Surface-plasmon ejection of Ag^+ ions from laser irradiation of a roughened silver surface

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The kinetic-energy distribution of Ag^+ ions ejected from a roughened silver surface irradiated with *p*-polarized laser light at 532 and 355 nm shows two prominent peaks: thermal Ag^+ ions in the range of 0 to 0.5 eV and Ag^+ ions with a mean kinetic energy of ~ 3.6 eV (2 eV full width at half maximum). Irradiation with 266-nm light shows only the thermal peak. The dependence of the 3.6-eV peak on surface roughness, light polarization, and wavelength implicates a coupling to surface plasmons (SP's); the SP energy for Ag is also ~ 3.7 eV.

In recent years, the study of the interaction of light with silver spheroids has received considerable attention, both on its own merit[1-3] and in investigations of the mechanisms responsible for surface-enhanced Raman scattering.[4-6] Silver is an exceptional material because it exhibits pronounced size effects[7] and has plasmons in the near-UV. Silver manifests its intense bulk and surface plasmons at approximately 3.7 eV. Electron-energy-loss spectroscopy for single crystals of silver shows that the energy of small-momentum surface plasmons depends upon the crystal face and, for Ag $\langle 110 \rangle$, upon crystal orientation.[8,9]

The coupling of photons to surface plasmons requires a mechanism which allows the optical and plasmon dispersion curves to intersect, simultaneously satisfying conservation of energy and momentum. Such conditions can be created by attenuated total reflection or surface roughening.[10,11] Particles of all shapes allow the coupling of light and surface plasmons to some degree; however, spheriods with diameters small compared to the wavelength of light are most efficient. Theory also enjoys computational simplicity for small spheroids.[12] Previous experiments involving the laser-induced ejection of Ag^+ and Ag_2^+ ions have been interpreted in terms of the Ag surface-plasmon resonance.[13] In that experiment, a single-crystal silver surface was irradiated with laser light, and the kinetic energies of the ions were measured by time-of-flight analysis. A mean kinetic energy of 9 eV was found well above the known surface- or bulk-plasmon energy for silver. Other studies have concentrated on the ejection of neutral atoms attributed to surface plasmons. In one experiment, desorption of Al atoms was studied using the method of attenuated total reflection from a thin aluminum film deposited on a glass prism.[14] In yet another experiment, Na atoms were desorbed from Na spheriods.[15] The Na atom desorption rate from particles with 50-nm average radius exhibited a resonant behavior with a maximum at 490 nm. The desorption was found to be nonthermal, and the authors presented evidence that Na atoms were ejected after decay of the collective electron oscillation into a single-electron state. A more recent paper[16] describes how the collective electronic excitation in a small Na particle results in electric-field enhancement at the surface, which could induce electronic transitions leading to the desorption of atoms.

Very recently, there has been considerable interest in plasmon excitations of size-selected small metal-atom clusters. Of particular relevance to this study is the observation of so-called giant resonances in the photofragmentation cross sections of small silver cluster ions (Ag_9^+ and Ag_{21}^+).[17] The peak in the photoabsorption cross section exhibits a reasonably large "blue" shift relative to the respective experimental surface-plasmon peak. Specifically, the parameters were for Ag_9^+ $\hbar\omega_0 = 4.02$ eV, $\Gamma = 0.62$ eV, and Ag_{21}^+ $\hbar\omega_0 = 3.82$ eV and $\Gamma = 0.56$ eV. ($\hbar\omega_0$ and Γ are the energy and widths of the giant resonance, respectively.)

In this Brief Report, studies of the ejection of Ag^+ ions attributed to the decay of surface plasmons following the laser irradiation of a roughened silver surface are presented. A pulsed Quantel YG571C Nd: YAG (yttrium aluminum garnet) laser capable of generating both 10-ns and 30-ps laser pulses was employed. The second, third, and fourth harmonics were used with wavelengths of 532, 355, and 266 nm, respectively. A double Fresnel rhomb was used to rotate the light polarization from *s* to *p* polarization. The direction of the laser light was incident at 45° to the surface normal. Ions emitted normal to the silver surface were detected through a 160° spherical-sector electrostatic energy analyzer, which also acted as a time-of-flight mass spectrometer. Thus, mass-resolved kinetic-energy distributions were recorded. The experimental apparatus and computer data-acquisition procedures have been described previously.[18]

