for a coldly condensed film with pyridine preadsorption after post-annealing at room temperature. Columnar structures ~5–15 nm in length separated by trench-like channels 1–3 nm in width are clearly resolved. The STM picture of the channels represents a convolution of the channel and tip structure. Penetration of the tip into these sites is limited by the tip geometry. However, close inspection of the channels in Figure 5 reveals areas where the channel bottoms are relatively flat structures, indicating that here the tip tunnels at the bottom of the channel sites. In other cases, the V-shaped structures reflect predominantly the tip structure. A schematic illustration of this point is shown in **Figure 6**. Consequently, the channel depths are estimated at 3 to >4.5 nm. Apart from the channel sites, the overall topography of the crystallites is fairly flat, i.e., within the resolution limit of most scanning electron microscope (SEM) techniques. These films have a surface topography similar to the model for *cold* films proposed by Albano et al., based on PAX and other data [4, 15].

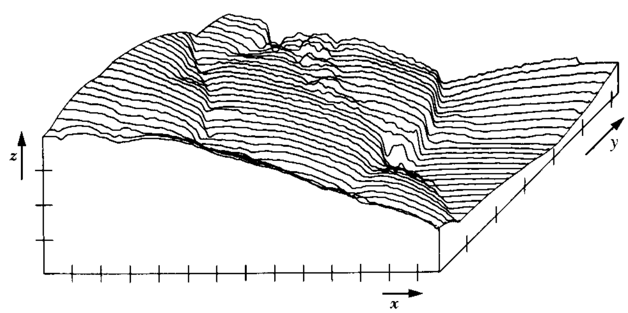

Figure 7

STM graph of a Type-II Ag film. Divisions on axes correspond to 50 Å. A W-tip operated at $V_t = +350$ mV, $i = 10$ nA [11]. ©Elsevier Science Publishers B. V. (North-Holland Physics Publishing Division), 1985; reprinted with permission.

Type-II films **Figure 7** shows a typical STM picture for a coldly condensed film. The absence of pyridine preadsorption results in an almost complete annihilation of the pore structure, although occasionally isolated pores similar to those shown in Figure 5 were observed. Post-annealing of the films gives rise to compact grain boundaries and crystallites of ~10–20 nm in size.

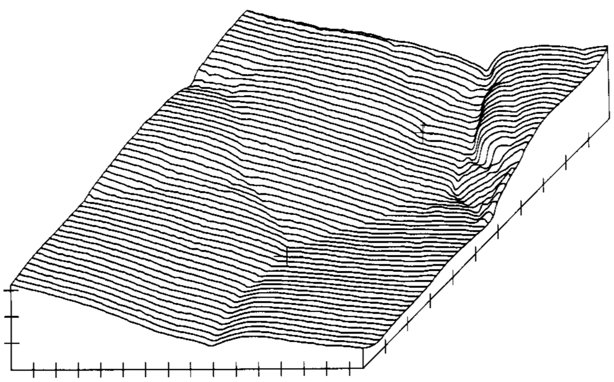

Figure 8

STM graph of a Type-III Ag film. Divisions on axes correspond to 100 Å. A W-tip operated at $V_t = +350$ mV, $i = 10$ nA.

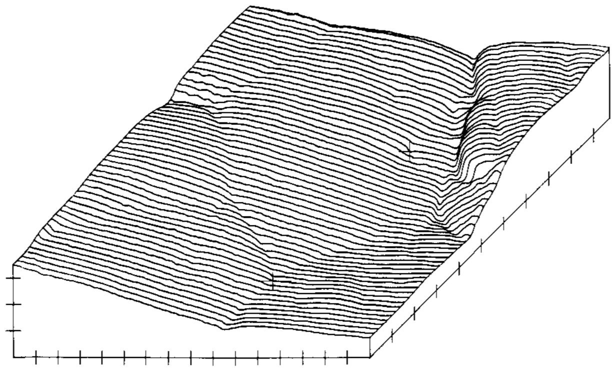

Figure 9

Repeat STM graph of Figure 8, recorded 20 minutes later. Divisions on axes correspond to 100 Å.

Type-III films **Figures 8** and **9** show typical STM pictures for a film condensed at room temperature. The pictures are very similar to Figure 7: No pores are observed, and the compact grain boundaries connect crystallites of larger dimensions than those of Type-II films. Typical grain sizes of ~500–1000 Å agree with TEM data for similarly prepared films [22]. The two figures were recorded on the same area of the sample. Although a small offset occurred in the image window owing to drifts, the reproducibility of the STM data is excellent.

The clearly observable differences in the surface topographies of Type-I and Type-II films give direct evidence for the role of pyridine adsorption in pore retention after post-annealing. These data are consistent with conclusions reached by Seki and Chuang [16], based on TDS, that pyridine plays a role in pore formation. Furthermore, the model proposed by Albano et al. [4, 15] based on PAX measurements for *cold* films closely resembles the topographic features of post-annealed Type-I films. However, our results show that pore structure is at least partially preserved by pyridine adsorption. Our data were recorded after ~15–20 hours of annealing at room temperature in UHV. The relevant time scale for pore annihilation due to annealing effects is an open question under investigation. The high self-diffusion rate of silver at room temperature should result in a time dependence of the surface topography.

In the absence of pyridine preadsorption, the pore structure is almost completely annihilated. The resulting surface of Type-II films is relatively flat, with compact grain boundaries. The observation of smaller crystallites for Type-II films compared with Type-I films indicates that although pore annihilation occurs, the coldly condensed films retain some memory of their porous structure in the absence of pyridine adsorption. The grain boundaries are probably evidence of channels that have been annealed out.

4. Outlook

The two systems discussed in this paper serve well to illustrate some of the capabilities of STM for studying disordered and randomly rough surfaces. A correlation with existing techniques for investigating μc- and nc-materials is demonstrated. STM reveals surface topographic structures not accessible by other methods.

As discussed previously, the problems encountered in studying rough surfaces differ somewhat from those related to single crystals. Limitations include the contribution to tunneling played by the shank in addition to the tip apex which complicates interpretation. Furthermore, if tip and surface are of comparable roughness, then it may be difficult to separate the resulting convoluted image.

Despite these apparent drawbacks, the new information obtained using STM, and the importance of disorder, randomness, and surface microstructure make the study of rough surfaces a worthwhile pursuit. Direct applications to metallurgical, optical-energy-conversion, and electronic thin-film surfaces or interfaces are foreseen.

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