Light emission from small metal particles and thin metal films excited by tunneling electrons

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(Received 5 December 1980)

We have measured the light intensity versus photon energy of six types of electron tunnel junctions and compared the experimental results to the localized plasmon model of Rendell, Mühlschlegel, and Scalapino, and to the smooth and slightly roughened junction model of Laks and Mills. The types of junctions used to test the theories were Al-Al_2O_3 junctions completed with a top electrode consisting of either an evaporated metal film of Au or Ag, or evaporated Au or Ag particles that were electrically connected by an evaporated Au or Ag film. The p-s–polarized light emitted by junctions with Au or Ag particles is consistent with the localized plasmon model. The "s"-polarized light of the particle junctions and the essentially unpolarized light of the Au and Ag film junctions may be consistent with the theory of Laks and Mills for slightly roughened junctions.

I. INTRODUCTION

There are both theoretical and practical reasons for studying thin-film structures that can convert electrical energy into light. Experiments by Hwang, Schwarz, and Jain[1] and McCarthy[2] stimulated recent work on light emission from metal-insulator-metal tunnel junctions. The light emission has been enhanced by roughening with CaF_2,[3] by using a rough Mg bottom electrode,[4] by introducing small metal particles,[3,5-7] and by fabricating junctions on holographic gratings.[8] Even with this enhancement, however, the junctions are inefficient, being in the 10^{-5} range at best.

Despite their present poor efficiencies, the junctions are promising for future matrix addressable thin-film displays (such as flat-screen televisions or computer output terminals). They involve very little material, only a 50-nm-thick film of aluminum and roughly 10-nm mass thickness of silver or gold. They can be run with low voltage dc since they will produce light up to a photon energy equal to the applied bias. Thus, the entire visible range of the spectrum can be covered with applied bias voltages of less than three volts. The color is tunable throughout the visible range. In fact, junctions can be voltage tuned to produce light from the infrared well into the ultraviolet. The switching time of the junctions should be limited only by their RC time constant; a typical value for a 0.2-m $\times$ 0.2-mm junction would be 10^{-7} seconds. This time could be decreased for smaller junctions.

This experimental work on light-emitting tunnel junctions has been accompanied and stimulated by theoretical work.[9-16] Two basic approaches that have emerged in recent theoretical work are (1) to treat microstructures on the junction (e.g., balls) as small antennae driven by the noise power spectrum of the tunnel junction,[9-11] and (2) to treat roughness on the top electrode as a perturbation that allows radiation from plasmons excited by the tunneling electrons in the top film.[12,13] Here we examine the applicability of these theories to new data on new types of light-emitting tunnel junctions.

We made Al-Al_2O_3 tunnel junctions with top metal electrodes of Au and Ag films and with Au or Ag particles connected by Au or Ag overlayer films. We measured the polarization, frequency spectrum, and angular distribution of the emitted light. The light output of the junctions with top metal electrodes without particles may be consistent with Laks and Mills's theory[12] for slightly roughened tunnel junctions. Junctions with top electrodes containing particles seem to emit unpolarized light due to random surface roughness[12] and mostly p-polarized light due to localized plasmons as predicted by Rendell, Scalapino, and Mühlschlegel.[10]

II. EXPERIMENTAL

Gold-particle electron tunneling junctions were prepared as previously described.[5,7] An Al film, 50–100 nm thick by 2 mm wide, was evaporated onto a glass slide and oxidized by brief air exposure at 200 °C. Gold was evaporated on the entire glass slide in a 2000-Pa (15-Torr) argon atmosphere to form gold particles. If the oxidation step followed particle deposition, the junctions were sometimes more efficient while their spectrum was essentially unchanged. Five conducting Au or Ag cross strips, 15 nm thick by 3.5 mm wide, were evaporated in vacuum to electrically connect the particles and form five completed junctions. Thinner Au or Ag strips were not reliably conductive over the particles, while thicker Au or Ag strips gave junctions with lower efficiencies. Silver-particle tunnel junctions were prepared similarly by evaporating Ag rather than Au in a 2000-Pa (15-Torr) argon atmosphere after the Al oxidation step. On some runs the junctions were completed without particles, yielding junctions that were smoother and less efficient.

