Surface Science Letters 297 (1993) L84–L90
North-Holland

surface science
letters

Surface Science Letters

Direct and roughness-induced indirect transitions in photoemission from silver films

Constantine Douketis, Tom L. Haslett, J. Todd Stuckless, Martin Moskovits
Department of Chemistry, University of Toronto, and Ontario Laser and Lightwave Research Centre, Toronto, Ont. M5S 1A1, Canada

and

Vladimir M. Shalaev [1]
Department of Physics, New Mexico State University, Las Cruces, NM 88003, USA

Received 24 May 1993; accepted for publication 9 August 1993

One-photon and two-photon electron emission spectra from vapour deposited rough and smooth Ag films are compared. Photoemission from rough films is strongly enhanced due to the participation of localized surface plasmons (LSP). A theory is outlined that successfully estimates the enhancement and predicts that LSP-initiated photoemission would involve momentum non-conserving transitions.

Photoemission has been widely used to provide detailed information on the electronic properties of metals. Recently, with the introduction of multi-photon excitation, its scope has been expanded to include unoccupied states [1]. The process has been successfully described in terms of a three-step model consisting of excitation of the photoelectron, migration to the metal surface with inelastic collisions en route, and escape overcoming the appropriate potential barriers [2]. Within this model, developed by Berglund and Spicer, it is important to determine (1) the contribution of momentum non-conserving (indirect) optical transitions resulting from the break in symmetry at the surface, and (2) the nature of the absorption – whether it is a simultaneous n-photon process or an n-step cascade?

In this Letter we present experimental results and theoretical arguments that distinguish between the above possibilities. This is achieved by comparing 1-photon and 2-photon electron emission spectra from both rough and smooth Ag films under conditions of constant total photon energy, light penetration depth and light polarization. We find that for smooth films, photoemission is initiated by simultaneous 2-photon, direct transitions, while on roughened surfaces, photoemission results largely from the excitation of localized surface plasmon (LSP) modes leading both to simultaneous and sequential 2-photon absorption via resonant intermediate states with indirect transitions dominating.

Ag surfaces formed by condensation of atomic beams onto a low temperature substrate are char-

[1] Also with: L.V. Kirensky Institute of Physics, Siberian Branch of the Russian Academy of Sciences, 660036 Krasnoyarsk, Russia.

acterized by microscopic surface roughness [3]. Films prepared in this way will be referred to as "rough" films, while Ag films formed at temperatures higher than 250 K where there is sufficient thermal mobility for self-annealing will be called "smooth" films. Recent evidence suggests that rough Ag films are self-affine [4]. Rough films are known to exhibit an enhanced optical response, the dominant mechanism for which is thought to involve LSP excitation [3]. For Ag, LSP excitations induce a strong broad absorption in the normally weakly absorbing visible part of the spectrum [5], which has been successfully modelled in terms of plasmon excitations of interacting spherical surface particles [6]. With a fractal arrangement of features capable of sustaining LSP resonances it has been shown that SP normal modes arising from dipole–dipole coupling are strongly localized spatially [7]. Although rough films are, at best, self-affine rather than self-similar we will assume that the results of ref. [7] apply to these films as well because, as indicated in ref. [8], the high local fields responsible for surface enhanced optical phenomena are a consequence of mode localization.

In a previous paper we reported enhanced 2-photon electron emission quantum yields from rough Ag films [9]. It was found that, at a photon energy of approximately 2.2 eV, the 2-photon quantum yield from rough films exceeded that from smooth films (examined under identical ultra-high-vacuum conditions) by a factor of up to several thousand. This enhancement was ascribed to LSP excitation. Here we present *energy resolved* photoelectron data obtained with laser-excited time-of-flight electron energy analysis from similar Ag film systems. The present data provide strong evidence that LSPs are key participants in the 2-photon photoemission process occurring on roughened surfaces.

Photoemission from a smooth film is dominated by direct transitions. This is because the wave vector of the incident light, $\boldsymbol{q}$, is much less than the electron momentum, $\boldsymbol{k}$. Consequently one can ignore the spatial variation of the exciting field. Therefore, matrix elements of the interaction operator $(e/2mc)[\hat{A}\hat{p} + \hat{p}\hat{A}]$ for transitions between Bloch states are nonzero only for direct electron transitions. Since the light penetrates tens to hundreds of atomic layers, while translational invariance is broken only for few atomic layers near the boundary, photoemission in smooth films can be successfully interpreted in terms of direct transitions in the bulk [10].

