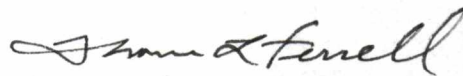


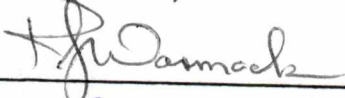
To the Graduate Council:

I am submitting herewith a dissertation written by Mark Joseph Bloemer entitled "Light Emission from Microstructured Tunnel Junctions." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Physics.

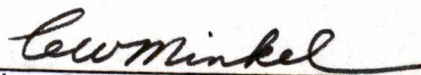


T. L. Ferrell, Major Professor

We have read this dissertation
and recommend its acceptance:



Accepted for the Council:



Vice Provost
and Dean of the Graduate School

LIGHT EMISSION FROM MICROSTRUCTURED
TUNNEL JUNCTIONS

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Mark Joseph Bloemer

December 1986

ACKNOWLEDGMENT

I wish to express my gratitude to Dr. T. L. Ferrell for his invaluable time and advice throughout the course of this endeavor. I would also like to thank Dr. R. J. Warmack for his patient instruction of experimental techniques and Dr. R. H. Ritchie for helpful discussions.

Finally, I would like to thank my co-workers and staff members of the Biological and Radiation Physics Section at Oak Ridge National Laboratory for making this a truly enjoyable experience.

ABSTRACT

Metal-insulator-metal tunnel junctions of aluminum-aluminum oxide-gold are fabricated with silver particulates positioned above the gold electrode by means of a magnesium fluoride spacer. The particulates are formed on the spacer by annealing a thin film of silver. Light emission is observed from these junctions when a bias voltage is applied across the oxide. Data are presented showing emitted light intensity as a function of wavelength, polarization, and angle of emission. A simple model is described in which tunneling current fluctuations are characterized by a single uniformly moving electron which stimulates surface plasmons in the gold electrode. The surface plasmon field is obtained and its effects on micro-particulates are described as driving surface plasmon modes in these microparticulates. While all aspects of the theory are not completely matched to the experimental conditions, the results are a new basis for qualitatively understanding the junction spectra.

TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION	1
Brief History	1
Surface Roughness and Microstructures	3
The Light Emission Process	4
Scope of the Present Research	6
II. THEORY	10
Absorbance Versus Emission	10
Geometry of the Model	11
The Driving Field	13
The Moments Induced in the Particulate	16
The Energy Radiated	18
III. SAMPLE PREPARATION	20
Substrate Preparation and Evaporation Masks	20
The Oxidation Process	22
The Electrode Thickness	23
Measurement Procedures	26
IV. RESULTS AND CONCLUSIONS	28
Comparison of Theory and Experiment	28
Effects of Shifting the Resonant Energy	37
The Radiation Pattern	39
Summary	41
REFERENCES	43
APPENDIXES	48
A. REVIEW OF TUNNEL JUNCTIONS	49
B. THE ALUMINUM OXIDE BARRIER	61
VITA	68

LIST OF FIGURES

FIGURE	PAGE
1. Cross Section of a Tunnel Junction	2
2. Diagram of the Coordinates	12
3. Tunnel Junctions on a 1x3 Inch Quartz Slide	21
4. Electron Micrograph of a 100 nm Thick Aluminum Film on a Quartz Substrate	24
5. Electron Micrograph of a 20 nm Thick Aluminum Film on Quartz	25
6. Spectra from Aluminum-Alumina-Gold Tunnel Junctions Described in the Text with Annealed Silver Films of Thickness (a) 9 nm, (b) 3 nm, and (c) No Silver Layer but Annealed	29
7. Electron Micrograph of a 9 nm Thick Annealed Silver Film	30
8. Electron Micrograph of a 3 nm Thick Annealed Silver Film	31
9. Solid Line: Calculation of the Power Radiated from a 3 nm Silver-Island Film on a 6 nm Magnesium Fluoride Spacer Above a 10 nm Gold Foil. Dotted Line: Experiment for the Same Structure but on an Aluminum-Alumina Layer	33
10. Calculation of the Power Radiated from a Silver Spheroid whose Minor-to-Major Axis Length Ratio is 0.4 and whose Major Axis Length is 35 nm	35
11. Calculation of the Power Radiated from a Gold Spheroid whose Minor-to-Major Axis Length Ratio is 0.4 and whose Major Axis Length is 35 nm	36
12. Radiation Pattern for a 9 nm Silver-Island Film on a 6 nm Magnesium Fluoride Spacer (0 Degrees Lies Along the Junction Normal)	40

CHAPTER I

INTRODUCTION

A. BRIEF HISTORY

Early work on tunnel junctions which emit radiation was concerned with transition radiation. Transition radiation results from changes in the photon field surrounding a charged particle when crossing the interface between two media. In the case of tunnel junctions, radiation may result when the electrons undergo the transition from the oxide to a noble-metal electrode. Transition radiation from metal-insulator-metal (MIM) tunnel junctions was first reported by Hwang, Schwarz, and Jain in 1976 [1]. Their tunnel junction consisted of aluminum (75 nm thick), aluminum oxide (3 nm thick), and silver (17 nm thick), as shown in Figure 1. Applying a bias voltage V , established a current with electrons of maximum energy equal to $|eV|$. For $|eV| \geq \hbar\omega_p$, where ω_p is the bulk plasma frequency of silver [2], photons of energy $\hbar\omega_p$ could be detected. The photons detected by these investigators had the energy, radiation pattern, and polarization characteristic of radiation emitted from silver foils bombarded by high energy electrons [3,4].

In the 1960s it was found that if rough silver films are bombarded by energetic electrons then, in addition to transition radiation, photons of energy less than $\hbar\omega_p$ are observed [5]. Later, this was also observed in the case of low energy incident electrons

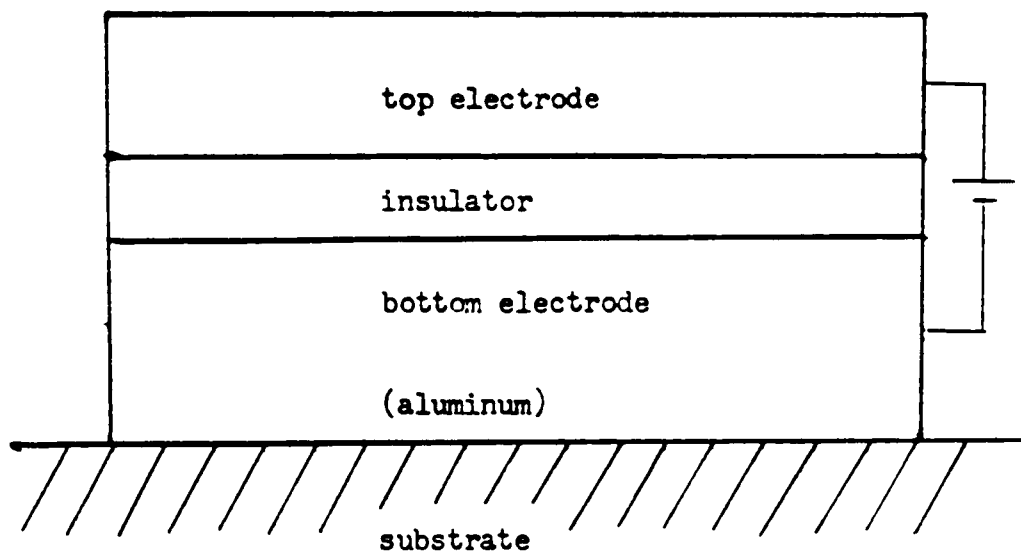


Figure 1. Cross section of a tunnel junction.