We used carbon-coated-nickel electron-microscope grids that were magnetically held next to junctions during particle deposition to determine particle size and distribution. The grids were covered with Al before the particle deposition and Au or Ag afterwards to resemble junctions. However, the metal films were only about half as thick as junction films to allow enough electron-beam transmission for electron microscopy. Figure 1 shows electron micrographs of typical Au and Ag particles. Au- and Ag-particle sizes ranged from about 10 to 90 nm. Surface coverage by particles on light-emitting junctions varied from 10-30 %. Gold particles (~40-nm diameter) tended to form agglomerations that were often several hundred nanometers across. Silver particles tended to form larger (~70-nm diameter) particles separated from each other by many small particles ($\lesssim$10 nm across).

Spectra of the light emitted from the junctions were taken from $\lambda = 350$ to 830 nm ($E \approx 3.5$ to 1.5 eV) with a monochromator of ~2-nm resolution and were stored on a data acquisition system. Bias voltages on the junctions were varied between 2.0 and 3.7 V (current between 8 and 100 mA). Below this range of voltage and current little or no light was observed; above this range the junctions tended to burn out quickly. Spectra were taken at different angles, θ, relative to the normal of the junction and for two polarizations, s and p. In orientation s the transmitting axis of the Polaroid filter was parallel to the plane of the junction and perpendicular to the line of observation. In orientation p the transmitting axis of the filter was in the same plane as s but rotated 90° about the line of observation.

Background noise was subtracted from the raw data with the use of the data acquisition system. Each spectrum was then corrected for the photo-

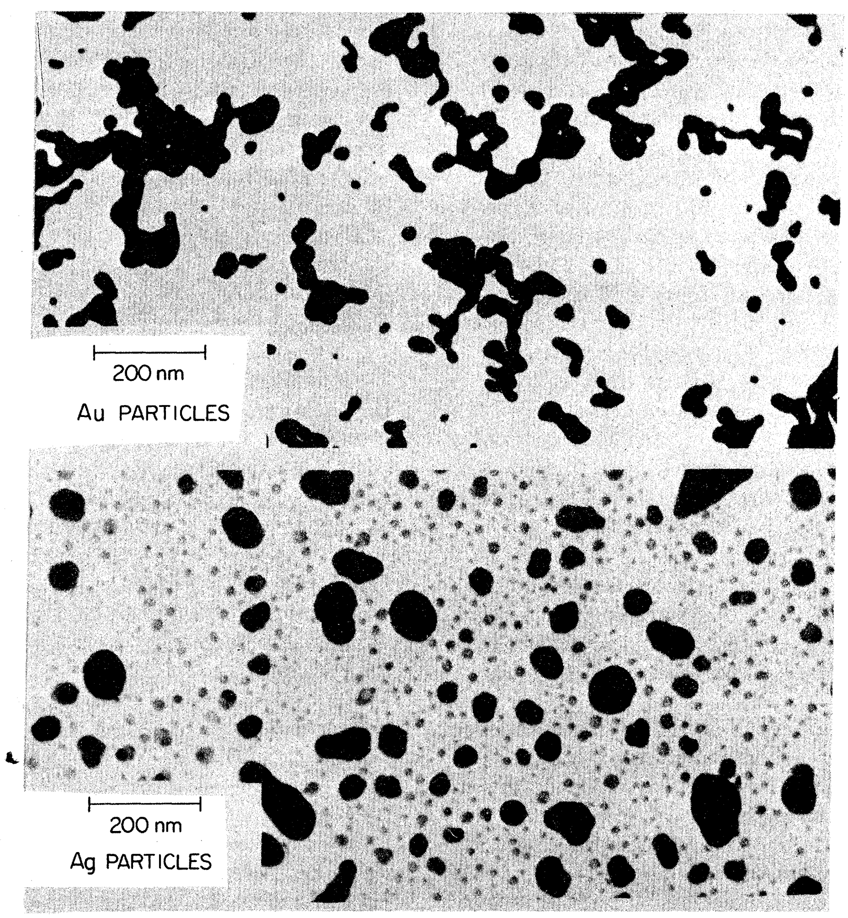

FIG. 1. Electron micrographs of gold particles (top) and silver particles (bottom). The particles were prepared by evaporation in an argon atmosphere (pressure $\approx$2000 Pa $\approx$15 Torr).

response of the monochromator, photomultiplier tube, and optical components by dividing the data by the spectrum of a calibrated tungsten lamp. The resultant quotient was multiplied by the known calibrated intensity function of the lamp yielding the true light intensity of the junctions as a function of wavelength. The efficiency of the junctions was measured with a calibrated silicon diode which measured the total light output (typically 0.01 to 10 μW).

