Fractal character and direct and indirect transitions in photoemission from silver films

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Abstract

We have examined the linear and nonlinear photoelectric response as well as low-temperature scanning tunnelling microscope (STM) images of rough (coldly deposited) and smooth (annealed) Ag films. Our one-photon and two-photon optical excitation wavelengths were chosen to induce photoemission with common total photon energy, polarization and light penetration depth. Direct optical transitions dominate one-photon and two-photon photoemission from smooth films and one-photon photoemission from rough films; this leads to energy distribution curves that are adequately modelled using well established theory. In contrast, photoelectron emission from rough films induced by two-photon absorption is mediated by the excitation of localized surface-plasmon (LSP) modes centred on roughness features. This photoelectric response is strongly enhanced and it involves indirect, momentum nonconserving transitions. STM images of rough films show an apparently fractal arrangement of structures which support the plasmon activity.

Certain rough metal film surfaces display a great deal of structural inhomogeneity in the form of surface microroughness as well as extensive porosity below the surface. These films have been the subject of a good deal of the surface science literature during the seventies and eighties because of the remarkably large enhancement effects they display in a number of optical experiments [1]; in Ag films the enhancements are particularly pronounced. Models to explain the enhancements have been published [1]. But recently, a new twist has been introduced: fractal character has been ascribed to the rough metal surface. X-ray

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reflectivity measurements [2] and light scattering experiments [3] on vacuum (coldly) deposited films, and even roughening induced from ion bombardment of the surface [4] all indicate a fundamental fractility. Moreover, theories based specifically on this characteristic of the film do well at explaining features of the optical excitation that previous theories could not deal with effectively [3,5].

A complete understanding of low-temperature rough films will only be achieved, however, when the detailed structure is observed and the optical response determined directly from it. At the heart of the optical enhancement effects on rough surfaces is surface-plasmon excitation, an intense resonant excitation with a broad spectral response. In this paper we support the view that rough films are a fractal arrangement of structural features. In Ref. [5] it is shown that surface-plasmon modes localized on roughness features couple through a dipole–dipole interaction such that the roughness features collectively contribute to a net excitation which, when the system is fractal, appears as an overall modulation of the film-surface charge density with strong spatial localization. That is, roughness features over the entire irradiated zone respond to the optical excitation, but the effective modulation of the charge density is still restricted to certain domains and involves only roughness features within those domains. Although rough films are probably self-affine systems, rather than self-similar, we will assume that the results of Ref. [5] are applicable because in rough films the high local fields responsible for surface enhanced optical phenomena have been shown to be a consequence of mode localization [3].

The signature of LSP excitation is evident in a photoemission experiment. This process has been successfully described with a three-step model involving (a) photoexcitation of the electron, (b) migration to the surface and (c) escape over potential barriers at that location [6]. With respect to the first step, there are two important questions one may ask. Fist, is photoemission initiated by direct optical transitions that conserve electron momentum, or are indirect transitions involved? Of course, the surface boundary itself acts to break translational invariance and, if photoemission is predominantly a surface effect, the indirect excitation path is favoured. On the other hand, the depth of light penetration into the metal is on the order of tens of nm and, therefore, one might anticipate a strong volume contribution involving direct transitions. Second, does the multiphoton excitation that leads to photoelectron ejection involve a true n-photon (simultaneous) absorption or an n-step (cascade) absorption process?

In this paper we attempt to answer the above by comparing one-photon and two-photon electron emission spectra from both rough and smooth Ag films under conditions of constant total photon energy, light penetration depth and light polarization. For smooth films our data is consistent with the view that photoemission is initiated by simultaneous, two-photon, direct transitions. On roughened surfaces, however, photoemission is induced largely from the decay of excited LSP modes into one-electron excitations and involves two-photon absorption via resonant intermediate states with indirect transitions dominating. Scanning

tunnelling microscopy images of rough films show in detail the structural features that support LSP activity.