The procedure used was to first roughen a single-crystal surface of silver by focusing the laser on the surface at high power density ($> 5 \times 10^9$ W/cm^2), which was sufficient to form a visible plasma plume. One feature of these laser-produced plasmas is that about 15% of the ablated material is redeposited back onto the surface. The redeposited atoms and molecules reconstruct into interesting morphology. This procedure formed a variety

of features on the surface, ranging from a rough structure to individual well-defined spheriods. Figure 1 shows a scanning electron micrograph of one of the laser ablated surfaces used in the experiment. The important feature is that spheroids were formed on the surface with diameters (450–70 nm) comparable to and smaller than the wavelength of laser light (700–450 nm). Such structures would allow direct optical coupling to surface plasmons.

After forming the roughened surface, the laser power density was reduced to the point at which no ions were detected, and gradually increased until a thermal peak was observed. A further increase in laser power showed the emergence of the Ag^+ peak at ~ 3.6 eV. The kinetic-energy distribution of the Ag^+ ions is shown in Fig. 2 at a laser power of 3×10^7 W/cm^2 for a wavelength of 355 nm and a pulse duration of 30 ps. The first peak has a low kinetic energy (<0.5 eV) and is designated the "thermal peak." This thermal peak was observed for all the other metals which we have studied thus far (Mg, Bi, Pd, Al, Cu, and Au). A detailed study of Pd has been published.[18] The second peak is centered at ~ 3.6 eV. We refer to this as the "plasmon peak" in the discussion that follows. Both of the peaks grew in height with increasing laser power, the thermal peak growing linearly while the plasmon peak increased approximately as the cube of the laser power. The advent of the thermal peak preceded that of the plasmon peak, but the plasmon peak soon dwarfed the thermal peak as the laser power was increased. The same behavior was observed for 10-ns and 30-ps pulse durations at both 532 and 355 nm, the difference being that the longer pulse duration and shorter wavelength required a lower power density to form the plasmon peak. Using 266-nm radiation, the thermal peak was evident, yet the 3.6-eV peak was never observed. The theoretical energy resolution of the analyzer at a 50-eV pass energy is 0.67 eV, which accounts for part of the width of the thermal peak. The ion kinetic-energy distributions are also broadened somewhat by space-charge

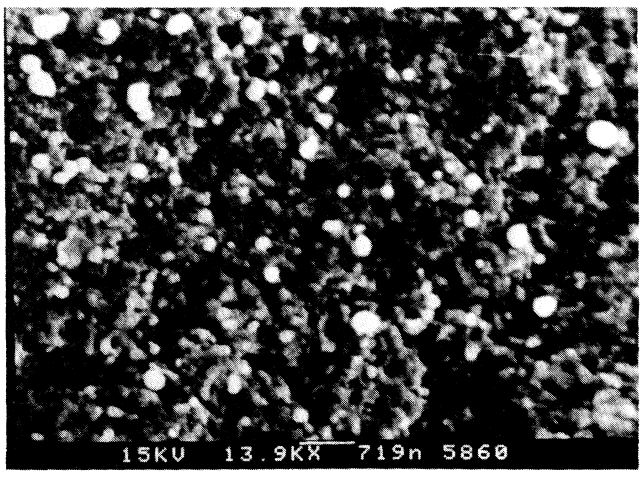

FIG. 1. The scanning electron micrograph of a roughened silver surface used in these studies. The small silver particles are produced by laser irradiation of a smooth silver surface at laser power densities sufficient to produce a plasma ($>5\times10^9$ W/cm^2).

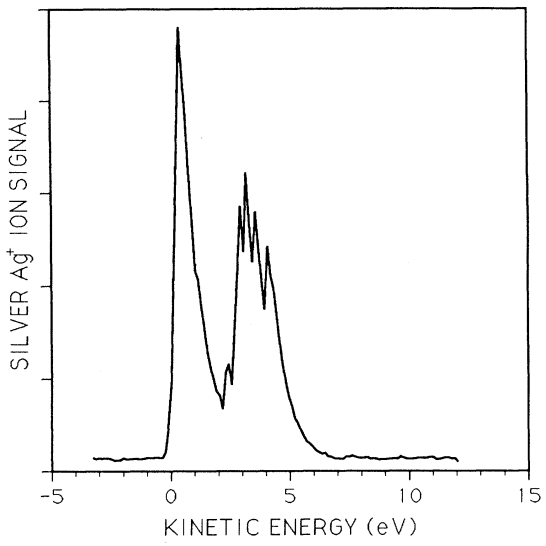

FIG. 2. The kinetic-energy distribution of Ag^+ ions at a wavelength of 355 nm, a pulse duration of 30 ps, and a power density of 3×10^7 W/cm^2.

