of spin in φ should be considered). The final potential application we mentioned is the two-band Hubbard model called the Anderson-lattice model, currently the vogue in the mixed-valence problem.

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[a]Permanent address: Michigan State University, East Lansing, Mich. 48824.

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Image of the Electron Energy-Loss Function in Light Emitted from Tunnel Junctions

D. G. Walmsley, H. F. Quinn, and P. Dawson
School of Physical Sciences, New University of Ulster, Coleraine BT52 1SA, Northern Ireland
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Tunnel junctions of the type Al-I-M ($M \equiv$ Au, Cu, Ag) prepared on CaF_2-roughened substrates emit broadband visible light. It is found that the light intensity variation with wavelength in the range 350 to 700 nm images the electron energy-loss function, $\mathrm{Im}(-1/\epsilon)$, of each metal M as calculated from its optical constants. It is concluded that surface plasmons are damped above the interband transition in Au at 2.5 V and in Cu at 2.25 V. The findings are in harmony with data from surface-enhanced Raman spectroscopy.

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Tunnel junctions with randomly rough metal surfaces emit broadband visible light when they are subjected to a voltage bias.[1] The maximum energy of the emitted photons, $h\nu_{max}$, is determined by the applied bias, V_a, according to the quantum condition $h\nu_{max} = eV_a$. Initially[1] it was thought that the tunneling electrons excite slow junction plasmon modes which then decay by photon emission. More recent studies,[2] particularly on junctions with sinusoidal surface profiles,[3,4] point to fast surface-plasmon polaritons (SPP) as the intermediate state. Possible effects due to local plasmon modes excited in small particles also have been reported.[5] A theoretical description of these processes has been developed by Laks and Mills (LM).[6]

As yet, however, there is no satisfactory explanation of the spectral form of the light emitted

from different metals. Here we confirm the characteristic form of the broadband spectra from randomly rough Ag and Au films and report for the first time the light spectrum from Cu. We offer a simple explanation of these spectra in terms of the so-called electron energy-loss function,[7] $\mathrm{Im}(-1/\epsilon)$, familiar in the study of fast-electron scattering. This insight complements and extends the LM theoretical model.

Observation in a tunneling experiment of the dielectric response of the interacting electron gas in a real metal is an exciting development. It provides the opportunity to explore with slow (quantum regime) probe electrons, at high resolution, the low-energy (< 5 eV) region of the dielectric response function.[8] Thus another spectroscopy becomes amenable to the tunneling method.

In our experiments a 120-nm-thick layer of CaF_2 is deposited on a glass substrate in a vacuum of $\sim 2\times10^{-4}$ Pa. Next, a 40-nm-thick film of Al, 7 mm wide, is laid down and this is oxidized in an oxygen glow discharge at a pressure of ~6 Pa with a current of 10 mA for a period of 5 min. Finally a top metal film of Au, Cu, or Ag, 30 nm thick and 7 mm wide, is deposited at a pressure of 2×10^{-3} Pa. Usually it is necessary to allow the tunnel sandwiches prepared in this way to age at room temperature for up to a week in order to obtain an adequately high resistance; a square-wave (± 10 mA) current through the sandwiches often expedites the aging process. Occasionally we oxidized the Al film in air at 100 °C for 30 min instead of using the glow discharge and this was particularly useful when Ag top films were used.

Measurements of light output were made with the sample immersed in liquid nitrogen in a slit-silvered glass Dewar. The light emitted normal to the sandwich plane was focused on the input slit of a Jobin Yvon model H25 monochromator operated with a 10-nm pass band. Subsequently the light, after being chopped at 400 Hz, was incident on an EMI9659B photomultiplier and the signal was synchronously detected by a Brookdeal model 9503 lock-in amplifier from which the output was fed to the y axis of a recorder. The recorder x axis displayed monochromator wavelength. Later, the recorded intensity was corrected for monochromator throughput and photomultiplier sensitivity.

The light output from a Ag top film under a bias current of 50 mA is shown in Fig. 1(a). The maximum energy of emitted photons, at 412 nm, corresponds closely to the voltage bias applied to the junction, 3.0 V. There is good agreement of the spectral form with that calculated by Laks and Mills[6] if one assumes the transverse correlation length, ξ_0, of the current fluctuations to be 10 nm and that of the surface roughness, a, to be 3.5 nm. The decrease in emission intensity at longer wavelength has its origin in the small value of a which does not allow long-wavelength SPP's to decouple efficiently from the surface.