Theoretically we have shown that photoemission is distinctly different when the excitation frequency of the laser falls within the LSP resonance profile [7]. The photoemission process is considered within a slowly varying envelope approximation for light. That is, the wave vector of the incident light is much less than the electron momentum and, therefore, the spatial dependence of the exciting radiation field can be neglected. Since the light penetrates tens to hundreds of atomic layers, while translational invariance is broken only for a few atomic layers near the boundary, photoemission in smooth films can be, and has been, successfully interpreted in terms of direct transitions in the bulk [8]. Bloch states appropriately describe the system and transitions with nonzero matrix elements are restricted to being direct and momentum-conserving. The theory extends the two-orthogonal plane-wave approach of Koyama and Smith [8] to include two-photon excitation. It first yields $P(E, \omega)$, the number of excited electrons per unit time, unit volume, and unit energy interval. Electron escape and transmission is then included through the function $T_0(E)$ using already established physical relations [9b].

We then consider the photoemission process in a rough film at excitation frequencies effective in activating LSP modes of the system. The fractal character of the film enters the theory at the outset [7]. We consider the optical response in the vicinity of the rapidly varying fields around roughness features. These fields break translational invariance allowing indirect transitions to take place. Matrix elements for rough film transitions are related to those of smooth films, again as a function of the appropriate response variables, amounting to an expression involving a quality factor for resonant eigenmodes of rough surfaces. We show that the photoemission probability for a rough film depends on a product of initial and final density-of-states and, because of the indirect character of the transitions involved, the product also involves the intermediate density-of-states. Averaging the optical response over a fractal arrangement of roughness features of 12 nm average size, we estimate that the photoemission probability from rough films excited within the LSP resonance band is enhanced by a factor of 10^2 to 10^4. This is in excellent agreement with experiment. In a previous paper we reported enhanced two-photon electron emission quantum yields from rough Ag films [10]. At a photon energy of approximately 2.2 eV it was found that the two-photon quantum yield from rough films exceeded that from smooth films (examined under identical ultra-high-vacuum conditions) by up to a factor of several thousand. This enhancement was ascribed to LSP excitation.

The time-of-flight electron photoemission experiments were carried out at 7×10^{-11} Torr base pressure. Ag films 200 nm thick were deposited onto a polished Cu substrate using an effusive beam of Ag atoms. The substrate could be cooled (through an intervening slap of sapphire) down to 30 K within a 4 h period.

In order to observe near-threshold photoelectrons the time-of-flight tube was biased to $V_B = +2.00$ V. In the observed spectra the low energy cutoff is given by $\Phi_{S,R} - \Phi_A + V_B$, where $\Phi_{S,R}$ denotes the work functions of the smooth or rough surfaces and Φ_A is the work function of the detector surface, and the high energy cutoff is $2\hbar\omega - \Phi_A + V_B$. The photoelectron arrival rate at the microchannel plate detector was limited to a few Hz to prevent space-charge effects. Cubic weighting was used to convert the time-of flight data to an energy spectrum. No smoothing was used.

Polarized light from a (10 ns pulse width) dye laser or from a second harmonic generator was focused onto the Cu substrate at 35° incidence. The dye laser power was kept below 0.5 μJ/pulse for rough films, and below 20 μJ/pulse for smooth films. At 510 nm (dye laser) and at 255 nm (doubler) the penetration depth of light in Ag is 12.4 nm and 14.0 nm respectively, based on well-known optical constants [11].

Photoelectron spectra for smooth films were recorded at room temperature immediately after deposition and at approximately 0.5 h intervals during the 4 h cool-down period to 30 K. Stepwise dosing with H_2O to a total of 5 L reduced the low energy cutoff by 0.6 eV, beyond which no further change was observed. (The high energy cutoff remains fixed indicating that Φ_A is not affected.) No H_2O electronically excited states are accessible with the laser excitation used here.

The scanning tunnelling microscopy was performed under UHV conditions in a chamber containing an STM and a cryostat. The sample is mounted on a rotating stage so that Ag films can be deposited and then rotated for examination by the tunnelling tip. The sample is in good thermal contact with the cryogenic fluid dewar but thermally isolated from the rotating mount. With liquid nitrogen in the dewar the sample temperature reaches 100 K. Although thermal gradients are clearly generated in the apparatus, they are stable at steady state as demonstrated by high quality graphite images that show single-atom resolution.

In Fig. 1 we present one-photon and two-photon spectra of a smooth film at 30 K dosed with 5 L H_2O (A) and of a rough film at 30 K (B). The one-photon and two-photon spectra of a smooth film are superimposable to within the signal-to-noise level. This is the expected spectrum for photoemission initiated by direct transitions for which the energy distribution curve (EDC) is a product of a rectangular-shaped $P(E, \omega)$ function with a triangular-shaped $T_0(E)$ function [7]. The influence of $T_0(E)$ is not apparent in smooth film spectra unless the work function of the surface is reduced by the introduction of an adsorbate molecule. In our case the photoelectric window is extended through lowering of Φ_S by dosing with H_2O.

