Nature of Surface-Enhanced-Raman-Scattering Active Sites on Coldly Condensed Ag Films

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Evidence is presented that coldly deposited Ag films are highly porous and that the pores persist up to 170 K but are heated out at 250 K. Diffusion of adsorbed pyridine into the pores is negligible below 60 K but readily takes place at 130 K. Theoretical results on the classical electromagnetic enhancement of the Raman cross section within the pores as well as a survey of published surface-enhanced Raman-scattering data lead the authors to conclude that the surface-enhanced Raman-scattering active sites of coldly deposited Ag films are within the pores.

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The enhancement mechanism producing surface-enhanced Raman scattering (SERS), i.e., classical electromagnetic effect versus chemical charge transfer effect, is currently under heavy debate.[1-6] Although general agreement exists on the crucial role of surface roughness in SERS, the relevent scale of roughness remains controversial. Strong SERS signals have been reported from pyridine adsorbed on coldly condensed Ag films under UHV. The SERS activity of these films disappeared irreversibly after the sample was annealed to room temperature.[4] Surprisingly, no fruitful attempt to characterize the structure of these coldly evaporated Ag films has been reported.

In this Letter we report on the geometrical and electronic structure of Ag films evaporated in UHV and annealed at temperatures ranging from 58 to 330 K. We characterized the films by means of Xe and pyridine adsorption as studied with ultraviolet photoelectron spectroscopy (UPS), Auger-electron spectroscopy (AES), thermal desorption (TDS), and work-function (WF) measurements.

The results show that (a) Ag films evaporated at temperatures lower than 170 K are *porous*. (b) The first monolayer of pyridine, the one exhibiting SERS in these films,[2] is *inside* the pores. (c) When no SERS is observed, either the pyridine molecules are not in the pores or the film is not porous. (d) The enhancement of the Raman cross section due to the classical electromagnetic effect is a factor of 10^4–10^5 larger at the bottom of the pores than on the surface. We conclude that only molecules *within* the pores of coldly condensed Ag films are SERS active.

The measurements were performed in a UHV system. For every experiment a 150-Å Ag film was deposited at 58 K onto a Ag substrate with a controlled evaporation rate[7] and then annealed at a given temperature (T_{an}). The WF of the films was found to increase continuously from 4.25 eV (T_{an} = 60 K) to 4.72 eV (T_{an} = 330 K). As deduced from photoemisssion of adsorbed xenon[8] and WF measurements the film annealed at 330 K is composed of (111) grains with only small amounts of defects.

(a) *Coldly condensed Ag films are porous.*—After Xe adsorption at 58 K on films annealed at $T_{an} \leq 170$ K *no Xe signal is detected* with either UPS, AES, or WF changes for exposures below 7 L. [1 L (langmuir) = 10^{-6} Torr sec; all reported exposures were calculated with uncorrected pressures. The gauge sensitivity is 2.8 for Xe]. *Only* for $T_{an} \geq 250$ K are adsorbed Xe atoms detected with all these techniques from the very beginning of exposure (less than 1 L), as, e.g., evidence by Fig. 1(a). The Xe emission shifts in binding energy with the WF of the substrate.[8] Figure 1(b) shows TDS spectra taken with a small-aperture, differentially pumped mass spectrometer immediately after the UPS data in Fig. 1(a) were recorded. All four peaks enclose the same area proving that Xe in fact is adsorbed and that the amount of adsorbed Xe is independent of T_{an}.[9] However, for $T_{an} \leq 170$ K the adsorbed Xe is not detected with the *other surface-sensitive* techniques. Taking into account the kinetic energies of Xe photoelectrons (~ 9 eV) and Auger electrons (~ 530 eV) we conclude that *Xe is adsorbed below the surface in deep (≥20 Å) intercrystallite gaps (pores)*. This conclusion is consistent with the unusually high desorption temperature of the Xe atoms from these Ag films with $T_{an} \leq 170$ K [see

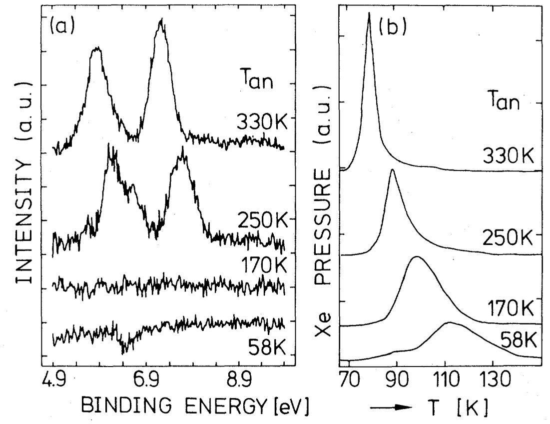

FIG. 1. (a) UPS Xe $5p_{3/2,1/2}$ difference spectra and (b) TDS spectra taken after the same exposure of 3-L xenon (1 L $= 10^{-6}$ Torr sec) at 58 K to Ag films annealed at the indicated temperatures T_{an}.