In a separate publication [11] we extend the two-orthogonal plane wave (OPW) approach of Koyama and Smith [10] to the case of 2-photon excitation. Additionally, we develop simple expressions for $P(E, \omega)$, the number of excited electrons per unit time, unit volume, and unit energy interval for both 1- and 2-photon excitation in smooth and rough films. $P(E, \omega)$ is proportional to the photoemission probability which, in turn, is proportional to the experimentally measured electron energy distribution curve (EDC).

We show in ref. [11] that for a polycrystalline film:

$$P^{(1p)}(E, \omega') = \frac{n_G}{24\hbar\pi}\left(\frac{eE^{(0)}}{\hbar\omega'}\right)^2 \frac{G}{1-\gamma}\left(\frac{V_G}{\hbar\omega'}\right)^2, \tag{1}$$

for a 1-photon process in a smooth film. G is the reciprocal lattice vector, n_G is the number of symmetrically equivalent G planes, $2V_G$ is the L_2' to L_1 energy gap, $E^{(0)}$ denotes the radiation field strength at photon energy $\hbar\omega'$, and $1-\gamma = [(\hbar\omega')^2 - 4V_G^2]^{1/2}/\hbar\omega'$. $P^{(1p)}(E, \omega')$ is non-zero only within the energy interval $E_{min} < E < E_F$, where $E_{min} = [(\hbar\omega' - (\hbar^2/2m)G^2)^2 - 4V_G^2]/[2(\hbar^2/m)G^2]$, m being the electron mass, and E_F is the Fermi energy. Multiplying $P^{(1p)}(E, \omega')$ by the electron transmission and the electron escape functions produces a quantity proportional to the EDC. The electron transmission function is essentially constant over the narrow range of electron energies studied here. On the other hand, the escape function takes the form $T_0(E) = \frac{1}{2}\{1 - [(E_F + \Phi)/E]^{1/2}\}$ for $E > E_F + \Phi$ and is zero otherwise [2].

The band structure of Ag is shown in fig. 1 in the vicinity of the L symmetry point. The dispersion curves are based on the fully relativistic augmented plane-wave calculations of Chris-

tensen [12], scaled so that E_F is located 0.3 eV above the L'_2 saddle point and $2V_G$ is 4.15 eV as determined by piezo-reflectance measurements [13]. Two vacuum levels are included, E_0^R and E_0^S, corresponding to the two values of the work function that we have measured for rough and smooth Ag films [9]. At our photon energy it is possible to draw only one direct transition on this diagram, shown slightly displaced to the left of the L point. Other possible direct transitions of constant interband energy can be represented in a three dimensional view of the band structure of which fig. 1 is a cross-section. Those transitions are incorporated in the range $E_F - E_{min} = 0.67$ eV, indicated by the shaded region in the figure; the value of 0.67 eV has been calculated using the piezo-reflectance data and assuming $\boldsymbol{G}$ along $\langle 111 \rangle$ [10]. Schematic photoemission spectra for rough and smooth films are included in fig. 1 to illustrate that photoemission signal is observed