The good agreement between the predicted and observed shape of the EDCs in Fig. 1A suggests that photoemission from a smooth film is initiated by direct (and simultaneous) transitions in the bulk metal both for the one-photon and the two-photon processes. For the one-photon process this conclusion is not new since
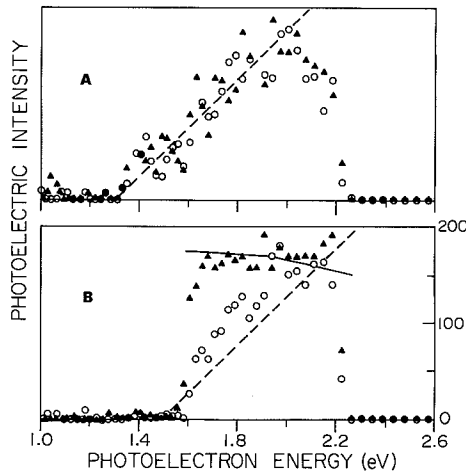
Fig. 1. Normalized two-photon (triangles) and one-photon (open circles) spectra for (A) a smooth Ag film at 30 K dosed with 5 L H_2O, and (B) a rough film at 30 K. The dashed line is $T_0(E)$; the solid line in B is the DOS product (right-hand ordinate) in Ry^{-4} $atom^{-4}$.

no one-electron transitions are observed in the absorption spectrum of Ag below the plasma edge at approximately 3.8 eV [12], the well-known weak absorption in the visible being entirely due to the Drude response.

The one-photon and two-photon spectra of a rough Ag film, shown in Fig. 1B, are strikingly different from those of the smooth films. The one-photon spectrum is largely triangular in shape and resembles the smooth film EDCs. However, a small positive departure from the triangular shape is evident. The two-photon spectrum on the other hand is distinctly rectangular, and this shape is weakly dependent on the presence of adsorbate and independent of light polarization. These observations can be understood by assuming the one-photon response in rough films to be due to direct transitions while the two-photon response, over a rough surface with power-law distribution functions characterizing fractal structures, originates from LSP-mediated, indirect transitions.

The roughness features that support LSP activity in rough Ag films are observable in low-temperature scanning tunnelling micrographs. In Ref. [13] we will report the actual two-dimensional images of the rough and smooth films. If a cut is taken along an arbitrary plane perpendicular to the surface, the variation of height in the film becomes apparent. In Fig. 2 we present such height profiles for smooth (A) and rough (B) films. In the case of the smooth film, surface undulations of size on the order of 100–200 nm are evident. In sharp contrast to this, a rough film shows structural inhomogeneities that are on a much smaller size range, 5–20 nm. We believe that it is on roughness structures such as these that LSP excitation is centred. Similar structures present below the surface, which constitute the porosity of the film, and which are within the penetration depth of the light, also must contribute, but they are clearly not observed in an STM
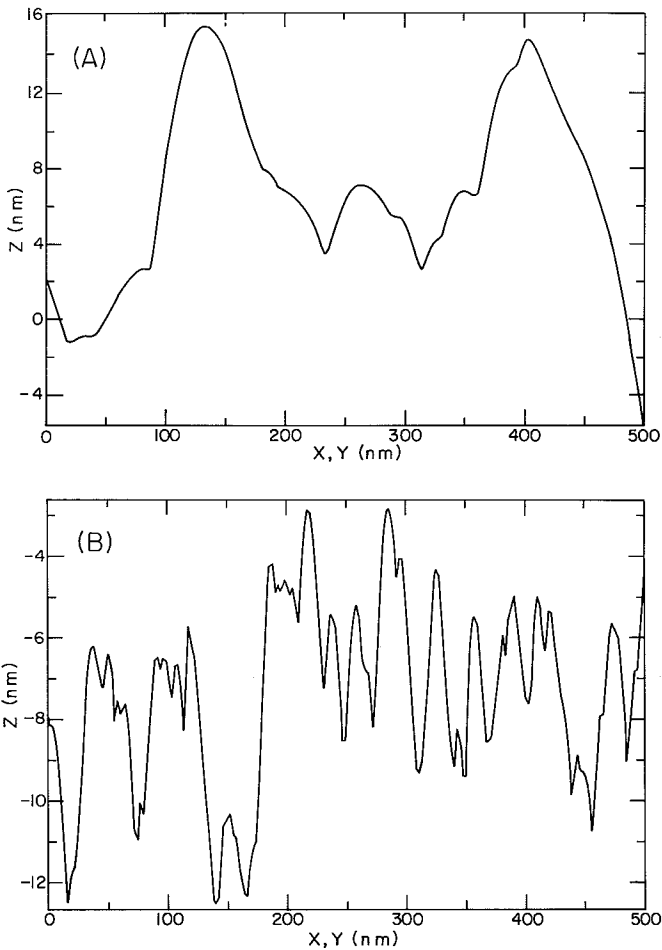
Fig. 2. STM height profiles of 200 nm thick films; (A) smooth Ag film deposited at 300 K and imaged at 100 K; (B) rough film deposited at 100 K.