conditions. A parametric least-squares-fitting routine was used to fit a Gaussian curve to the plasmon peak. This established the centroid of the plasmon peak to be 3.6 ± 0.15 eV.

At a planar, vacuum/solid interface, direct photon-plasmon coupling is forbidden[10,11] since it is impossible to match simultaneously the energy and momentum of the incident photon and surface plasmon. However, such matching is possible for a roughened surface. The broken symmetry allows the electric field of the incident light to couple to the plasmons.[3] The treatment of this effect is appropriate for spheres that have a diameter equal to or smaller than the wavelength of light, which is the realm of our experimental data. A measure of the strength of the coupling is found in the induced dipole moment of the roughening feature, which scales, in the simplest case of a dielectric sphere suspended in free space, as $(\epsilon+2)^{-1}$, where ϵ is the complex dielectric function $(\epsilon_1+i\epsilon_2)$. The important feature is that when $(\epsilon+2)$ becomes small, i.e., $\epsilon_1\simeq-2$ and $\epsilon_2\simeq0$, the induced dipole strength becomes very large, and plasmons can be resonantly excited. For a silver sphere of 10-nm diameter, the plasmon resonance occurs at ~ 3.5 eV with a full width at one-half height of ~ 0.5 eV.

In addition to perfect spheres, ellipsoids are known to facilitate the excitation of surface plasmons; however, the wavelengths for optical stimulation are shifted to longer wavelengths. Thus the ellipsoidal shapes shown in Fig. 1 give a redshift to the coupling of light to plasmons, extending the wavelength range from 355 to 700 nm. The plasmon peak was also observed for 532-nm light, which falls into a region of shapes observed from our scanning electron microscopy (SEM).

The Ag^+ ion plasmon peak was observed for both 355- and 532-nm light. This was explained in terms of the roughening features observed in the SEM. The experiment was repeated with 266-nm light, but no plasmon

peak was observed. Although spheroids of the type shown in Fig. 1 were produced, only the thermal Ag^+ signal was detected. This observation is consistent with the fact that 266-nm light will not excite surface plasmons. Thus the observed wavelength dependence is consistent with the wavelength criteria of coupling to surface plasmons through roughening. A major question remains as to how light at 355 or 532 nm could produce Ag^+ ions with kinetic energy above the photon energy. Clearly more than one photon would be responsible for the Ag^+ ion ejection. The details of how photons excite surface plasmons at one photon energy (e.g., 532 nm) and eject Ag^+ ions with energies corresponding to the surface-plasmon energy (~ 3.7 eV) is a matter for future consideration.

The production of surface plasmons is favored by using p-polarized light.[1] Although p and s polarization are undefined for a single sphere suspended in space, when spheres or spheroids are laid down on a plane the symmetry is reduced and the definition of s and p polarization retains meaning. Figure 3 shows the polarization dependence of the plasmon peak. The peak was a maximum for p-polarized light, i.e., light with its electric vector in the plane of incidence. For s-polarized light, the signal reached a minimum but did not vanish entirely. The Ag^+ intensity versus polarization angle fits very closely to a $\sin^2\theta$ function. The thermal peak also exhibited a $\sin^2\theta$ dependence, as expected, since light absorption is maximum for p-polarized light. Thus, the observation that the 3.6-eV Ag^+ ion signal is a maximum for p-polarized light is a necessary but not a sufficient condition for attributing its occurrence to surface-plasmon decay.

We have attempted to estimate the efficiency for producing Ag^+ ions from laser desorption via surface-plasmon decay. Assuming that Ag^+ is ejected isotropically from a point in front of the surface, the fraction of ions that enter the analyzer is $\sim 6\times 10^{-5}$. From measurements of the number of ions detected per laser shot through the analyzer, we estimate the total number of ions as 3.2×10^6 per laser pulse. The laser power of 10^7 W corresponds roughly to 8×10^{14} photons for a 30-ps laser pulse. From this we obtain $\sim 10^8$ photons per Ag^+ ion ejected or alternately 10^{-8} ions/incident photon.

