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Enhanced two-photon photoemission from coldly deposited silver films

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Photoemission measurements were performed on thick silver films vapor deposited under ultrahigh-vacuum conditions onto cold or warm substrates and on samples subsequently annealed. Laser powers were adjusted so that linear photoemission is produced with 4.5-eV (above-threshold) photons and quadratic photoemission with 2.3-eV (below-threshold) photons. Coldly deposited films were found to produce two-photon photoelectron yields 3 orders of magnitude greater than annealed films. By contrast, only a small enhancement was found for one-photon photoemission produced by the cold films over those of annealed or room-temperature films.

Microscopic roughness of silver metal is known to enhance a variety of optical scattering processes at the surface, notably Raman emission from admolecules, but also surface second-harmonic generation, etc.[1–5] This effect is usually attributed to an increased optical field strength at the surface due to the excitation of localized surface plasmons of the roughness features, electromagnetic resonances which have dipolar character. Silver which has been vapor deposited onto low-temperature substrates, so that there is little thermal annealing of the ballistically aggregating metal, can show a 10^6-fold Raman enhancement.[6] The structures of such films have not been well characterized. Their optical resonance, as indicated by an increased absorbance, is broadly ranged between 2 and 3.5 eV, and peaked near 2.5 eV.[7]

Clean silver has a photoelectric threshold of 4.1 eV or higher, depending on the crystal face exposed.[8] This threshold, however, is sensitive to adsorption, especially of charged species. Furtak and Sass have studied photoemission from roughened silver electrode-electrolyte interfaces, accessing the planar surface plasmon with photon energies near 3.5 eV.[9] A small yield enhancement was observed. More recent works have extended the photon energies into the visible range, where a stronger resonance would be expected. Funtikov, Sigalaev, and Kazarinov have studied photoemission from the electrode-electrolyte interface and report a large roughness induced enhancement, increasing down to 2.3 eV.[10] However, Lopez-Rios and Hincelin report that there is no significant enhancement at these energies for coldly deposited cesiated silver films in UHV.[11] Both sets of results might depend in a complicated fashion upon interaction with the adsorbate.

Using very intense laser radiation it is possible to induce nonlinear effects, among them the emission of photoelectrons which have gained the energy of two (or more) photons. We report here on two-photon photoemission from clean silver at photon energies near 2.3 eV.

Experiments were carried out under ultrahigh-vacuum conditions with a base pressure below 7×10^{-11} Torr. Silver films were made by evaporation from 99.99+% wire in a resistively heated tantalum basket, with pressure excursions to the low 10^{-9}-Torr scale during evaporation. Deposition was at normal incidence onto a polished oxygen-free high-conductivity (OFHC) copper mirror, at a rate of about 6 Å/s for 200 s. The substrate could be cooled from room temperature down to 100 K. A Lumonics excimer-pumped dye laser, along with tracking fre-

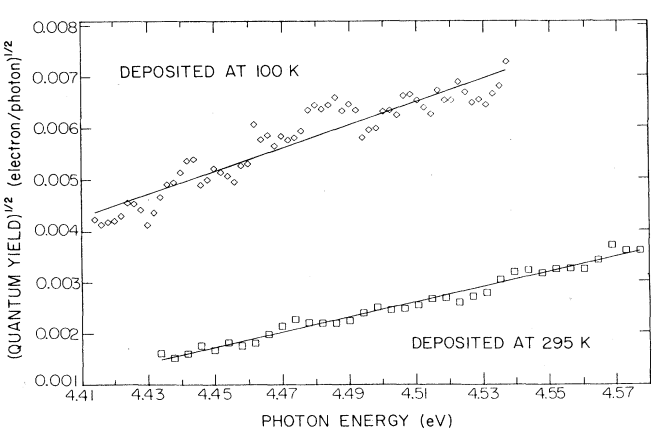

FIG. 1. Fowler plot for one-photon photoemission (measured at 100 K).