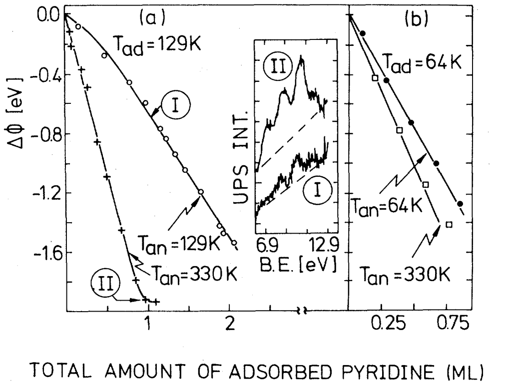

FIG. 2. Pyridine-induced WF changes ($\Delta\varphi$) as a function of the total amount of adsorbed pyridine. (1 monolayer corresponds to the monolayer capacity of the film annealed at 330 K.) (a) Adsorption of pyridine at $T_{ad} = 129$ K on films annealed at 129 and 330 K. Inset: Pyridine UPS signals corresponding to the points I and II, on the $\Delta\varphi$ curves. (b) Adsorption of pyridine at $T_{ad} = 64$ K on films annealed at 64 and 330 K.

Fig. 1(b)], because within the pores the Xe atoms are highly coordinated to the substrate. It was actually suggested many years ago[10] that metal films evaporated at low temperatures consist of columnar crystals separated by gaps. As surface self-diffusion comes into play on raising the temperature [at ~ 210 K for Ag (Ref. 10)], diffusing atoms fill the narrow gaps between crystallites and thus normal grain boundaries are formed. From our data, the pores disappear in the range 170 K $\leq T_{an} \leq$ 250 K, and the minimum thickness of the evaporated Ag films needed to develop pores is ~ 100 Å.[7]

(b) *Under the conditions of SERS activity the pyridine molecules are inside the pores.*—Figure 2(a) shows the WF changes ($\Delta\varphi$) as a function of the *total amount* of adsorbed pyridine after dosing both a nonporous ($T_{an} = 300$ K) and a porous ($T_{an} = 129$ K) Ag film with pyridine at 129 K. In the following, one monolayer (ML) corresponds to the monolayer capacity of the film annealed at 330 K as determined from $\Delta\varphi$ and UPS measurements. The WF decrease induced by one monolayer of pyridine on the porous film is smaller than on the flat film (~ 33%). The corresponding UPS data in the energy range of the pyridine emission are depicted in the inset in Fig. 2(a). The signal from the flat film is approximately three times larger than that from the porous sample in agreement with the $\Delta\varphi$ results. Obviously, for the film annealed at 129 K an amount of pyridine equivalent to ~ $\frac{1}{3}$ ML is adsorbed on the surface and the remaining $\frac{2}{3}$ ML are inside the pores. For the highest pyridine coverage in Fig. 2(a), i.e., 2 ML, the distribution of adsorbed molecules is ~ 0.8 ML on the surface and 1.2 ML in the pores. Figure 2(b) displays the $\Delta\varphi$ caused by pyridine adsorbed at 64 K on a flat and a porous film. Here the two curves are much closer

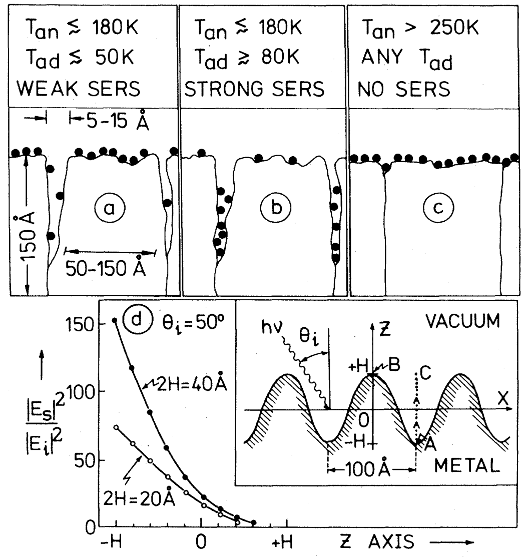

FIG. 3. (a)–(c) Schematic drawing of the geometrical structure of Ag films annealed at different temperatures including the relevant dimensions (Ref. 7). Dark balls represent pyridine molecules. (d) Plot of the variation of the enhancement E along the line A-C of the inset. The results depend only slightly on the incident angle (θ_i) of the light. Inset: The model topography of the film used in the calculations.