(20-1500 eV) [6,7]. This light originates from the decay of charge density oscillations at the surface of the foil (surface plasmons). The existence of surface plasmons was first described by Ritchie in 1957 [8]. These quanta of collective electronic oscillations are readily excited by charged particles. However, the probability that a photon normally incident on a semi-infinite free electron gas will be absorbed by the excitation of a surface plasmon is very small [9]. Simultaneous conservation of energy and momentum cannot be satisfied in this case unless an indirect process or other mechanism is involved. Roughness on the interface provides the necessary vehicle to enhance this coupling as it provides a sink for the momentum [10].

Shortly after Hwang et al. [1] published their results, Lambe and McCarthy [11] submitted an experimental paper on broadband visible light emission from roughened tunnel junctions. The silver electrode was mildly etched to provide roughness. They confirmed that the light results from tunneling electrons exciting surface plasmon modes in the junction and that these modes radiatively decay through the roughness.

B. SURFACE ROUGHNESS AND MICROSTRUCTURES

Since Lambe and McCarthy's [11] first paper a variety of roughness features have been incorporated in tunnel junctions. Three categories of roughness have dominated: holographic gratings, random or statistical roughness, and discrete microstructures.

Tunnel junctions on holographic gratings have groove spacing on the order of hundreds of nanometers. This roughness is well defined and can easily be viewed in a conventional scanning electron microscope (SEM).

Random or statistical roughness is most often provided by an underlayer of calcium fluoride. The surface of calcium fluoride has an irregular profile which is quantified in terms of its statistical properties. It has features with sizes between a few nanometers and tens of nanometers. All of the interfaces for tunnel junctions fabricated on calcium fluoride are rough on this scale.

Discrete microstructures incorporated in tunnel junctions are usually in the form of metal spheres or spheroids. The major axis diameter for spheroids is on the scale of tens of nanometers. These structures are termed "discrete" due to the discontinuous nature of the surface plasmon dispersion relation. The surface plasmons are "localized" to the microstructure, being described as multipolar modes, and have energies dependent on the geometry and dielectric function of the material. These microstructures are placed within or above the top electrode leaving planar interfaces below.

C. THE LIGHT EMISSION PROCESS

Numerous articles have attempted to quantitatively interpret light emission from roughened tunnel junctions. To date, no theory can describe all the features of the emission process. A difficult problem is the calculation of the excitation probability of surface

plasmons by tunneling electrons. Most investigators employ a driving term first developed by Hone, Muhlschlegel, and Scalapino [12]. If a dc bias voltage is applied to a tunnel junction a current is established. This current is not steady and fluctuations about the average current exist. There are fluctuations in the current up to the frequency $\omega = eV/\hbar$, as dictated by conservation of energy. This is also the maximum frequency found experimentally for the photons emitted from the junction. The spatial extent of these fluctuations must also be defined in some manner. This method of modeling tunnel current fluctuations as driving surface plasmons has had some success but is not a complete representation of the excitation process.

Further difficulties arise in calculating the dispersion relation for surface plasmons on a rough interface. There are two avenues of solutions to the problem. One is to solve the dispersion relation for a planar interface and treat the roughness as a perturbation. This technique is valid for small amplitude roughness. Approaching the problem from the other extreme is to solve the surface plasmon dispersion relation for an isolated particulate, and to incoherently superimpose the results for several such particulates across the area of the junction. Real tunnel junctions are frequently situated between these two extreme conditions.

Once the dispersion relations are calculated, the question remains as to which mode is responsible for the light emission. This question is especially difficult in tunnel junctions in which all interfaces are rough.

Although tunnel junctions are complex systems, there has been success in modeling, especially for junctions on gratings where the roughness is well defined. A more complete review of MIM tunnel junctions is presented in Appendix A.

D. SCOPE OF THE PRESENT RESEARCH

Light emission from metal-insulator-metal tunnel junctions incorporating metal particulates has been reported by a number of investigators [13-16]. In Refs. 14-16, metal spheres of silver or gold were deposited directly on the insulating layer and subsequently buried under a noble metal, or top, electrode. A theoretical model appropriate for microstructures placed on the oxide was developed in a series of papers [12,17,18]. In this model, surface plasmons localized in the microstructure are excited by a fluctuating current produced by the tunneling electrons. The currents induced in these miniature antennae radiate the observed light. One disadvantage of this model is that it neglects the interaction with the top (noble metal) electrode, which is necessary in order to carry the tunneling charge away.

In another experiment by McCarthy and Lambe [13], a thin insulating layer was deposited on the top electrode. Metal particulates situated on this layer were pictured as coupling nonlocal surface plasmons to the photon field via surface plasmon decay. For this geometry, both the microstructures and the upper electrode are expected to be important in understanding the light emission. That

is, surface plasmons in the noble-metal electrode couple to surface plasmons in the particulates, and the spectrum of the emitted photons depends primarily upon the thin-film surface plasmons while the intensity depends upon the radiating particulates.

Recent articles [19-23] on surface plasmon modes in metal island films have provided the impetus for further investigations of tunnel junctions utilizing the geometry of McCarthy and Lambe [13]. These papers present experimental and theoretical results on the excitation and radiative decay of surface plasmons on thin annealed films. Modeling the islands as oblate spheroids was shown to yield good agreement between theory and experiment.

Light emission from metal oblate spheroids above tunnel junctions may be modeled as the last in a series of stages of energy transfer. At each stage losses are introduced. This sequence accounts for the low efficiency of these light-emitting devices. In a planar junction, tunneling electrons excite nonlocal, thin-film, surface plasmon modes in the top electrode. The fields associated with these modes decay exponentially with distance from the electrode. If metal islands are in the vicinity of this interface, localized modes may be stimulated. Radiative decay of surface plasmon modes in the islands is the final step of the emission process. Thus, in this model the particulates of the island film are driven off-resonance by the thin-film, surface plasmon field induced by tunneling electrons.