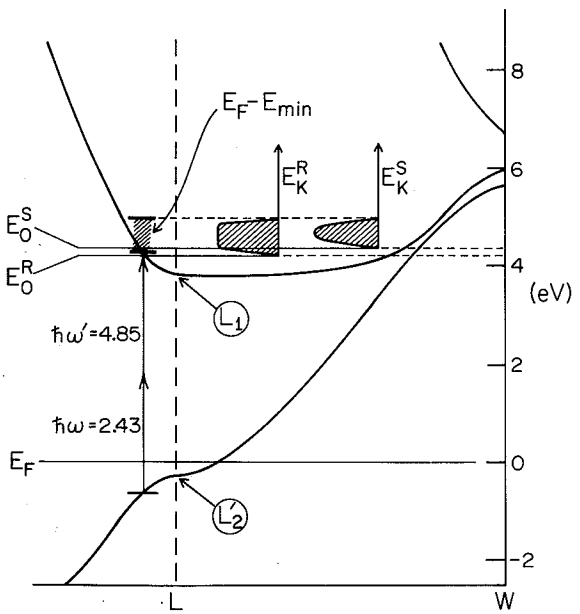

Fig. 1. Band structure of Ag near the L symmetry point. Direct 1-photon and 2-photon transitions at 4.85 eV total energy are shown. E_0^S and E_0^R mark the vacuum level of smooth and rough films with respect to the Fermi level. EDCs for rough and smooth films and the photoelectric window $E_F - E_{min}$ are also shown.

within the rectangular shaped box bounded by $E_F - E_{min}$.

For direct, 2-photon excitations in the $L'_2 \rightarrow L_1$ region of Ag with $\omega = \omega'/2$ we determine $P^{(2p)}(E, \omega)$ to be [11]:

$$P_S^{(2p)}(E, \omega) = \frac{n_G}{20\pi(1-\gamma)} \frac{(eE^{(0)})^4 G}{m\hbar^4\omega^5} \left(\frac{V_G}{\hbar\omega}\right)^2 \left(\frac{V_n}{\hbar\omega}\right), \quad (2)$$

in the range $E_{min} < E < E_F$ and zero otherwise. $V_n = \hbar^2 k_n^2/(2m)$ where k_n is the radius of the Fermi surface "neck". We assume throughout that we are near threshold. This function (eq. 2) is also box-like. It too must be multiplied by $T_0(E)$ to give the 2-photon EDC.

The rough film was modeled as a fractal arrangement of polarizable objects [8]. The field close to a surface roughness feature (the near zone) is given by $E_\alpha^{(nz)} = E_{\beta'}^{(0)} r^{-3}(\delta_{\alpha\beta} - 3n_\alpha n_\beta)\eta_{\beta\beta'}$ where $\boldsymbol{r}$ is a position vector originating at the center of the roughness feature, $\boldsymbol{n} = \boldsymbol{r}/r$, and η is the polarizability of the roughness feature. The Fourier transform of r^{-3} includes components with high $\boldsymbol{q}$ values, even comparable to $\boldsymbol{k}$. This breaks translational symmetry and weakens the momentum conservation requirement. Because the fields in the near zone are greatly enhanced compared to the incident field, photoemission from rough films will be dominated by transitions (which need no longer be direct) initiated by the absorption of near-zone photons.

For direct electron transitions, the matrix elements $V_S \sim eE^{(0)}k(\hbar/m\omega)$. The corresponding matrix elements for a rough film, V_R, include contributions from all transitions, even those with a change in momentum as large as $|\boldsymbol{G}| \approx a^{-1}$. In ref. [11] we show that $V_R/V_S \sim (a/R_0)^2(R_0^3/v_{loc})\chi$ where R_0 is the linear size of the roughness feature, v_{loc} is the volume within which the electron is localized, $\chi > \eta/R_0^3$ is the susceptibility associated with dipolar modes on the roughness features, and a is the lattice constant. At resonance $\chi \sim Q$, where Q is the quality factor. For noble metals $Q \sim 10^2$ and the ratio V_R/V_S is close to unity if $v_{loc} \sim R_0^3$.

Assuming that for a rough film V_R is completely independent of Δk, one finds:

$$\frac{P_R^{(2p)}(E,\omega)}{P_S^{(2p)}(E,\omega)} \sim \left\langle \left| \frac{a^3}{V} \right| \chi \left(\frac{a}{R_0} \right)^2 \frac{R_0^3}{v_{loc}} \right|^4 \Bigg\rangle \times (\hbar\omega)^4 D_i(E_i) D_m(E_i + \hbar\omega) \times D_f(E_i + \hbar\omega') \times \left[\frac{2}{\hbar \Gamma_{mm}} + D_m(E_i + \hbar\omega) \right],$$

where V is the sample volume, Γ_{mm}^{-1} is the lifetime in the intermediate state, m, the angle brackets denote an average over the random positions and sizes of the roughness features, and $D_i(E_i)$, $D_m(E_i + \hbar\omega)$, and $D_f(E_i + \hbar\omega')$ are the density of initial, intermediate and final states, respectively. In contrast to the situation with smooth films (eqs. 1 and 2), the shape of the EDC is determined by the density of states. The presence of the two terms in the square brackets in (3) reflect the contribution to photoemission of two channels of 2-photon excitation, cascade (sequential) and simultaneous. Eq. 3 was obtained by assuming near-threshold excitation and accordingly that $\hbar\omega \sim V_G \sim V_n/(1-\gamma) \sim \hbar^2 G^2/(8m)$.

