Silver Films Condensed at 300 and 90 K: Scanning Tunneling Microscopy of Their Surface Topography

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Scanning tunneling microscopy shows that warm-condensed Ag films consist of a gently rolling surface topography with compact boundary regions. In contrast, cold-condensed films retain structure on the nanometer scale after annealing to room temperature: These intercrystallite channels or trenches show a strong similarity in width (<1–3 nm), separation (5–15 nm), and possibly depth [3–(>4.5) nm] to the surface topographic models for surface-enhanced–Raman-scattering activated films. This suggests that postannealing does not imply the annihilation of channels, also termed "pores" or "cavities," postulated by some current models.

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The renewed interest, during the last few years, in metallic films condensed on low-temperature substrates can be ascribed mainly to the strong surface-enhanced Raman scattering (SERS) observed from molecules adsorbed on their surfaces.[1,2] Although general agreement exists on the fact that some type of roughness is a necessary prerequisite for SERS,[3] the relevant scale of roughness is still under debate. Unfortunately, the experimental difficulties associated with *in-situ* low-temperature measurement of the topography of cold-condensed films appear to represent a major obstacle for electron microscopic investigations. Furthermore, until recently there was a lack of suitable microscopic methods to study nonideal surface topographies in real space with the required near-atomic resolution. One attempt to overcome these difficulties was to stabilize the roughness relevant to SERS by overcoating cold-condensed Ag films with a thin layer of aluminum oxide and then warming the film to room temperature[4] (postannealing). Subsequent transmission electron microscopic (TEM) studies of carbon replicas of the overcoated films revealed a high density of roughness by features with lateral dimensions ≈ 10–20 nm, whereas uncoated Ag films were smooth on this scale. At present, it is unclear whether the aluminum-oxide coating itself contributes to the features observed.[2] TEM investigations of thick continuous Ag films have been reported for samples condensed at room temperature or above.[5] Several indirect methods have been recently applied to the investigation of cold-condensed Ag surfaces, including photoemission,[6,7] Auger electron spectroscopy,[6] work function,[6,8] thermal desorption,[9] and optical measurements.[4] Despite the activity, the models reported for the surface topography are mainly speculative. Albano *et al.*,[6] for example, have postulated that cold-condensed Ag films are "porous" in the sense that the surface consists of almost-flat plateaus (5–15-nm width) separated by crevices about 0.5–1.5 nm wide. Seki and Chuang[9] envision the pores to be 1–3 nm wide and ~ 15 nm deep and call them "cavity sites." For Otto *et al.*,[10] the pores are of atomic-scale dimensions with "boundaries between crystallites corresponding roughly to two-dimensional nets of vacancies."

It is important to note that SERS activity of cold-condensed films is irreversibly lost upon annealing to room temperature.[1,6,9,11] For Albano *et al.*,[6] this gives evidence of the disappearance of pores.

The purpose of this Letter is to report, for the first time, on the experimentally measured topographies of warm-condensed and cold-condensed Ag films, post-annealed after pyridine adsorption, in a comparative fashion by use of the technique of scanning tunneling microscopy (STM).[12] The development of STM by Binnig, Rohrer, and co-workers has opened new possibilities for the study of three-dimensional real-space images of surfaces with a lateral resolution of several angstroms. The results demonstrate that, for cold-condensed films, the preanneal surface structure does not completely "heal." Atomic-scale trenches <1–3 nm in width, 3–(>4.5) nm in depth, and separated by 5–15 nm are clearly resolved, although the trench depth is underestimated by the limitation of tip penetration. In contrast, warm-condensed films are rather flat with gently rolling areas separated by boundaries. On the basis of the good agreement in the shape and size between postannealed films and the model postulated for surface topography of cold-condensed SERS-active surfaces, we interpret the trenches as evidence for remaining pores.