In the experiment detailed below, the tunnel junction geometry used by McCarthy and Lambe [13] is employed to present evidence for

light emission due to radiative decay of localized plasmon modes driven off resonance by fields associated with the upper electrode. A straightforward calculation is given which predicts the peak position of the emission spectra. However, the calculation neglects retardation effects for large particulates, and for the size of particulates used in this experiment. Retardation effects in silver particulates can have measurable effects for particulates with dimensions on the order or greater than 40 nm. If one uses Mie theory for spherical particulates, the shift in the silver dipole surface plasmon resonance has been found to be small [24]. The main effects are the enhancement of the quadrupole mode and subsequent effects on the radiation pattern. Nonetheless, with the light emission being primarily determined by the driving frequency, the nonretarded calculation does yield a reasonable spectrum due to the large slope of the real part of the dielectric function of silver as it depends on frequency in the visible range. This implies a small shift in the spectrum for a large change in the value of the real part of the dielectric function.

A good deal of the motivation for the studies presented here lies in the attractiveness of tunnel junctions for studies of the high-field breakdown of insulators. With a thin insulating film one can attain high electric fields at low voltages. Tunnel junctions offer the thinnest practical films and permit field strengths of 10^7 volts/cm. The emitted light may be used diagnostically once it is well characterized. Thus, for example, if microstructures provide

seed sites for breakdown, and if the microstructures undergo physical changes, the radiation provides a means of analyzing the changes with spatial and temporal localization advantages. Since low voltages are used it would be then possible to use extremely rapid pulses to resolve small time intervals immediately prior to breakdown. Thus, this work concentrates on understanding the radiation and producing tunnel junctions which can be operated at higher voltages than hitherto reported.

The phenomenon of vacuum breakdown can also be much better understood if the role of microstructures can be delineated. In many nonlinear effects, such as surface-enhanced Raman scattering [2], microstructures produce amplification of local fields. Even with dc voltages a "lightning rod" effect is present due to microstructures. At this point there has been very little quantitative progress toward understanding such effects. Tunnel junction data may be of considerable use in elucidating the importance of microstructures.

CHAPTER II

THEORY

A. ABSORBANCE VERSUS EMISSION

The energies for the two dipole modes of an oblate spheroidal particulate on a tunnel junction (or multiple thin film system) are calculated in Ref. 25. The energies of the modes depend on the thickness of the magnesium fluoride spacer and on the shape of the particulate. Absorbance experiments confirmed the validity of this model for silver oblate spheroids on transparent substrates. However, the model is not directly applicable to the emission measurements from tunnel junctions presented in Chapter IV. Nevertheless, some features of the model are very useful, and for the tunnel junctions prepared for the present work, certain results of the research on absorbance are even essential.

Differences between absorbance investigations and emission investigations result from the nature of the measurement process. In an absorbance experiment the light transmitted through the sample is detected and normalized to the incident beam intensity. In this way any peak in the frequency spectrum of the source is cancelled by the normalization procedure. The frequency spectrum of the driving field in a tunnel junction cannot be measured except through measurements of the spectrum of the emitted light or other indirect means.

In view of these considerations, a peak in the absorbance spectra of a tunnel junction would not be expected to match a peak

in the emission spectra unless the driving field of the junction had a constant intensity at all frequencies. Therefore any theoretical model of light emission from particulates on a tunnel junction must include analysis of the driving fields that excite the surface-charge oscillations in an off-resonance manner. That is, the driving field in general will not have a peak in its frequency spectrum at the surface plasmon frequency observed in absorbance measurements.

B. GEOMETRY OF THE MODEL

The following sections present a simple calculation of the power radiated from an oblate spheroidal metal particulate located on an insulating layer above a tunnel junction. The tunneling electron is treated as a classical particle [26] which traverses a straight line path through the oxide layer from the lower electrode to the upper electrode. It is taken as the source of the driving field as mediated by the upper electrode.

For analyzing the reaction of the spheroid, the trajectory is taken to lie along a line which coincides with a surface normal that passes through the center of a metal spheroid (Figure 2). The origin of the coordinate system is taken to be at the center of the metal particulate. The plane $z = -z_0$ passes through the center of the electrode. The distance between points z' and $-(z_0 + L/2)$ is equal to the oxide thickness.

The upper electrode of thickness L has a complex dielectric response function $\epsilon_F(\omega)$. In order to simplify the equations, the dielectric functions of the oxide layer and insulating spacer have

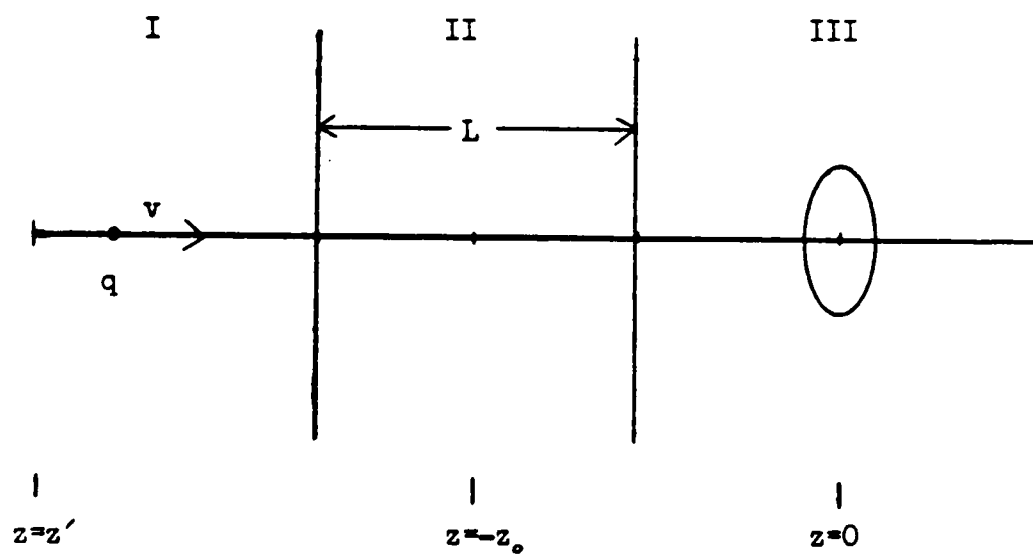


Figure 2. Diagram of the coordinates.

been set equal to unity. The particulate has a complex dielectric response function $\epsilon_p(\omega)$.