All junctions could be run at room temperature exposed to air at low voltages. The Au-particle junctions with Au top electrodes were fairly stable for many months at voltages as high as 3.5 V, as were the Au-film junctions with no particles. The junctions containing Ag particles or films were not very hardy in air, however, and were protected with a viscous index-matching oil or operated in vacuum when running at voltages above 2 V. When operated in vacuum ($P \approx 10^{-7}$ Pa $\approx 10^{-9}$ Torr), they were usually cooled to 50 K using a helium recirculating refrigerator. This resulted in the junction's current-voltage characteristics being more stable than the oil-protected junctions or noncooled junctions. It also allowed operation at higher voltages, up to 3.7 V.

III. RESULTS AND DISCUSSION

Figure 2 curve *a* shows the intensity as a function of photon energy of p-s-polarized photons emitted at 60° from the junction normal from an Au-particle tunnel junction with an Au top electrode. The dc bias voltage was 3.01 V. p-s-polarized photons are photons emitted by a dipole with its dipole moment perpendicular to the surface. As shown previously,[7] the angular distribution and spectrum of p-s photons emitted by junctions composed of Au particles with an Au top electrode is consistent with the localized plasmon model.[9,10] This model explains the broad peak in the intensity near 1.9 eV as due to a plasmon resonance localized in a cavity formed at the Au-particle–insulator interface. This mode can be excited by optical frequency fluctuations of the tunneling current through the junction and may emit a photon on decay due to the plasmon's localized nature. The measured p-s-polarized photon intensity peaks at an angle $\theta \approx 55°$, as would be expected from a perpendicular dipole radiating just above a metal surface. The calculated and observed efficiencies are both in the 10^{-5} range. (Generally, the efficiencies of the particle junctions were in the 10^{-5} range while the efficiencies of film junctions were in the 10^{-7} range.) The theoretical width of the peak in the observed spectrum depends on particle-size distribution and agrees well with the experimentally observed spectral width and particle-size distribution. (The peak position in energy should depend roughly on the $-\frac{1}{4}$ power of the particle size.[9,10]) However, the localized plasmon theory does not account for the extra s-polarized light emitted by the junction which is nearly equal in intensity to the p-s-polarized light.

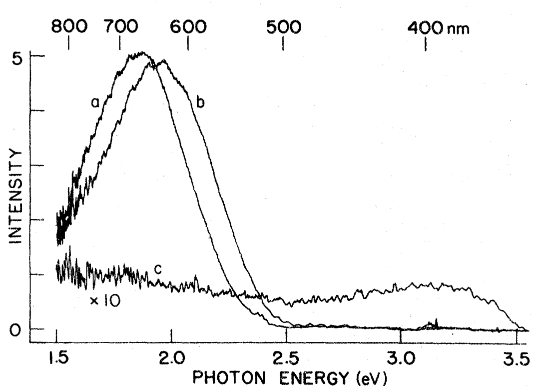

FIG. 2. Intensity of p-s-polarized light versus photon energy at $\theta = 60°$ relative to the junction normal. Each unit on the intensity axis represents approximately 1×10^{-4} W/Sr eV. Curve *a*: gold-particle junction with gold top electrode, 3.01-V bias. Curve *b*: gold-particle junction with Ag top electrode, 3.01-V bias. Curve *c*: unpolarized light, gold top electrode, no particles, 3.50-V bias.

Figure 2 curve *b* shows the p-s intensity versus photon energy at $\theta = 60°$ for an Au-particle junction with an Ag top electrode. The junctions used for Fig. 2 curves *a* and *b* were both constructed on the same glass slide so their particle distributions are nearly identical. They both had a bias voltage of 3.01 V applied to them. Their spectra are nearly identical except for the peak intensity in curve *b* being about 0.1 eV higher in energy. The reason for this small peak shift may be due to (1) a change in the effective dielectric constant of the particles due to the addition of the top metal electrode or (2) emission or absorbance by the top metal electrode. Both show a peak that appears to be due to a localized plasmon resonance associated with Au particles.