Our results differ from a previous report in Ref. 13 of plasmon-induced ejection of Ag^+ and Ag_2^+ ions. In that case, using much lower intensity light at 351 and 248 nm, the Ag^+ ions from an unroughened silver surface had a kinetic energy of 9 eV. Much more work is needed to determine if the 9- and 3.6-eV Ag^+ ion-ejection mechanisms are related. It would seem not. Others have reported the ejection of neutrals due to plasmon decay.[15,14] In these two cases, the kinetic energy of the neutrals ejected was considerably less than the surface-plasmon energy.

The occurrence of the Ag^+ peak at 3.6 eV has a simple physical interpretation. Ions which are in the process of being thermally liberated from the roughened surface

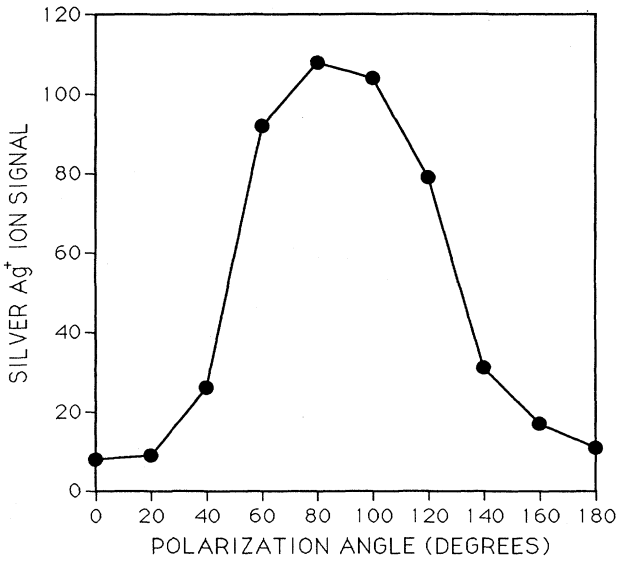

FIG. 3. The laser polarization dependence of the "plasmon peak" (the ~ 3.6-eV peak shown in Fig. 2). The Ag^+ ion yield is a maximum for p-polarized light, i.e., light with its electric vector in the plane of incidence.

subsequently absorb a quantum of energy from the surface plasmon. The presence of the thermal ions combined with the fact that the plasmon peak does not extend down to 0 eV suggests that free ions residing near the surface receive a liberating impulse from the plasmon decay. Ritchie, Manson, and Echenique[19] have considered such an ion ejection as an inverse bremsstrahlung-type absorption of the surface-plasmon quantum by an Ag^+ ion which undergoes a collision with the surface.

This paper represents definitive experimental evidence for the direct conversion of the surface plasmon into ionic kinetic energy. In addition to the observed Ag^+ ion emission, it is expected that neutral silver atoms are also ejected from the surface with an energy equal to or less than (plasmon energy minus the Ag^0 surface binding energy) the surface-plasmon energy. Future studies are designed to examine neutral ejection under low laser power conditions.

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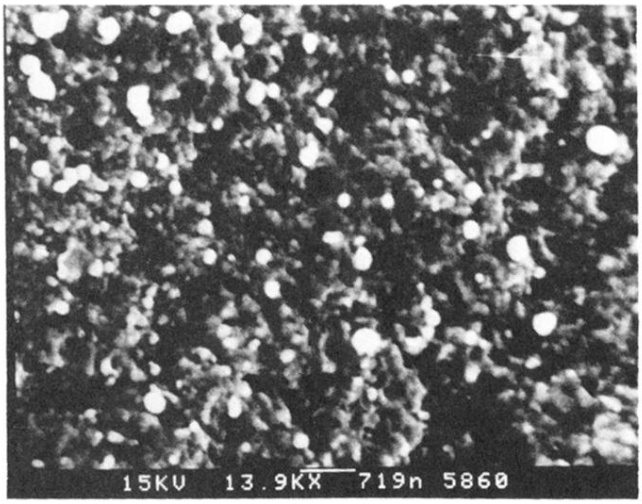

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