C. THE DRIVING FIELD

First it is necessary to find the Fourier components of the nonretarded potential due to an electron normally incident on the top electrode. The potential must be known everywhere. The Fourier transform of a function is assumed to exist and can be defined as

$$f(x,y,z,t) = \int_{-\infty}^{\infty} \frac{dK_x}{2\pi} \int_{-\infty}^{\infty} \frac{dK_y}{2\pi} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{i(\vec{K} \cdot \vec{R} - \omega t)} \tilde{f}(K,\omega,z) \quad (1)$$

and

$$\tilde{f}(K,\omega,z) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dt e^{-i(\vec{K} \cdot \vec{R} - \omega t)} f(x,y,z,t) \quad (2)$$

where

$$\vec{R} = x\hat{i} + y\hat{j} \quad (3)$$

and

$$\vec{K} = K_x\hat{i} + K_y\hat{j} . \quad (4)$$

In Region I of Figure 2 the charge density can be expressed as

$$\rho(x,y,z,t) = q\delta(x) \delta(y) \delta(z - z' - vt) \quad (5)$$

where q is the charge of the tunneling electron. The electron travels with constant velocity from the lower to the upper electrode. The velocity v , corresponds to that of an electron with kinetic energy

equal to $|qV|$, where V is the dc bias voltage applied to the junction.

The Fourier transform of Eq. (5) is

$$\tilde{\rho}(K, \omega, z) = \frac{q}{v} e^{i \frac{\omega}{v} (z-z')} . \quad (6)$$

Poisson's equation for a time-dependent charge density is

$$\nabla^2 \phi(x, y, z, t) = -4\pi\rho(x, y, z, t) . \quad (7)$$

The left hand side of Eq. (7) can be written as

$$\nabla^2 \phi(x, y, z, t) = \int_{-\infty}^{\infty} \frac{dK^2}{(2\pi)^2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \nabla^2 [e^{i(\vec{K} \cdot \vec{R} - \omega t)} \tilde{\phi}(K, \omega, z)] . \quad (8)$$

Similarly, the right hand side of Poisson's equation, for Region I can be expressed as

$$-4\pi\rho(r, t) = -4\pi \int_{-\infty}^{\infty} \frac{dK^2}{(2\pi)^2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{i(\vec{K} \cdot \vec{R} - \omega t)} \frac{q}{v} e^{i \frac{\omega}{v} (z-z')} . \quad (9)$$

Equations (7), (8), and (9) yield

$$[-K^2 + \frac{\partial^2}{\partial z^2}] \tilde{\phi}_I(K, \omega, z) = - \frac{4\pi q}{v} e^{i \frac{\omega}{v} (z-z')} . \quad (10)$$

Solving Eq. (10) for the Fourier components of the potential in Region I gives

$$\tilde{\phi}_I(K, \omega, z) = \frac{4\pi q/v}{K^2 + (\frac{\omega}{v})^2} e^{i \frac{\omega}{v} (z-z')} + A(K, \omega) e^{K(z+z_0+\frac{L}{2})} \quad (11)$$

where $A(K, \omega)$ is the Fourier amplitude of the potential. Proceeding in a like manner for Regions II and III it is found that

$$\tilde{\phi}_{II}(K, \omega, z) = B(K, \omega) e^{K(z+z_0+\frac{L}{2})} + C(K, \omega) e^{-K(z+z_0+\frac{L}{2})} \quad (12)$$

and

$$\tilde{\phi}_{III}(K, \omega, z) = E(K, \omega) e^{-K(z+z_0-\frac{L}{2})} \quad (13)$$

Now that the Fourier components of the potential have been formally specified in all three regions, the boundary conditions can be utilized to find the Fourier amplitudes. At the interface $z = -z_0 - L/2$ the following two conditions hold:

$$\tilde{\phi}_I(K, \omega, z = -z_0 - \frac{L}{2}) = \tilde{\phi}_{II}(K, \omega, z = -z_0 - \frac{L}{2}) \quad (14)$$

and

$$\left. \frac{\partial \tilde{\phi}_I(K, \omega, z)}{\partial z} \right|_{z=-z_0-\frac{L}{2}} = \epsilon_F(\omega) \left. \frac{\partial \tilde{\phi}_{II}(K, \omega, z)}{\partial z} \right|_{z=-z_0-\frac{L}{2}} \quad (15)$$

Similar boundary conditions prevail at the interface $z = -z_0 + L/2$ for the Fourier components of the potentials in Regions II and III.

After some manipulation, the nonretarded potential in Region III is found to be

$$\phi_{III}(R, z, \omega) = \frac{q}{v} \epsilon_F(\omega) e^{-i \frac{\omega}{v} (z_0 + \frac{L}{2} + z')} \int_0^\infty dK \frac{J_0(KR)}{K + i \frac{\omega}{v}} T(K, \omega) e^{-K(z + z_0 - \frac{L}{2})} \quad (16)$$

where $J_0(KR)$ is the zero order Bessel function and

$$T(K, \omega) = [\epsilon_F(\omega) + \tanh(\frac{KL}{2})]^{-1} - [\epsilon_F(\omega) + \coth(\frac{KL}{2})]^{-1} . \quad (17)$$

The potential is symmetric about the z -axis, and is expressed in cylindrical coordinates z and R , where $R = (x^2 + y^2)^{1/2}$. The use of cylindrical coordinates facilitates the transformation to oblate spheroidal coordinates which are useful for the geometry of the metal particulate.

D. THE MOMENTS INDUCED IN THE PARTICULATE

The potential in Eq. (16) is applied to a metal particulate which is situated above the thin film at $z = 0$. The applied field induces multipole moments of various strengths in the metal island. Only the induced electric dipole and quadrupole moments are considered in the computation.

The transformation of the potential from cylindrical to oblate spheroidal coordinates is straightforward. The cylindrical coordinates become (η, μ, a) . Oblate spheroidal coordinates have confocal ellipsoids, single-sheeted hyperboloids, and half planes as the mutually orthogonal surfaces. For an oblate spheroidal particle (a flattened sphere), the coordinate " a " is the focal length and $\eta = \eta_0$ defines its surface. The following relation from Smythe [27] is used in the transformation of coordinates:

$$e^{-Kz} J_m(KR) = -\left(\frac{\pi}{2Ka}\right)^{1/2} \sum_{n=m}^{\infty} (2 - \delta_{m,n}) (-1)^{m-n} (i)^{-n} (2n+1) \frac{(n-m)!}{(n+m)!} J_{n+\frac{1}{2}}(Ka) P_n^m(\mu) P_n^m(in) \quad (18)$$

where P_n^m are associated Legendre functions.