Figure 2 curve *c* shows the spectrum of an Au-film junction with no particles on it. No resonance appears here and the only structure besides noise is due to (1) a quantum cutoff at 3.5 V (there are no photons with $E > 3.5$ eV) and (2) an Au interband transition near 2.5 eV that causes a slight dip in the light output at 2.5 eV (the imaginary part of the Au dielectric constant is rapidly increasing with energy while the real part is increasing toward zero with energy).[17] This may be a cause of the sharp dropoff of the high-energy side of the peak in curves *a* and *b* of Fig. 2 (especially curve *a* since it has an Au top electrode).

Figure 3 curves *a* and *b* show the intensity of *p*-*s*-polarized photons versus photon energy at $\theta = 60°$ relative to the junction normal for Ag-particle tunnel junctions with a 3.5-V bias applied. Curve *a* shows the effect of an Au top electrode; curve *b* shows the effect of an Ag top electrode. Figure 3 curve *b* resembles the calculated absolute dipole-moment squared of a plasmon localized at the Ag-particle–Al_2O_3 interface above an Al surface.[11] The calculated dipole-moment squared shows two broad overlapping peaks at about 1.9 and 2.6 eV, the peak at 2.6 eV being nearly twice the peak at 1.9 eV. When realistic particle sizes and distributions (obtained from Fig. 1 curve *b*) are roughly put into the theory, there is enough smearing of the peak positions to yield a plot of the dipole-moment squared similar to Fig. 3, curve *b*.

Figure 3, curve *a* (Ag particles, Au top electrode) has a peak near 1.9 eV but then decreased to about $\frac{1}{3}$ the peak value at 2.5 eV and then remains constant until near the quantum cutoff at 3.5 eV. This behavior is similar to the spectrum of Ag particles placed 5 nm above an Au top electrode by means of a MgF_2 spacer layer as reported by McCarthy and Lambe.[3] It appears in each case that the Au electrode absorbs photons with energies near 2.5 eV (i.e., gold appears yellowish since it absorbs blue-green light).

Figure 3 curve *c* is the spectrum of unpolarized photons at $\theta = 60°$ for an Ag-film junction with no particles and an applied bias voltage of 3.5 V. This spectrum shows no structure except for noise

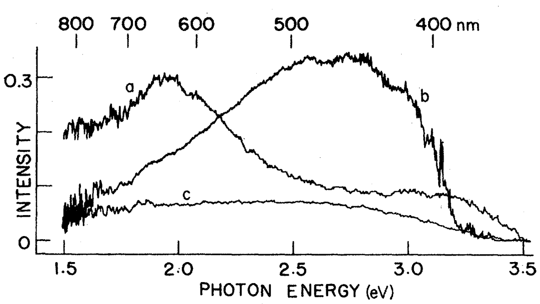

FIG. 3. Intensity of *p*-*s*–polarized light versus photon energy at $\theta = 60°$ relative to the junction normal. Each unit on the intensity axis represents approximately 1×10^{-4} W/Sr eV. Curve *a*: silver-particle junction, gold top electrode, 3.50-V bias. Curve *b*: silver-particle junction, silver top electrode, 3.50-V bias. Curve *c*: Unpolarized light, silver top electrode, no particles, 3.50-V bias.

and a cutoff slightly below the quantum cutoff at 3.5 eV. The film junctions (curve *c* in Figs. 2 and 3) gave about 10% more *p*-polarized than *s*-polarized light. This "excess" *p*-polarized light had essentially the same spectrum as the no-Polaroid spectrum. Note also that the spectrum in Fig. 3, curve *a* extends to the quantum cutoff at 3.5 eV while the spectra in Fig. 3, curve *b* or *c* do not. This may be due to emission by the gold film as seen in Fig. 2, curve *c* or to the Au film being less absorbing than the Ag film near 3.5 eV. We note that from 3 to 3.8 eV the real part of the dielectric constant of Ag rapidly increases from about -5 to +0.4, while the imaginary part decreases from about +1 to +0.4. Thus Ag has a large absorbance in this spectral region.[18] The spectra of smooth and slightly rough Ag- and Au-film tunnel junctions have been calculated by Laks and Mills[12] and the observed thin-film spectra (curves *c* of Figs. 2 and 3) do not resemble their calculations for perfectly smooth junctions. In fact, the calculations give peaks where we see dips and yield *p*-polarized light when we observe predominantly unpolarized light). The calculated spectra of slightly rough junctions are qualitatively similar to the observed spectra, but quantitative comparison will depend on the adjustment of the parameters of the theory. The angular distributions and polarization properties are in agreement with the calculations for slightly rough junctions.[12]

IV. SUMMARY

In our study of the light emitted from tunnel junctions we have shown the following.