than after adsorption at 129 K. At 64 K the pyridine molecules are not mobile enough to migrate into the pores while at 129 K the molecules are thermally activated to diffuse. In fact, at 78 K 25% of a monolayer of pyridine is found to diffuse into pores within ~ 200 min. Accordingly Fig. 3 shows our proposed model for the adsorption of pyridine on Ag films. The amount of pyridine capable of being trapped in the pores is ~ 1.5 ML in agreement with the Xe measurements.[7] Thermal-desorption traces of pyridine from differently annealed Ag films[7, 11] can also be interpreted straightforwardly on the basis of our model for the porosity of coldly deposited films.

(c) *The field of the incident light is enhanced inside the pores.*—We have performed a calculation based on the extinction-theorem formalism[12] for the classical enhancement of the electrical field near a surface which is defined by a local dielectric constant, $\epsilon(\omega)$.[13] The film topography was modeled by a one-dimensional cosine-shaped grating [see inset in Fig. 3(d)] with a periodicity of 100 Å and a corrugation ($2H$) of 40 Å as suggested by the mean crystallite and pore size of the Ag films characterized above. Figure 3(d) shows the electrical field increase E, defined as the ratio of the modulus squared of the field at the surface (E_s) to the modulus squared of the incident field (E_i), along the line A-C in the inset. Note that E is large at the bottom of the valleys, decreasing strongly towards the mouth of the pores. On top of the crystallite (point B) only very weak enhancement is found. Since the Raman cross section varies with the fourth power of E_s, this crude, classical model predicts an enhancement factor of 3×10^4 (6×10^3 for $2H=20$ Å) for the choosen geometry in good agreement with SERS experiments.[2] The enhancement for periodic gratings much smaller than the incident wavelength (5145 Å), which is the case in our calculation, is due to large-Q plasmons appearing as the amplitude of the grating is increased with respect to the period.[14] Summarizing, strong SERS signals are observed when several enhancement mechanisms work simultaneously as for pyridine on coldly deposited Ag films. Our data prove that in this case the major source of SERS is the electromagnetic enhancement ($\sim 3\times10^4$) within the pores of the Ag film. However, the chemical specificity of SERS cannot be explained by this mechanism which should work equally well for any kind of molecules adsorbed within the cavities. There is evidence[15-17] pointing to the existence of an additional, short-range, charge-transfer-excitation contribution to the total Raman cross sections, which, though small, would explain the chemical specificity. This charge-transfer-excitation mechanism is visualized as originating in photon-driven electron transitions from occupied metal states into empty molecular levels. Experimentally[18] and theoretically[19] the corresponding enhancement factors are only 50–100.

(d) *Discussion of selected SERS measurements.*—Adsorption of pyridine at 18 K on porous Ag films was found to yield only weak SERS signals.[6] At 18 K adsorbed pyridine is certainly immobile and only those few molecules can reach the pores which are impinging directly into them from the gas phase [see Fig. 3(a)]. Only after the substrate was warmed from 18 K to 70–90 K did SERS develop maximum intensity.[6] This activation cycle of the *adsorbate* obviously promotes diffusion of pyridine into pores. The resulting situation is illustrated in Fig. 3(b).

Thick Ag films condensed at temperatures lower than ~ 180 K show strong SERS signals for pyridine adsorbed at temperatures between ~ 70 and 180 K. However, the active sites for SERS are irreversibly annihilated when the films were annealed at $T_{an} \geqslant 250$ K.[2, 4] From our data the annihilation of pores in coldly evaporated Ag films takes place in the range 170 K$\leqslant T_{an} \leqslant$ 250 K, after which pyridine can only adsorb on the outer surface [Fig. 3(c)]. Obviously, atomic-scale roughness (ASR) is also annihilated within the above-mentioned interval of T_{an}. Nevertheless, the lack of SERS signals from coldly deposited 10-Å-thick Ag films,[5] which should have the highest density of ASR, but no pores because of the small thickness, rules out ASR as the major origin for SERS.[5] Furthermore, enhanced Raman signals have been observed only after deposition of 150-Å Ag films,[5] i.e., when the gaps between crystallites have already been developed as we have demonstrated. Moreover, Ag single crystals,[3] stepped surfaces,[3] and polycrystalline slugs,[2] where the presence of pores can certainly be ruled out, do not exhibit SERS.

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[9] This statement is strictly valid for exposures below 10 L where for flat films monolayer saturation takes place; i.e., 150-Å-thick films deposited at 58 K have a surface area 2.8 times larger than flat films and the first monolayer becomes saturated for ~1-5 L of Xe exposure.

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