To find the multipole expansion coefficients of the applied field it is necessary to calculate the potential inside and outside the metal particulate and apply the boundary conditions at the surface. Employing the notation used by Kennerly et al. [22] the coefficients are found to be

$$E_{\ell mp} = \frac{i\sqrt{3}q}{av} \delta_{m,0} \delta_{p,1} (2 - \delta_{\ell,0}) (-i)^{-\ell} (2\ell+1)^{1/2} \epsilon_F(\omega) I(\omega) \quad (19)$$

where

$$I(\omega) = e^{-i\frac{\omega}{v}(z_0 + \frac{L}{2} + z')} \int_0^{\infty} dK (K + i\frac{\omega}{v})^{-1} T(K, \omega) e^{-K(z_0 - \frac{L}{2})} j_{\ell}(Ka) \quad (20)$$

The fact that only the coefficients for which $m = 0$ and $p = 1$ are nonzero results from conservation of angular momentum and the symmetry of the potential about the z -axis. Therefore, only the electric dipole moment p_z and quadrupole moment Q_{zz} are nonzero. More general cases, for the particle displaced from the z -axis, are intractable.

The z -component of the dipole polarizability for an oblate spheroidal particulate with a complex dielectric function $\epsilon_p(\omega)$ is given in Ref. [22] as

$$\alpha_z = -\frac{a^3}{3} \frac{\eta_0}{Q_{10}(i\eta_0)} \frac{\epsilon_p(\omega) - 1}{\epsilon_p(\omega) - \epsilon_{10}} \quad (21)$$

where

$$\epsilon_{\ell,m} = \frac{P_{\ell m}(i\eta_0)Q'_{\ell m}(i\eta_0)}{Q_{\ell m}(i\eta_0)P'_{\ell m}(i\eta_0)} \quad (22)$$

The $P_{\ell m}(i\eta_0)$ and $Q_{\ell m}(i\eta_0)$ are associated Legendre functions of imaginary argument as given in Smythe [27] and $\eta = \eta_0$ describes the surface of the particulate. In a similar fashion it is found that

$$\alpha_{zz} = \frac{-2a^4}{3i\sqrt{15}} \frac{1 + 3\eta_0^3}{Q_{20}(i\eta_0)} \frac{\epsilon_p(\omega) - 1}{\epsilon_p(\omega) - \epsilon_{20}} \quad (23)$$

The moments induced in the particulate are

$$p_z = \alpha_z E_{101} \quad (24)$$

and

$$Q_{zz} = \alpha_{zz} E_{201} \quad (25)$$

where $E_{\ell mp}$ is given in Eq. (19).

E. THE ENERGY RADIATED

The energy radiated per solid angle from the metal particulates is calculated in the usual manner [28] neglecting multiple scattering of the radiation by other particulates. The energy radiated per unit solid angle per unit frequency interval from an electric dipole is

$$\frac{d^2 P_{\text{dip}}}{d\Omega d\omega} = \frac{c}{8\pi} \left(\frac{\omega}{c}\right)^4 \sin^2 \theta |p_z|^2 \quad (26)$$

where c is the speed of light and ω is the frequency of the emitted radiation at an observation angle θ with respect to the surface normal. The radiated energy per solid angle per unit frequency interval for an electric quadrupole is

$$\frac{d^2 P_{\text{quad}}}{d\Omega d\omega} = \frac{c}{128\pi} \left(\frac{\omega}{c}\right)^6 \sin^2 \theta \cos^2 \theta |Q_{zz}|^2. \quad (27)$$

The total energy radiated per solid angle per unit frequency interval is taken to be the sum of Eqs. (26) and (27).

CHAPTER III

SAMPLE PREPARATION

A. SUBSTRATE PREPARATION AND EVAPORATION MASKS

Tunnel junctions were fabricated on 1x3 inch glass or quartz microscope slides. The slides were washed in warm water with liquid detergent (Micro) and then rinsed in deionized water for ten minutes. An ultrasonic bath in methanol for fifteen minutes, followed by blow drying with nitrogen, provided clean substrates for the junctions. Slides were handled with tweezers or plastic gloves to prevent oil contamination.

Evaporation masks were made of 1/8 inch thick machined aluminum. Three different masks were required to make tunnel junctions. The first mask was necessary to form the solder pads for electrical contact to the junctions. The pads consisted of chromium (150 nm thick) overlayed with gold (150 nm thick).

The second mask had a 2x70 mm slot for the aluminum evaporation. The final mask had slots for eleven cross-strips which would form the top electrode. The junction area was four square mm. Figure 3 depicts a slide with the completed junctions. Direct contact of the mask to the substrate occurred only along the edge of the slide to avoid scratching the electrodes.

Film deposition took place in a cryopumped, electron beam evaporator at a pressure of 1×10^{-6} torr. Film thickness was measured by a quartz crystal monitor positioned near the substrate.

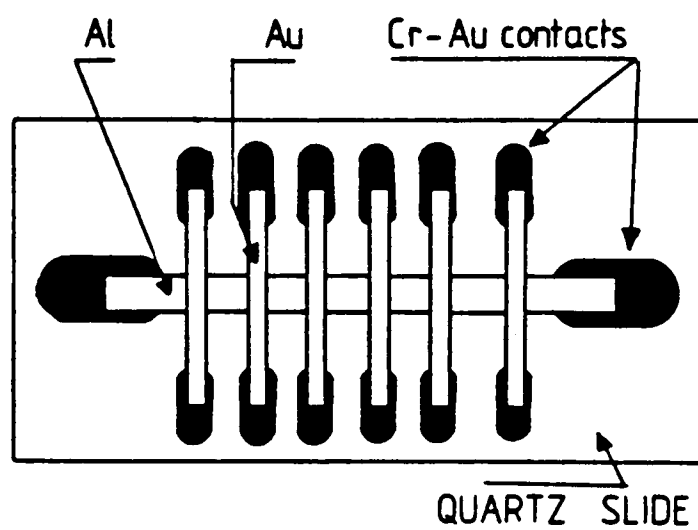


Figure 3. Tunnel junctions on a 1x3 inch quartz slide.

B. THE OXIDATION PROCESS

The evaporation rate for the aluminum electrode was 2 nm/sec. Thermal oxidation of the fresh aluminum film by venting the belljar to room air proved to be erratic. Exposure for periods >3 hours resulted in junctions with little or no resistance. A one hour exposure was optimum with a relative humidity ~60%. Some usable junctions were obtained but the success rate was low, ~20%.

Venting the belljar to high purity oxygen (99.99%) yielded similar results. Oxides formed in moist oxygen increased the success rate only slightly.

Heating the aluminum film on a hot plate at 325°C for one hour in room air gave thick reliable oxides. Unfortunately, tunnel junctions fabricated with these electrodes were good light emitters without intentional roughness. Inspection of the electrodes in a SEM capable of 3 nm resolution revealed no noticeable roughness. The roughness was either underneath the oxide or on a scale smaller than the resolution of the microscope. Annealing at lower temperatures or shorter times produced poor quality oxides.

Plasma anodization in a moist oxygen environment yielded favorable results. After aluminum deposition, the system was vented to oxygen for 15 minutes. The sample was then removed and placed in a r.f. discharge [29] for anodization. Plasma anodization at 0.85 torr with a discharge current of 20 mA for one hour was sufficient to produce stable junctions. Almost 70% of the junctions fabricated in this manner were usable. Aging the completed junctions for

several days on the shelf also proved helpful. For more details concerning the oxide see Appendix B.

