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RADIATIVE DECAY OF SURFACE PLASMONS
ON NONSPHERICAL SILVER PARTICLES*

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We have studied the radiation emitted by electron-bombarded silver particles. Electron micrographs have shown that the particles, obtained by heating thin (5 nm) silver films, were oblate (flattened) with minor axes aligned along the substrate normal. The characteristic wavelength obtained by bombarding these particles with 15-keV electrons was found to vary with angle of photon emission. We have modeled this wavelength shift as a result of the mixture of radiation from dipole and quadrupole surface-plasmon oscillations on oblate spheroids. Experimental observations of the energy, polarization, and angular distribution of the emitted radiation are in good agreement with theoretical calculations.

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Introduction

The interaction of electromagnetic radiation and charged particles with small metal spheres has been the subject of a great deal of research⁽¹⁻⁵⁾. The effects of different particle-shapes have been considered⁽⁶⁾, and regular nonspherical particles have been produced to study surface-enhanced Raman scattering⁽⁷⁾ and second-harmonic generation⁽⁸⁾. A study of the radiation emitted by electron-bombarded metal particles could yield important information on the effects of nonspherical shapes on surface plasmon related processes.

Experimental Apparatus

We have modified a Zeiss Novascan 30 scanning electron microscope so that the radiation from electron-bombarded samples can be analyzed as to wavelength, polarization, and angular distribution. The experimental apparatus is to be described in detail elsewhere⁽⁹⁾. We give a brief description below.

A beam of 1,5,15, or 30 keV electrons enters the evacuated sample chamber vertically. It can be positioned on a single spot or raster-scanned over an area on the sample. The sample stage is electrically isolated so that the incident electron beam current can be monitored. The stage can be rotated about a horizontal axis from outside of the vacuum so that the angle of electron incidence can be varied.

We have designed a periscope which allows us to collect the radiation emitted by the sample and analyze it in a GCA/McPherson scanning monochromator. The periscope uses a 45-degree mirror, a quartz focussing

lens, a polarizer, and a quartz fiber-optic bundle⁽¹⁰⁾ mounted in a cylindrical sleeve on a port in the sample chamber. The sleeve is mounted on o-rings and can be rotated without breaking vacuum. This rotates the optical axis of the periscope in an arc centered at the sample so that radiation emitted at any angle relative to the sample normal can be collected. One end of the fiber-optic bundle is spread into a 0.5 mm row of fibers which forms the entrance slit to the monochromator. A UV-sensitive photomultiplier tube detects the light at the exit slit.

The optical response of the system was obtained by using a tungsten light source calibrated for spectral intensities by the National Bureau of Standards. The photomultiplier current and the electron beam current are read by a PDP-11/23 computer which automatically normalizes the photomultiplier output to a constant electron beam current and corrects for the optical response of the system. The corrected current is displayed on a Tektronix 4025 graphics terminal from which a hard copy is obtained.

Sample Preparation

A 3-5 nm film of silver^{was} evaporated onto a highly-polished silicon chip⁽¹¹⁾. The sample^{was} placed into a 720 °C oven under an inert gas atmosphere for 5 seconds. Electron micrographs of the film before heating showed no detectable structure (to within the 10 nm resolution of the microscope). After flash-heating, the chip was covered with particles of about 40 nm ($\pm$ 7.5 nm) average size. The particles had circular cross section in the plane of the substrate surface and average center-to-center spacing of about 70 nm. The "shadows" cast by the particles

when silver was evaporated onto the samples from a near-grazing angle were found to be about half as long as they would be if the particles were spherical. This indicated that the particles were flattened out along the direction of the substrate normal. This result was also indicated by high-sample-tilt electron micrographs.

Experimental Results

The samples were bombarded with 15 keV electrons incident at 50° to the substrate normal. The intensity of the radiation was measured as a function of wavelength for various angles of emission. Figure 1 shows a typical set of spectra.