A description of the STM technique is given in Ref. 12. Our STM is based on the design by Binnig, Rohrer, and co-workers with minor differences for sample translation and transfer. Ag films were prepared in a standard UHV system by controlled condensation of a thick layer (>1000 Å) onto a polished copper substrate which could be cooled to 90 K. For the cold-condensed films, pyridine was adsorbed prior to annealing. The same substrate was used to prepare cold- and warm-condensed films which were characterized by photoemission spectroscopy.[13] A thick film of pyri-

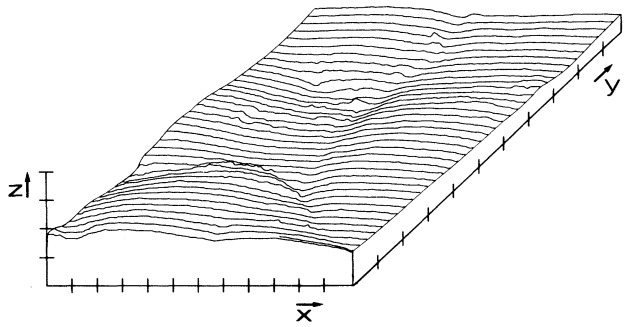

FIG. 1. An STM picture of a warm-condensed Ag surface. Divisions on the axes correspond to 5 nm.

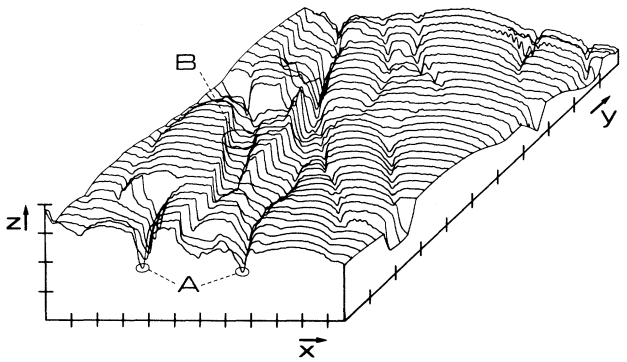

FIG. 2. An STM picture of a cold-condensed pyridine-treated Ag surface after annealing to 300 K: A, narrow trench sites where tip penetration limits topographic reproduction; B, trench sites where the tip tunnels with the bottom of the trench. Divisions on the axes correspond to 5 nm.

dine was adsorbed under 1-atm pressure of nitrogen on both films prior to transfer through air to the STM chamber. This latter pyridine preadsorption was used to avoid surface contamination. In contrast, the former low-temperature pyridine adsorption was used because of its reported role in shaping and maintaining cavities during low-temperature annealing ($T < 250$ K).[9] The STM experiments were conducted in a vacuum of $\sim 10^{-8}$ Torr, which results in subsequent desorption of the pyridine. After STM analysis, Auger electron spectroscopy was used to monitor the cleanliness of the surfaces studied. Submonolayer contamination by C, S, O, and Cl was found.

Several areas of five samples were measured by STM over a total area of several square micrometers. The results presented are typical of the data set.[14] Each of the $\sim 60\times 60$-nm^2 STM graphs presented were scanned carefully at least three times and the scan direction changed to ascertain that distortion due to thermal and other drifts is not important and, further, to establish good reproducibility of the images. For the data presented, a polycrystalline-W tip operated at a tip voltage of $V_t = 350$ mW and a constant tunnel current of $i_t = 10$ nA.

Figure 1 shows a typical STM graph of a warm-condensed film. The picture can be described in terms of a gently rolling surface topography. Various crystallite regions separated by compact low-angle boundaries are clearly resolved. Smaller features may also be seen corresponding to minor secondary roughness from defects, adsorbed species, or changes in tunnel-barrier height. The boundaries and secondary roughness indicate that the lateral resolution is < 1 nm. The typically observed grain size of ~ 50 nm is consistent with carbon-replica TEM micrographs of similarly prepared Ag films.[15]

Figure 2 was obtained with use of the same tunneling conditions for the cold-condensed film. Although the differences compared to Fig. 1 are striking, the surface appears nearly flat on the resolution scale of several tens of nanometers which is a typical value for most conventional scanning-electron-microscopic techniques (see also the TEM micrographs in Ref. 4). The high resolution of the STM reveals a new scale of roughness for the first time: We observe deep "trench"-like boundaries separating structures 5–15 nm apart. The trench widths show a distribution of < 1–4 nm with apparent depths of 1–4.5 nm.

Two effects must be considered when interpreting the STM graphs in relation to surface topography. Firstly, the graphs represent a convolution between tip and local sample morphology. From the lateral resolution observed, δ, of < 1 nm we estimate the tip radius, R, to be < 1 nm using the approximations $\delta \approx \pi[\hbar^2/2m\phi(R+s)]^{1/2}$ given by Stoll[16] (ϕ is the barrier height) and $\delta \approx (2\ \text{Å})(R+s)^{1/2}$ given by Tersoff and Hamann.[17] For such high-resolution STM graphs, the tip-to-sample separation s is in the subnanometer range.[16–18] The STM tip cannot penetrate the trenchlike features beyond a limiting depth governed by the tip radius, tip angle, and trench width and shape. Figure 3 shows a schematic illustration of this point: When the trench width is small compared to the tip dimensions, electrons tunnel on the two side walls of the trench site in the minimum vertical position [Fig. 3(a)].