C. THE ELECTRODE THICKNESS

Initially, tunnel junctions were fabricated with aluminum electrodes 80-100 nm thick. Electron micrographs of these junctions clearly displayed pronounced roughness, as shown in Figure 4. This texture is also reproduced on the surface of the upper gold electrode. Thinner aluminum electrodes in the 20-30 nm range reduced this roughness considerably, as shown in Figure 5. The reduction in roughness is significant, and not only produces junctions which may be better quantified, but also precludes any untoward high-field dielectric breakdown such as may be enhanced by roughness.

Thus, the thinner 20-30 nm thick aluminum electrode had the advantage of smooth junction interfaces and better junction stability at high bias voltages. This might be due to an oxide of increased uniformity as well as to a reduction of rough protrusions which would serve as high-field sites to enhance dielectric breakdown.

Additional micrographs of aluminum on various substrates demonstrated that some roughness is inherent in the aluminum. Three substrates were tested: polished silicon (Monsanto), quartz slides (Esco Products), and ordinary glass microscope slides (Curtin Matheson). Since all three substrates gave similar results, the inexpensive glass slides were chosen as substrates. The residual roughness did not prove to be nearly as severe a problem for junction stability as the roughness of the 80-100 nm aluminum.

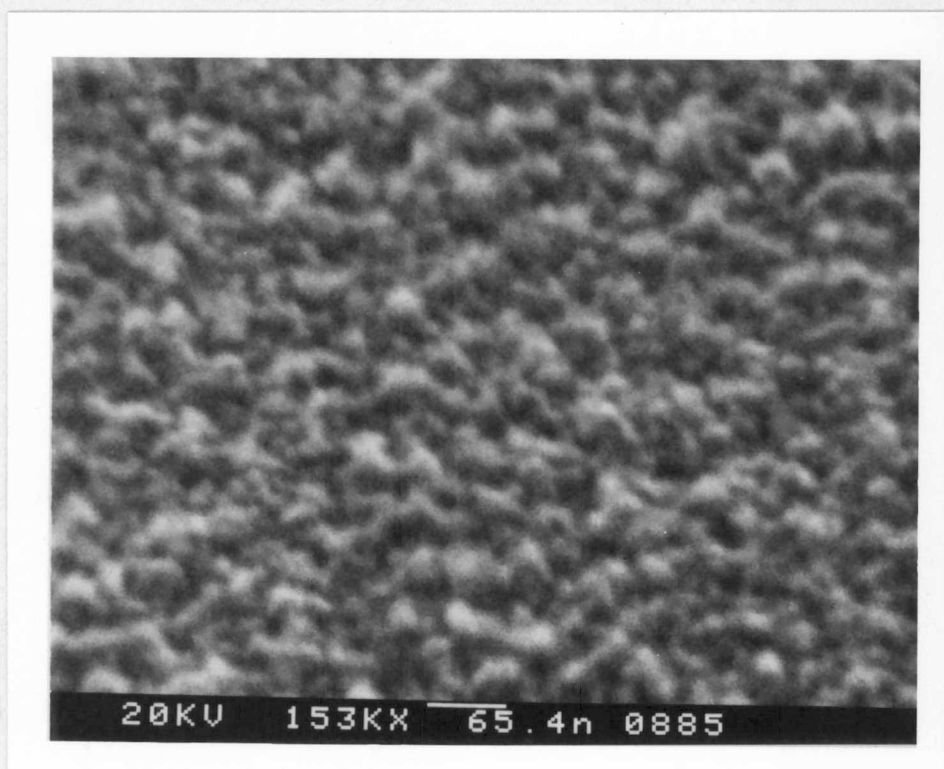


Figure 4. Electron micrograph of a 100 nm thick aluminum film on a quartz substrate. Angle of observation is 60 degrees from the substrate normal. The length of the bar corresponds to 65.4 nm.

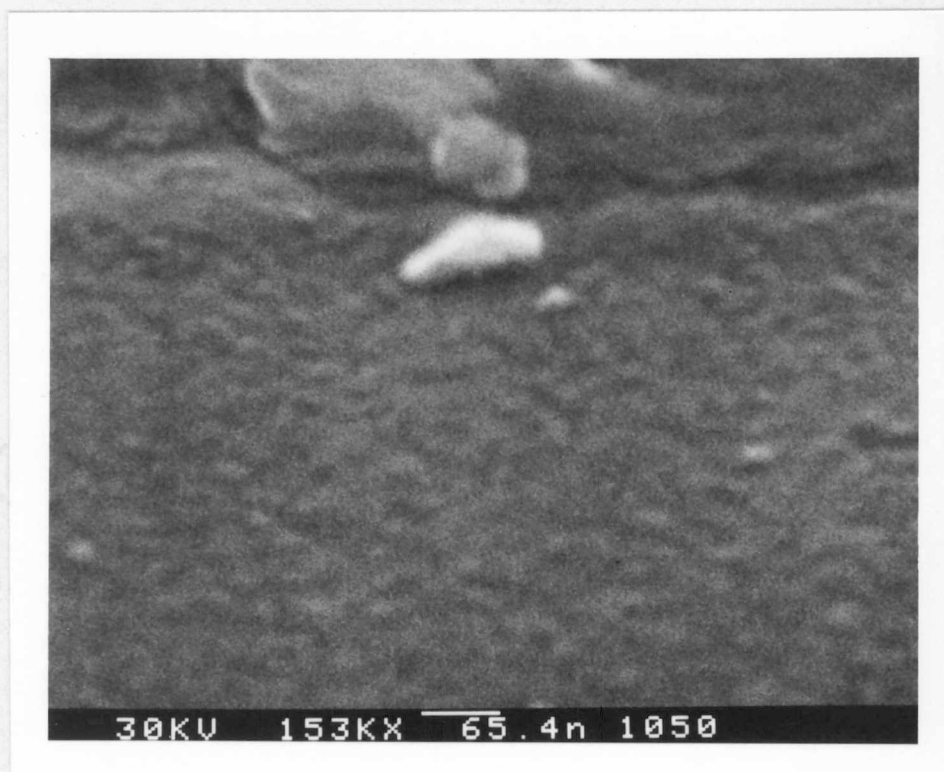


Figure 5. Electron micrograph of a 20 nm thick aluminum film on quartz. Observation angle is 60 degrees from the normal. Debris in the upper portion of the micrograph is for focusing purposes.