With a Au top film the light output at 50 mA bias current is as in Fig. 2(a). Superimposed on the general features seen in the Ag spectrum,

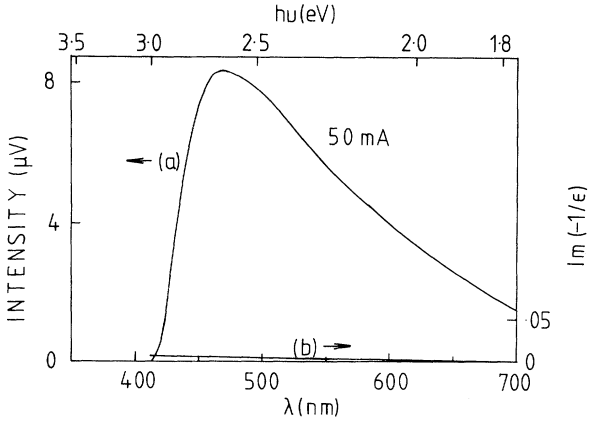

FIG. 1. (a) Variation of emitted light intensity with wavelength, λ, from Al-I-Ag junction biased at 3.00 V. Units correspond to signal input to lock-in detector but with optical-system response corrections applied. (b) Electron energy-loss function of Ag calculated from optical data (Ref. 10).

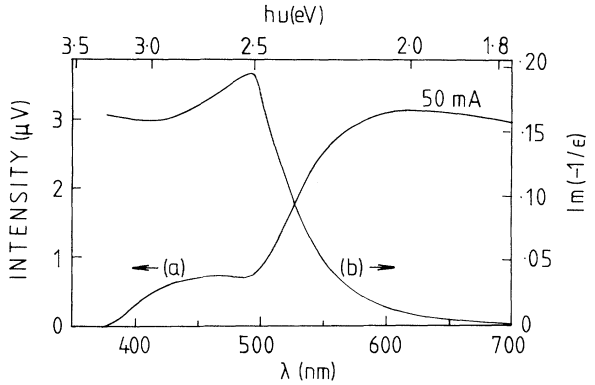

FIG. 2. (a) Variation of emitted light intensity with wavelength, λ, from Al-I-Au junction biased at 3.28 V. Units correspond to signal input to lock-in detector but with optical-system response corrections applied. (b) Electron energy-loss function of Au calculated from optical data (Ref. 10).

and described by the LM theory, is a pronounced drop in intensity near 500 nm (2.5 V). It has been reported before.[1,9] Adams and Hansma[9] attributed it to the absorption of light transmitted through the Au film. However, the optical absorption is too weakly wavelength dependent to produce the strong effect seen in Fig. 2(a). Besides, this interpretation assumes that decay of the junction plasmon mode is responsible for the emission and most evidence now points to the involvement of the fast SPP at the metal-vacuum surface. Laks and Mills[6] suggested that the sharp intensity drop in the spectrum corresponds to the maximum SPP energy in Au, and therefore the upper limit for photon emission mediated by plasmons. They introduced a second mechanism to account for emission at higher energy: direct coupling of the tunneling electrons to the radiation field. Inspection of the optical data[10] for Au shows that the real part of the dielectric constant remains less than -1 up to 4.9 V and SPP's can thus be excited up to that energy. They are not limited to energies below 2.2 V as LM suggest. We offer a different explanation.

The observed Au spectrum images quite directly a bulk material property, the electron energy-loss function. This quantity, $\mathrm{Im}(-1/\epsilon)$, can be calculated from the measured optical constants[10] and is shown for Au as Fig. 2(b). It exhibits a sharp increase at ~2.5 V in the very region where the light output drops off; the increase is attributable to an interband transition described by Christensen and Seraphin.[11]

Like Au, Cu has an interband transition in the visible[12] and an associated sharp increase is seen in its calculated electron loss function near 550 nm (2.25 V) as displayed in Fig. 3(b). We measured the light from a Cu top film and a drop in intensity is found at the same energy and over the same interval as the rise in $\mathrm{Im}(-1/\epsilon)$. The result at a bias current of 200 mA is shown in Fig. 3(a).