The required average over position is performed implicitly by using the result of ref. [8]: for fractal structures $\langle |\chi|^4 \rangle \sim Q^3$. This result was obtained for volume fractals. However, based on general considerations involving the inhomogeneous character of the spectral broadening for disordered systems like fractals and self-affine surfaces, one can show that this estimate is valid for self-affine surfaces as well [11]. By estimating the density of states $D \sim (v_{loc}/a^3)E^{-1}$, eq. 3 reduces to a simple form which can be used to estimate the roughness-induced photoemission enhancement:

$$\frac{P_R^{(2p)}(E,\omega)}{P_S^{(2p)}(E,\omega)} \sim f(R_S) Q^3(R_S) \left(\frac{a}{R_S} \right)^2 \times \left[\frac{2V_G}{\hbar \Gamma_{mm}} + \left(\frac{R_S}{a} \right)^3 \right]. \quad (4)$$

Here R_S is the depth of light penetration and $f(R_S)$ is the volume fraction filled by roughness features with size $\leq R_S$. It follows from (4) that approximately isotropic roughness features with $R_0 \sim R_S$ are predominantly responsible for the photoemission. For Ag at $\lambda = 510$ nm, R_S is less than the electron mean free path, l, and Q can be estimated as: $Q(R_S) \sim (R_S/(R_S + l))Q_{bulk}$. Using the following parameters for Ag: $a = 4$ Å, $R_S \approx 120$ Å, $l = 400$ Å, $Q_{bulk} \approx 120$, and assuming that $2V_G/\hbar\Gamma_{mm} \sim 10^2$ to 10^4, and that $f(R_S) \sim 10^{-3}$ to 10^{-1}, the enhancement ratio is calculated to lie between 10^2 and 10^4. Experimentally we observe 10^3.

The experiments were conducted with a time-of-flight photoelectron spectrometer described in detail elsewhere [14]. Ag films 200 nm thick were deposited at 1×10^{-10} Torr at a rate of 1 nm s^{-1} onto a polished Cu mirror using an effusive beam of atoms. Polarized light from a dye laser (10 ns pulse width) 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 to prevent space-charge effects. The second harmonic light power was severely attenuated to give similarly low count rates.

In order to observe near threshold photoelectrons, a +2.00 V bias (V_B) was applied to the time-of-flight tube. In the observed spectra the low energy cut-off is given by $\Phi_{S,R} - \Phi_A + V_B$ where $\Phi_{S,R}$ and Φ_A are the work functions of the smooth or rough surfaces, and the detector surface, respectively. The high energy cut-off is $2\hbar\omega - \Phi_A + V_B$. The photoelectron arrival rate at the microchannel plate detector was limited to a few counts per second. Cubic weighting converted the time-of-flight data to an energy spectrum. No smoothing was used.

The Cu substrate was cooled by means of a closed-cycle He refrigerator. Photoelectron spectra for smooth films were recorded at room temperature, immediately after deposition, and at 30 K after four hours of cool-down. Some smooth Ag films were dosed with H_2O to reduce Φ_S and, thereby, increase the energy window within which photoelectric signal appears. Only the low energy

cut-off shifts on dosing; the high energy cut-off remains fixed indicating that Φ_A is not affected. Step-wise dosing with H_2O to a total of 5 L reduced the low energy cut-off by 0.6 eV beyond which no further change was observed. H_2O does not have any electronically excited states that are accessible with the laser excitation used. Therefore, its presence does not affect the shape of the photoelectron spectrum. Moreover, similar results were obtained with other physisorbed molecules. Photoelectron spectra for rough films were recorded at 30 K immediately after deposition.