Gold was deposited to a 10 nm thickness to form the top electrode. A thin insulating layer of magnesium fluoride, 6 nm thick, was then evaporated onto the junction. Silver was deposited on the magnesium fluoride at a rate of 0.2 nm/sec. The silver-island films ranged in mass thickness from 3-9 nm. For all samples, three junctions were covered by a stainless steel plate and clamped to the mask during the metal island evaporation in order to serve as uncoated references. Heating the samples caused the silver-islands to bead, forming oblate spheroids. Annealing took place in an open-ended oven at 350°C for 45 seconds.

D. MEASUREMENT PROCEDURES

Spectra were obtained on a Spex monochromator equipped with a photon counting system. The relative efficiency of the detection system as a function of wavelength was measured using a NBS tungsten filament lamp. The data presented below were corrected by the relative efficiency.

Thin metallic films have considerable resistance, therefore the dc bias voltage was measured on the two noncurrent carrying leads. This four point probe technique for measuring current and voltage yields an accurate reading if the junction area is not too large.

Tunnel junctions of Al-Al₂O₃-Au operated at room temperature were stable for weeks if the applied dc bias is <2.5 V. When the bias voltage exceeds 3.5 V, the lifetime of the junction was reduced to a period of days. For a typical junction of <50 nm total thickness and

4.0 square mm area, the input power under normal operation is 0.1 watt. A portion of this is converted to light but most is dissipated through heat.

It was possible to prevent dielectric breakdown at these high voltages by applying a square wave bias with a 70% duty cycle, but this merely reflects the decrease in the power applied to the junction. Tunnel junctions mounted on a stage cooled to -150°C by rapid expansion of nitrogen gas proved helpful, but this technique requires the junction be fabricated on a good thermal conductor. Superior results were obtained by operating the junctions in liquid nitrogen. Electrical connections were made through the use of copper clamps instead of solder. Extended junction life and improved current stability were observed. The breakdown voltages also increased by 20% over junctions operated at room temperature. Therefore, all spectra presented in Chapter IV were acquired with the junctions immersed in liquid nitrogen.

CHAPTER IV

RESULTS AND CONCLUSIONS

A. COMPARISON OF THEORY AND EXPERIMENT

Figure 6 displays spectra detected along the substrate normal from junctions with various mass thicknesses of the silver-island film. The junctions were dc biased at 3.8 V (aluminum was the negative electrode) and had currents near 27 mA. Tunnel junctions incorporating metal islands have peaks in the spectra near 2.4 eV. The spectra from the junctions without particles have intensities that increase with energy. Junctions fabricated without particles by McCarthy and Lambe [13] have intensities that decrease with increasing photon energy. This can be attributed to a reduction in the mean correlation length of the roughness for thin aluminum films (30 nm) compared to the thicker aluminum films (60 nm) used by McCarthy and Lambe.

After emission measurements had been completed, the junctions were viewed in a SEM. The islands formed by annealing a 9 nm thick silver film are irregular in shape and clearly are not oblate spheroids (Figure 7). The particulates had major axis lengths ranging from 80-160 nm across. For the 3 nm thick annealed film, the particulates have a much narrower size and shape distribution, and are better modeled as oblate spheroids (Figure 8). The major axis length is ~ 35 nm and a minor-to-major axis length ratio of 0.4 is reasonable for these spheroids [20]. Although the size and shape

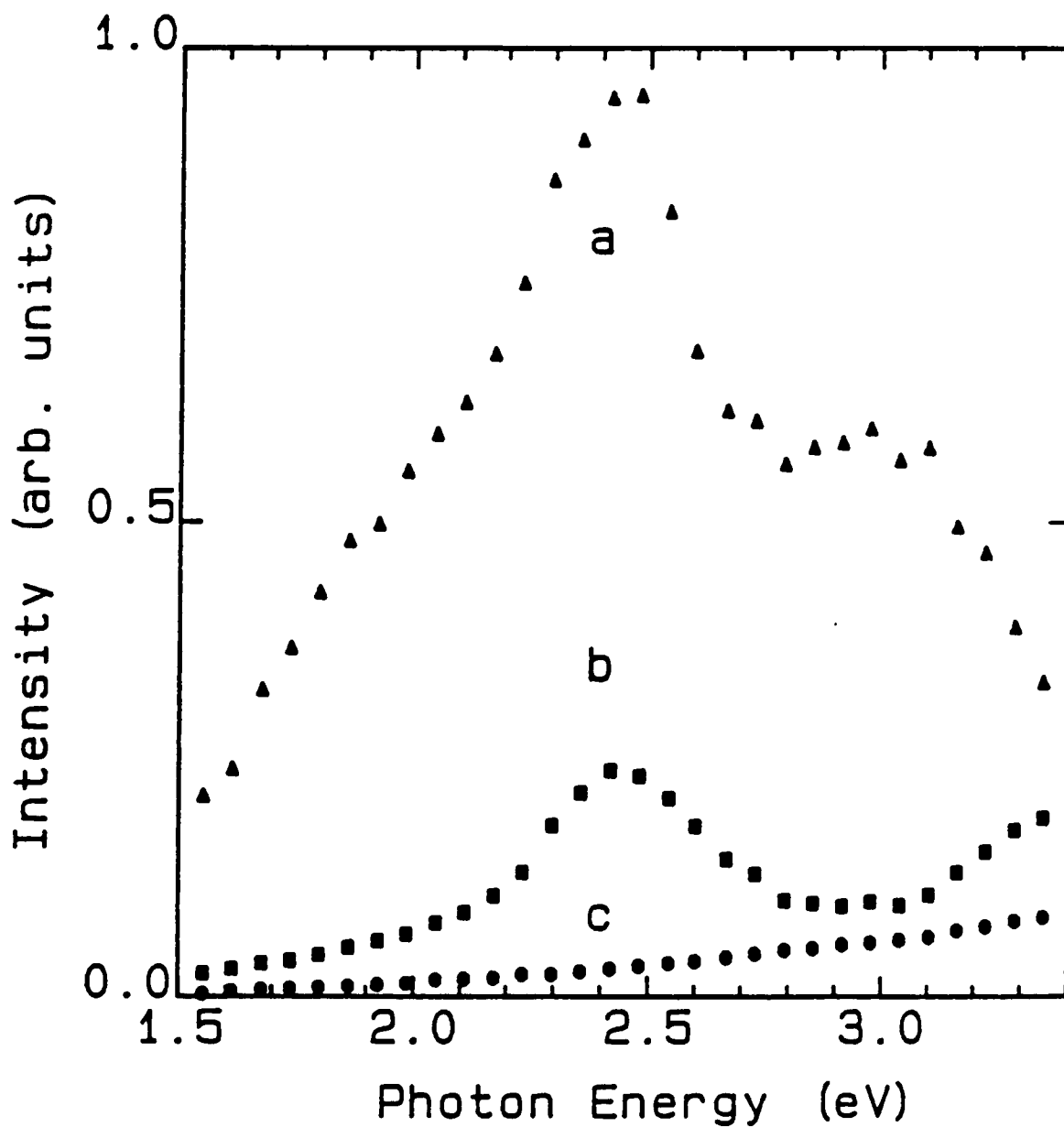


Figure 6. Spectra from aluminum-alumina-gold tunnel junctions in the text with annealed silver films of thickness (a) 9 nm, (b) 3 nm, and (c) no silver layer but annealed.