No intensity was observed along the normal. As the angle of emission increased (to about 10° - 20°), a peak in the P-polarized radiation (polarized in the plane defined by the normal and the direction of emission) was observed between 350 nm and 360 nm. At intermediate angles (40° - 50°), the peak had broadened, increased in intensity, and shifted to shorter wavelengths. For large angles (about 70° - 80°), the peak had shifted to still shorter wavelengths (to between 330 nm and 340 nm), but the width and intensity had decreased. No S-polarized radiation (perpendicular to P-polarized) was detected for these samples.

Comparison With Theory

Calculations for the radiation patterns resulting from the decay of surface plasmons on oblate spheroids⁽¹²⁾ show that the observed wavelength shift could be explained as a mixture of radiation from dipole

and quadrupole charge-density oscillations. For particles that are small compared with the wavelength of the emitted light, the patterns from these modes differ very little from those of the corresponding modes on spheres. Figure 2 shows the superposition of dipole and quadrupole radiation patterns of equal peak intensities. All of the radiation is P-polarized. We see that no radiation is emitted along the normal. At small angles, the radiation is dominated by the quadrupole mode. For intermediate angles, there is a mixture of radiation from the two modes. For large angles, the radiation is dominated by the dipole mode. This type of superposition of radiation could explain the observed results if the dipole mode had a higher energy (radiating at a shorter wavelength) than the quadrupole mode.

Using the values of the dielectric response function calculated for oblate spheroids⁽¹³⁾ and experimental optical data for silver⁽¹⁴⁾, we can obtain the mode energies appropriate for oblate silver particles. Figure 3 shows a plot of these energies for the dipole and quadrupole modes as a function of particle shape. The shape parameter is the "radial" coordinate in oblate spheroidal coordinates⁽¹⁵⁾, and can be defined by

$$\text{Shape Parameter} = [(A/B)-1.0]^{-1/2}, \quad (1)$$

where A is the particle major axis length, and B is the minor axis length. Large values of the shape parameter refer to spherical particles. Figure 3 shows that for spheres, the dipole mode has a lower energy than the quadrupole mode. This contradicts the experimental results. However, for particles with shape parameters of less than 0.9, the modes are reversed.

Figure 2 shows that the most nearly complete separation of the two modes is obtained by comparing radiation at small angles with radiation at large angles. The three sets of points labeled a, b, and c in Figure 3 show the peak-energies for small angle (low energy) and large angle (high energy) radiation from three samples. For each sample, the best fit to a single value of the shape parameter is indicated by a vertical line (the shape parameter must be the same for radiation from two modes on the same sample). The values shown for the shape parameters for a, b, and c give major-to-minor axis ratios of 4.1:1, 3.2:1, and 2.6:1, respectively. These values are consistent with values obtained for similar samples using the shadow-casting technique.

Conclusions

Particles formed by flash-heating thin silver films have been shown to be oblate with minor axes oriented along the substrate normal. This particle-alignment allows the angular dependence of the radiation to be measured. All of the features observed in the radiation emitted by the electron-bombarded particulates have been explained as the result of a mixture of radiation from two surface plasmon modes on oblate silver spheroids.

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Figure Captions

Fig. 1. Spectra obtained from electron-bombarded silver particles for three angles of emission. Radiation is dominated by the quadrupole surface plasmon mode for small angles and by the dipole mode for large angles. At intermediate angles, the mixture of the two modes gives two unresolved peaks.

Fig. 2. Radiation patterns from dipole and quadrupole plasmon modes on oblate spheroids. Radiation emitted in the directions indicated by the arrows should be predominantly single-mode.

Fig. 3 Mode-energy for surface plasmons on oblate silver spheroids as a function of particle shape. Large values of the shape parameter give spherical particles, and small values give disks. Vertical lines labeled a, b, and c give the best fits to single-values of the shape parameter for radiation from three samples. For each sample, the higher energy radiation was emitted at large angles ($\sim 80^\circ$), and the lower energy radiation was emitted at small angles ($\sim 20^\circ$).

FIGURE 1

FIGURE2

FIGURE 3