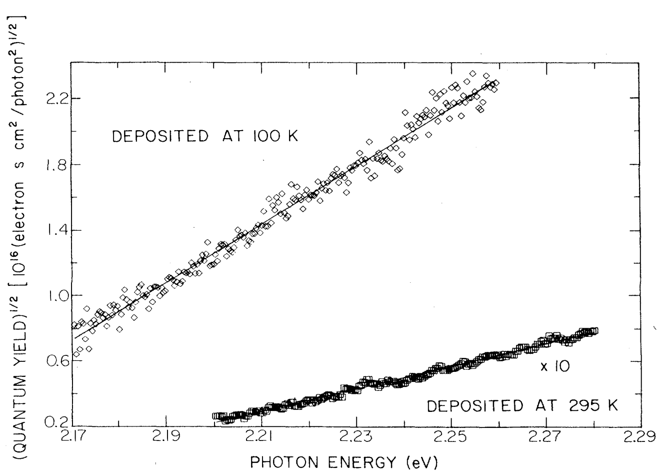

FIG. 2. Modified Fowler plot for two-photon photoemission (measured at 100 K).

TABLE I. Sample types, photoemission thresholds, and photoemission cross sections.

Sample (at 100 K)	ϕ (eV)	A_1 (electron/photon eV^2) (p polarization)	A_2 (electron $cm^2 s$/photon^2 eV^2) (p polarization)	(s polarization)
Deposited 100 K	4.24	5.8×10^{-4}	7.5×10^{-31}	3.1×10^{-31}
Deposited 100 K and annealed 295 K	4.19	2.3×10^{-4}	1.2×10^{-33}	2.4×10^{-34}
Deposited 295 K	4.33	2.3×10^{-4}	1.1×10^{-33}	. . .

quency doubler, provided pulsed laser radiation tunable throughout the visible and near uv spectrum. Light was incident on the sample at 45°, and either s or p polarizations could be generated using a Soleil-Babinet compensator. The incident laser intensity was determined for each pulse. The total emitted charge per pulse was measured using a charge-sensitive preamp between ground and sample, and with a large positive extraction voltage on a counterelectrode.

Linear, or one-photon, photoemission was readily observed at higher photon energies. Over a limited range of energies near threshold the photoelectron yield varied as the quadratic limit of Fowler's[12] law:

$$J/I = A_1(\hbar\omega - \phi)^2 ,$$

where J is the photoelectron flux, I the incident laser intensity, $\hbar\omega$ the photon energy, and ϕ the photoelectric threshold. The constant A_1 is effectively a measure of the cross section for electron excitation and transport to the surface within the metal. Linearized Fowler plots of the square root of the quantum yield versus the photon energy allow determination of the constants A_1 and ϕ. Fowler plots are shown in Fig. 1 for cold- and warm-deposited silver films. The absolute photoemissive quantum yield for the warm-deposited sample is 1×10^{-5} electrons per incident photon, at 4.54 eV.

For photon energies below threshold we could observe photoemission only at much higher laser fluences (but held under 5 $MW cm^{-2}$ peak local intensity). The emitted charge was quadratic with laser intensity for a given photon energy, indicating the absorption of two photons preceding the emission of an electron. For energies near one half the threshold energy, we find that the yield follows a modified Fowler's law:

$$J/I^2 = A_2(2\hbar\omega - \phi)^2 ,$$

where A_2 is the effective two-photon cross section. Modified Fowler plots are shown in Fig. 2. The photoemissive "two-photon quantum yield" of the warm-deposited sample is 5×10^{-35} electron $cm^2 s$ per incident photon squared at 2.27 eV.

In order to compare yields between sample types of different thresholds we use the values A_1 and A_2, as they are formally independent of $\hbar\omega$ and ϕ. Representative results are given in Table I. There are about 3 orders-of-magnitude enhancement of the two-photon cross section for coldly deposited films over those deposited on a room-temperature substrate. Importantly, there is only a small difference between the one-photon cross section for these films. Many of the factors which govern photoyield should affect the apparent cross section of both the one- and two-photon excitations. This includes the relative area of emitting patches (on a possibly higher-threshold surface) and other factors relating to the escape of the hot electron across the surface. However, any field enhancement depending upon resonant excitation of localized plasmons near 2.3 eV would only affect our two-photon cross section.

The nonlinear photoeffect which we observe might actually be a linear photoemission due to doubled energy photons created by second-harmonic generation in the material. However, present estimates of the cross section for second-harmonic generation by silver, enhanced by surface roughness,[13] imply that this indirect process would give rise to relatively negligible photocurrents.

The two-photon photoemission yield enhancement is most simply ascribed to an increased local-field strength near the surface upon resonant excitation of localized surface plasmons. We cannot rule out, however, the possibility that the yield enhancement is due to a roughness induced increase in the density of accessible intermediate one-electron states for a two-step absorption process.

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