(1) The spectrum and angular intensity distribution of *p*-*s*–polarized light emitted by junctions containing particles are consistent with the localized plasmon model.[9,10]

(2) The angular intensity distribution and perhaps the spectrum of *s*-polarized light emitted by junctions containing particles are qualitatively consistent with the slightly roughened tunnel junctions model.[12] Theoretical work matching the experimental conditions remains to be done for quantitative comparison.

(3) The angular distribution and perhaps the spectrum of unpolarized light emitted by thin-film junctions without particles may be consistent with the slightly roughened tunnel junction model.[12] More theoretical and experimental work needs to be done to describe the actual roughness spectrum of a junction.

(4) We see no evidence for photon emission that can be described by the perfectly smooth junction model.[12]

Interesting questions that remain are (1) Can the model of slightly rough junctions quantitatively reproduce the experimentally observed s-polarized spectra of particle junctions if the proper roughness parameters are put into the theory, or is the s-polarized light perhaps due to scattered p-s-polarized light or some other mechanism? (2) Can tunnel junctions be made more efficient (perhaps by building the proper microstructure on the junction)?

ACKNOWLEDGMENTS

We thank Professor D. J. Scalapino, Professor J. R. Schrieffer, and Professor H. Metiu for stimulating discussions and Professor J. Tinsman for suggesting improvements in the manuscript. This work was supported by NSF Grant No. DMR79-25430.

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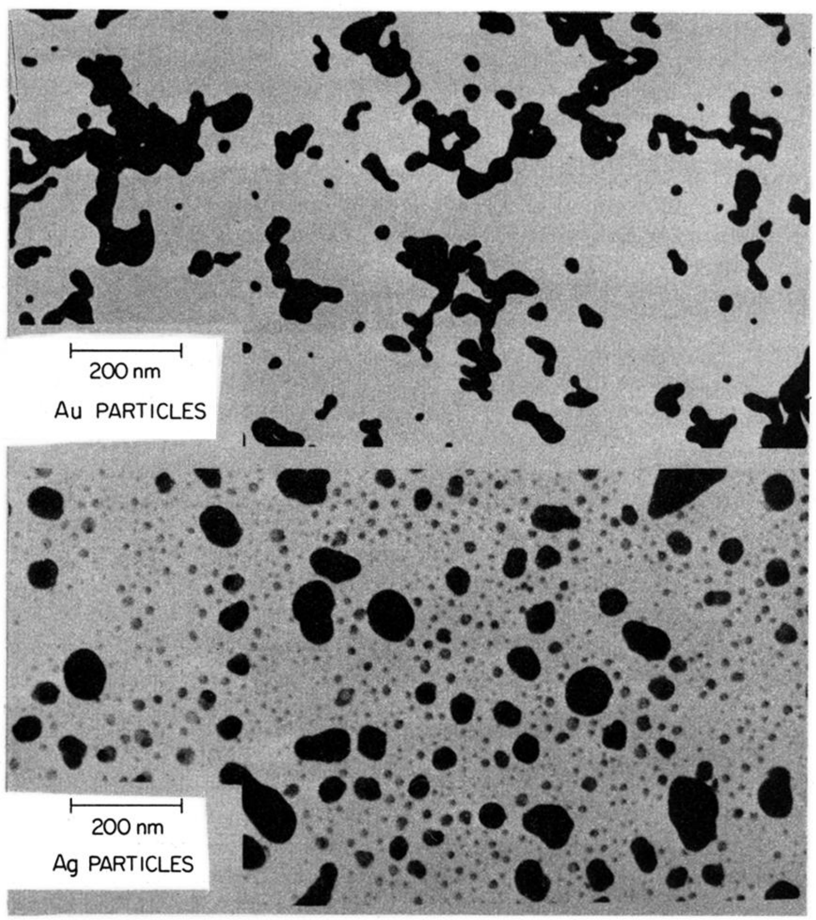

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