measurement. The direct observation of the roughness features on a coldly deposited Ag film has given us an estimate of the size range of roughness features in agreement with the value of 12 nm used previously to calculate the photoemission enhancement ratio between a rough and a smooth Ag film. The resultant ratio was found to be in excellent agreement with experiment.

We have used the height profiles of Fig. 2 in an analysis to determine the presence and extent of fractality. The profiles are treated as "fractal coastlines" and a fractal dimension determined [14]. We find that the rough film height profile is characterized by a fractal dimension of $D = 1.25$ while for the smooth film $D = 1.09$. This analysis is quite preliminary and will be presented in detail in a future publication [13]. But initial indicators are promising and suggest fractal character in the rough films.

In Fig. 1B the density-of-states product is drawn as the solid, nearly horizontal line. It is seen that the appearance of the two-photon EDC is very well explained by this product but only in the absence of any modification from $T_0(E)$. This implies that essentially all of the photoelectrons originate, in this case, near the surface of the roughness features where the field enhancement is largest.

That LSP excitation in rough films is only observed with visible photons is consistent with the report of an anomalous visible absorption in roughened Ag that has been ascribed to surface-plasmon excitations [1,3,7,15]. The nearly triangular one-photon response in Fig. 1B shows that direct transitions do take place in rough films but only if there is sufficient detuning from the LSP resonance. The small departure of the one-photon EDC from the purely triangular shape observed with smooth films strongly suggests that for rough films a greater fraction of even one-photon induced electron emission comes from the surface region. Consistent with other experiments that are sensitive to surface roughness (like surface-enhanced Raman scattering [1,15]), the photoemission spectra are not affected by the polarization of the laser, apart from the Fresnel reflectivity effect.

In explaining the difference between the two spectra of Fig. 1B one cannot ignore the possibility of roughness-induced surface states. We reject this explanation because surface states are expected to be strongly polarization-dependent as well as highly sensitive to adsorption of molecules on the surface; neither is observed to be the case. Furthermore, electron energy loss studies [16] and inverse photoemission measurements comparing rough and smooth [17] Ag show no evidence of surface states and indeed show that the bulk electronic structure of rough and smooth Ag films are very similar. Our results support that conclusion.

We have presented a unique photoemission study comparing one-photon and two-photon spectra of rough and smooth Ag films under conditions of equal total photon energy and nearly equal optical penetration depth. Our findings are consistent with a theory that incorporates the involvement of LSP excitation into existing and well developed theories of photoemission from metals. We interpret photoemission from smooth films as a process involving direct optical transitions. On rough films, however, where LSP resonances are excited, photoemission is dominated by the enhanced near-zone fields around surface roughness features where translational invariance breaks down. This, together with localization due to the fractality of the rough surface, leads to the conclusion that most of the photoelectrons originate from restricted regions of the irradiated surface. Using this theoretical framework we have estimated an enhancement factor that agrees very well with experiment. This does not mean that the system must be fractal in order to exhibit enhanced photoemission. Rather, we have shown that a theory based on a fractal arrangement of polarizable roughness features quantitatively describes the observed enhancement. The theory also incorporates an extension of the three-step photoemission model to encompass two-photon excitation.

We have also described STM images of the structures on a rough film that

support LSP oscillations. Preliminary analysis suggests fractal character for the rough films. The structures are found to be of a size in agreement with theoretical estimates that correctly describe rough film enhancement effects.

Acknowledgement

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