For completeness we show the calculated electron energy-loss function for Ag in Fig. 1(b). It is featureless throughout the visible, as is that for Al,[13] and is consistent with the observation of a simple pseudo-LM form for the emission over the spectral range shown.

We interpret the drop in light intensity above the interband transition energy in Au and Cu as the result of damping of the SPP's which mediate the transfer of energy from the tunneling electrons into visible radiation.[4] The interband transition offers an alternative decay mode for plasmons of higher energy. It is perhaps slightly surprising that the light intensity images the loss function in such a direct way. More commonly the loss function is used to describe low-energy (~10 eV) loss by fast (~100 keV) electrons in solids.[14] Both interband transitions and surface-plasmon maxima are then usually observed as separate features. Here we are seeing the interaction between the excitations; in effect the plasmon continuum has replaced the fast electron as the probe of the interband transition. Instead of a scattering peak we see an absorption. At 650 nm the observed light intensities normalized to unit tunnel current from the Cu, Au, and Ag are in the ratio 1:3:2 while at 450 nm the ratio is 1:3:23; the electron energy-loss function alone can account for this factor of 10 variation with wavelength. The potential emission efficiency of other metals can also be estimated from their measured optical constants by calculation of the electron energy-loss function. Of course the noble metals are among the most efficient emitters while Cu and Au show unusually dramatic changes in optical properties with wavelength in the visible.

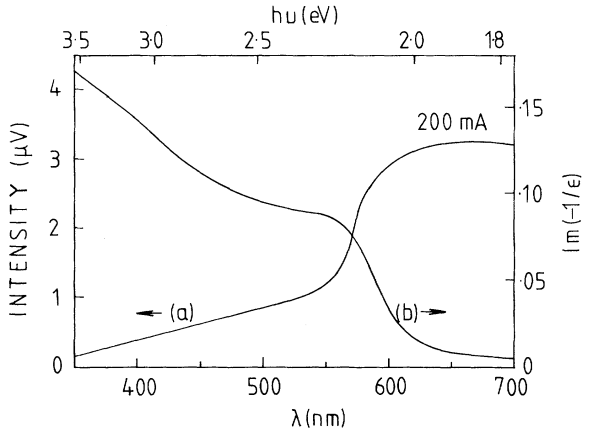

FIG. 3. (a) Variation of emitted light intensity with wavelength, λ, from Al-I-Cu junction biased at 3.80 V. Units correspond to signal input to lock-in detector but with optical-system response corrections applied. (b) Electron energy-loss function of Cu calculated from optical data (Ref. 10).

These results impinge on surface-enhanced Raman spectroscopy.[15] Surface plasmons are thought to be excited when the effect is observed. If so we should find that the effect is much reduced (by ~10^2) when Au or Cu substrates are used and the exciting wavelength lies beyond that of the interband transition. Indeed this is found to be the case.[16-19]

A simple consistent picture emerges. Surface plasmons are damped above the interband transition in Au and Cu. The effect is seen as a rather clear image of the electron energy-loss function in the spectrum of light emitted from tunnel junctions. The findings are in harmony with surface-enhanced Raman spectroscopy data.

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Initial Adsorption State for Al on GaAs(110) and Its Role in the Schottky Barrier Formation

R. R. Daniels, A. D. Katnani, Te-Xiu Zhao,[a] and G. Margaritondo
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

and

Alex Zunger
Solar Energy Research Institute, Golden, Colorado 80401, and Department of Physics, University of Colorado, Boulder, Colorado 80309

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Synchrotron-radiation experiments were performed at ultralow (< 0.1 monolayer) coverages to test the weakly-interacting-cluster model for Al adsorption on GaAs(110). The evolution of the Al 2*p* peak revealed *two* different submonolayer adsorption states, one below and one above 0.1 monolayer coverage, as predicted by the model. These results demonstrate that experiments at ultralow coverages are crucial to the understanding of the Schottky barrier formation.

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The traditional theoretical models described the Schottky barrier (SB) as the result of a charge redistribution between a metallic adlayer and a bulk semiconductor.[1] In contrast, modern experimental studies[2-9] have revealed that, in many cases, the barrier is already formed at *atomic* metal-adatom coverages (~1 Å), where the overlayer need not be metallic. These studies were performed on adlayers as thin as 0.1–1 Å while the more traditional thicknesses occurring in devices are ~10^3 Å. Their results have focused considerable attention on the local chem-