Fig. 2 shows normalized 1-photon and 2-photon spectra of a smooth film at room temperature (fig. 2a) and at 30 K dosed with 5 L H_2O (fig. 2b), and of a rough film at 30 K (fig. 2c). The 1-photon and 2-photon spectra of a smooth film are identical within the signal-to-noise level. This is the expected spectrum for photoemission initiated by direct transitions for which the EDC is a product of a "rectangular" $P(E, \omega)$ with a "triangular" $T_0(E)$ function [11]. The influence of $T_0(E)$ is not apparent in fig. 2a because of the narrow range over which photoelectron signal is observed; in fig. 2b, where this range is extended through lowering of Φ_S, $T_0(E)$ is included as a dashed line. The good agreement between the predicted and observed shape of the EDCs suggests that photoemission from a smooth film is initiated by direct (and simultaneous) transitions in the bulk metal both for the 1- and the 2-photon processes. For the 1-photon process this conclusion is not new since no 1-electron transitions are observed in the absorption spectrum of Ag below the plasma edge at approximately 3.8 eV [15]. The weak absorption of Ag in the visible is due entirely to the Drude response.

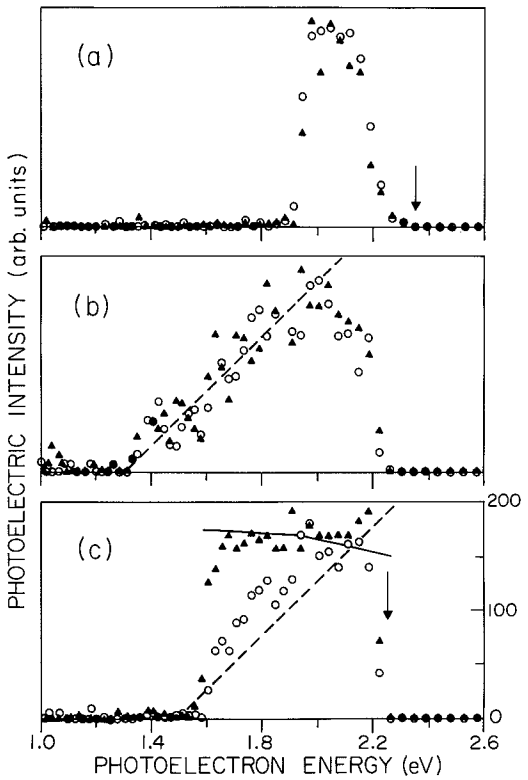

Fig. 2. Normalized 2-photon (triangles) and 1-photon (circles) spectra for (a) a smooth Ag film at room temperature, (b) a smooth film at 30 K dosed with 5 L H_2O, and (c) a rough film at 30 K. The dashed line in (b) and (c) is $T_0(E)$. The solid line in (c) is $D_i(E_i)D_m^2(E_i+\hbar\omega)D_f(E_i+2\hbar\omega)$. The right-hand ordinate in (c) refers to this DOS product in units of Ry^{-4} $atom^{-4}$. The arrows in (a) and (c) indicate the maximum photoelectron energy from the theory of ref. [10].

The 1-photon and 2-photon spectra of a rough Ag film, shown in fig. 2c, are strikingly different from those of the smooth films. The 1-photon spectrum is largely triangular in shape and resembles the smooth film EDCs, but with a small positive deviation clearly evident. The 2-photon spectrum is distinctly rectangular (this shape was reproduced with many films of varying thickness), it is found to be weakly dependent on the presence of adsorbate and it is independent of light polarization. These observations can be understood by assuming the 1-photon response in rough films to be essentially due to direct transitions while the 2-photon response originates from LSP-mediated, indirect transitions.