The V-shaped features are unresolved structures limited by the tip penetration, and have apparent depths of up to 4.5 nm (see feature A in Fig. 2). When the trench width is larger than the tip dimension, the bottom of the trench sites are resolved [Fig. 3(b)] giving rise to the features like B in Fig. 2. A closer examination of the trench-edge profiles shows similarities consistent with our interpretation that the tip shape dominates the convoluted STM profile at the

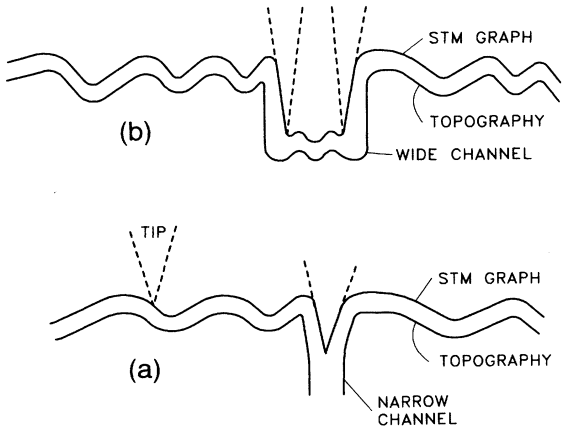

FIG. 3. A schematic illustration of the scanning of the tip across a trench site for (a) a narrow trench and (b) a wide trench with respect to the tip dimensions. Both topography and the corresponding STM graph are shown.

trench edges.[19]

The second important feature of STM is that surface topography is recorded by maintaining $-\phi^{1/2}s$ at a constant value.[12] For a W tip and Ag surface, ϕ is estimated to be ~ 4 eV. Local deviations in ϕ can give rise to apparent topographical effects. On the top of the trench sites in Fig. 2, s was estimated to be < 1 nm. Possible topographic changes corresponding to trenchlike structures would result from a local increase in ϕ. However, such an increase in ϕ would result in only a subnanometer displacement of the tip. This effect is of insufficient magnitude to account for the depths of the structures observed. As a result of the small tip-to-surface separation estimated above, we assign the trenches to topographic features.

To summarize our interpretation of the STM graphs, most of the features are surface topographical except in narrower trench sites as discussed previously. Deviations due to possible barrier-height variations are of negligible importance of the scale of the measurements presented.

Postannealing results in a surface topography very similar to the schematic model for cold-deposited SERS-active surfaces,[6] despite the fact that annealing causes a loss in SERS activity. However, parallel photoemission measurements at 300 K[13] clearly indicate that cold-condensed Ag films, where pyridine was preadsorbed at low temperature, retain spectral features characteristic[7] of SERS-active cold-condensed films. Our experiments show that "pore/cavity" structure is clearly evident after postannealing of thick cold-condensed Ag films pretreated by pyridine adsorption. Postannealing is known to cause a modification of the surface topography. However, the deactivation of SERS does not imply the complete disappearance of channels produced by cold condensation of Ag.

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[14]Approximately 100 STM pictures of warm- and cold-condensed Ag films were recorded, with both repeat of selected areas and study of other areas of the sample over a range of several micrometers. Five samples were studied. Four different tips were used, which consisted of Ag and W material. In some cases the same tip was used to study cold- and warm-condensed films and subsequent or previous experiments on polycrystalline gold, graphite, and silicon samples were conducted with tips that had been used to study the silver films. The characteristic channel or pore structures were only observed on cold-condensed Ag films, while the compact grain boundaries were observed on warm-condensed films.

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[19]Artifacts such as double or multiple tunneling during scanning, low barrier heights, whiskers, etc., are well known to us. The signatures of such effects are characteristic and do not resemble the data presented. The topography of a surface after deliberate tip-surface contact has been studied by us and others [G. F. A. Van de Wall, T. A. M. Benistant, H. Van Kempen, and P. Wyder, Europhys. Conf. Abstr. **9C**, 145 (1985)] for W on Ag. The resulting pattern is unrelated to the present data.