Photoemission initiated by LSP fields at rough surfaces is expected to be strongly enhanced due to the increase in the local field strength. Moreover the momentum conservation rules applicable to absorption will be relaxed. Hence, according to eq. 3, $P(E, \omega)$ should follow the product $D_i(E)D_m^2(E+\hbar\omega)D_f(E+2\hbar\omega)$, which is drawn as the solid, nearly horizontal line in fig. 2c, as outlined above. (The second term in the square brackets of (3) usually exceeds the first term.) It

is seen that the appearance of the 2-photon EDC is very well explained by the density of states 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 [6,7] that has been ascribed to surface plasmon excitations [7]. The nearly triangular 1-photon response in fig. 2c shows that direct transitions do take place in rough films when there is sufficient detuning from the LSP resonance. The small departure of the 1-photon EDC from the purely triangular shape observed with smooth films suggests (not unexpectedly) that for rough films a greater fraction of even 1-photon induced electron emission comes from the surface region. The photoemission enhancement might also be associated with propogating surface plasmons (surface polaritons). However, considerable scattering of surface polaritons is expected on surfaces with strong roughness and the corresponding enhancement should be dramatically suppressed. Moreover, the photoemission spectra of the rough films obtained in our experiment are not affected by the polarization of the laser, apart from the trivial Fresnel reflectivity effect. This is entirely consistent with LSP excitation in surface roughness and is evident in other experiments, for example, surface enhanced Raman scattering [4].

The different between the two spectra of fig. 2c might also be explained in terms of roughness-induced surface states. We believe this to be a less likely explanation because surface states are expected to be strongly polarization dependent and sensitive to adsorption contrary to what is observed. Furthermore, electron energy loss studies [16] and inverse photoemission measurements comparing rough and smooth [17] Ag show no evidence of surface states. Both studies show the bulk electronic structure of rough and smooth Ag films to be very similar. Our results support that conclusion. We see that the EDC cut-off points predicted by the upper limit of the range $E_F - E_{min}$ (indicated by the two vertical arrows in figs. 2a and 2c) are in good agreement with the high energy extreme of the observed EDCs of both films.

We have presented unique photoemission results comparing 1-photon and 2-photon spectra of rough and smooth Ag films under conditions of equal total photon energy and nearly equal optical penetration depth. Our findings indicate that with smooth films photoemission takes place following direct optical transitions while with rough films, where LSP resonances are excited, photoemission is dominated by absorption of photons in the near-zone fields around surface roughness features, and most of the photoelectrons originate from the surface region. The theory outlined describes all features of the experiments. It extends the three-step photoemission model to encompass 2-photon excitation.

We are grateful to NSERC for their financial support and to Mr. Valery Smelyansky for kindly supplying us with band structure calculations.

References

[1] K. Giesen, F. Hage, F.J. Himpsel, H.J. Riess and W. Steinmann, Phys. Rev. Lett. 55 (1985) 300.
[2] C.N. Berglund and W.E. Spicer, Phys. Rev. 136 (1964) 1030.
[3] M. Moskovits, Rev. Mod. Phys. 57 (1985) 783.
[4] R. Chiarello, V. Panella, J. Krim and C. Thompson, Phys. Rev. Lett. 67 (1991) 3408.
[5] Y. Borensztein, M. Jebari, G. Vuye and T. Lopez-Rios, Surf. Sci. 211/212 (1989) 775.
[6] P.H. McBreen and M. Moskovits, J. Appl. Phys. 54 (1983) 329.
[7] M.I. Stockman, T.F. George and V.M. Shalaev, Phys. Rev. B 44 (1991) 115.
[8] M.I. Stockman, V.M. Shalaev, M. Moskovits, R. Botet and T.F. George, Phys. Rev. B 46 (1992) 2821.
[9] J.T. Stuckless and M. Moskovits, Phys. Rev. B 40 (1989) 9997.
[10] R.Y. Koyama and N.V. Smith, Phys. Rev. B 2 (1970) 3049.
[11] V.M. Shalaev, C. Douketis and M. Moskovits, in preparation.
[12] N.E. Christensen, Phys. Status Solidi B 54 (1972) 551.
[13] C.E. Morris and D.W. Lynch, Phys. Rev. 182 (1969) 719.
[14] J.T. Stuckless, PhD Dissertation, University of Toronto (1991).

[15] P.B. Johnson and R.W. Christy, Phys. Rev. B 6 (1972) 4370.
[16] R.A. Wolkow and M. Moskovits, J. Chem. Phys. 96 (1992) 3966.
[17] (a) A. Otto, K.H. Frank and R. Reihl, Surf. Sci. 78 (1978) 591;
(b) R. Reihl and R.R. Schlittler, Phys. Rev. B 29 (1984) 2267.