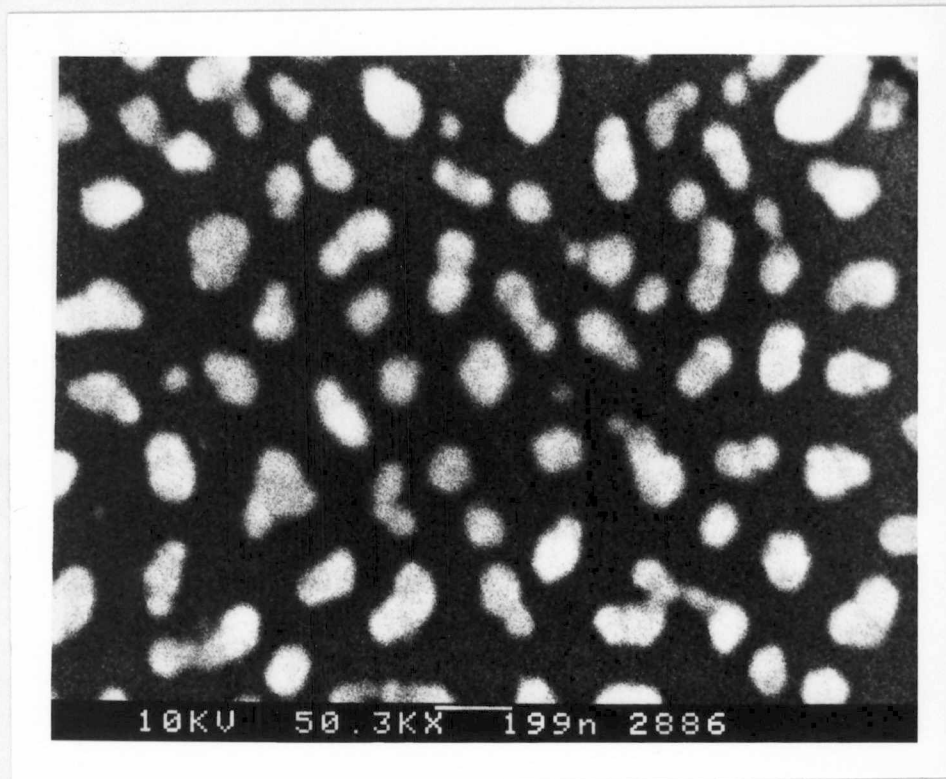


Figure 7. Electron micrograph of a 9 nm thick annealed silver film. Observation angle is along the junction normal.

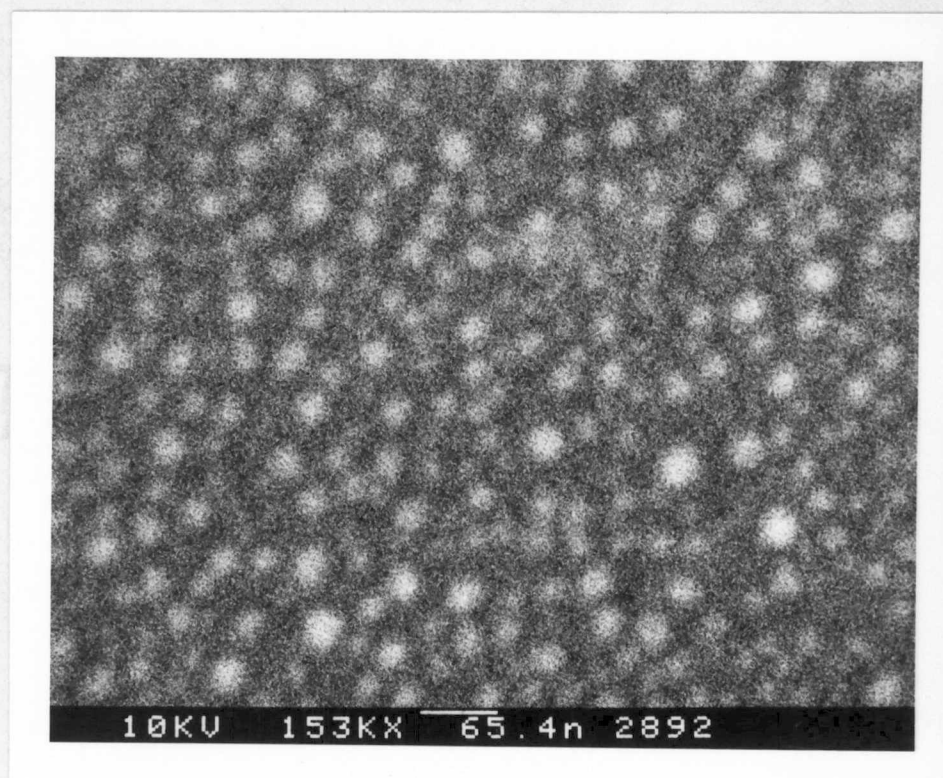


Figure 8. Electron micrograph of a 3 nm thick annealed silver film. Observation angle is along the junction normal.

distribution of the metal islands for the 3 nm and 9 nm annealed films differ substantially, both spectra have peaks at the same energy.

For driving fields of wavelengths much longer than the dimensions of the spheroids, only dipole moments are induced in the particle. Silver oblate spheroids can sustain two dipole modes: one with its dipole moment oriented along the minor axis ($\ell = 1, m = 0$), and the other with its dipole moment oriented along the major axis ($\ell = 1, m = 1$). The resonant energy of the (1,0) mode is near that of a sphere (i.e., at 3.5 eV) in the nonretarded regime for all minor-to-major axis length ratios, while the (1,1) mode is strongly dependent on shape and is at a lower energy.

Figure 9 shows the calculated total radiated power of the (1,0) mode induced in the silver spheroid by the junction's surface plasmon driving field using the experimental parameters. The silver particulates were modeled as noninteracting sources, each of which having an oblate spheroidal shape with a major axis length of 35 nm and a minor-to-major axis length ratio of 0.4. The slight discrepancy for experiment and theory may result from errors in the optical data for gold [30] or from other simplifying assumptions made in the calculation. A 15% increase in the real part of the dielectric function of gold would shift the theoretical peak to the observed value. We have also done the same calculation using the experimental parameters of McCarthy and Lambe [13], and have observed that the calculated power peaks near the experimentally observed energy for this case as well.

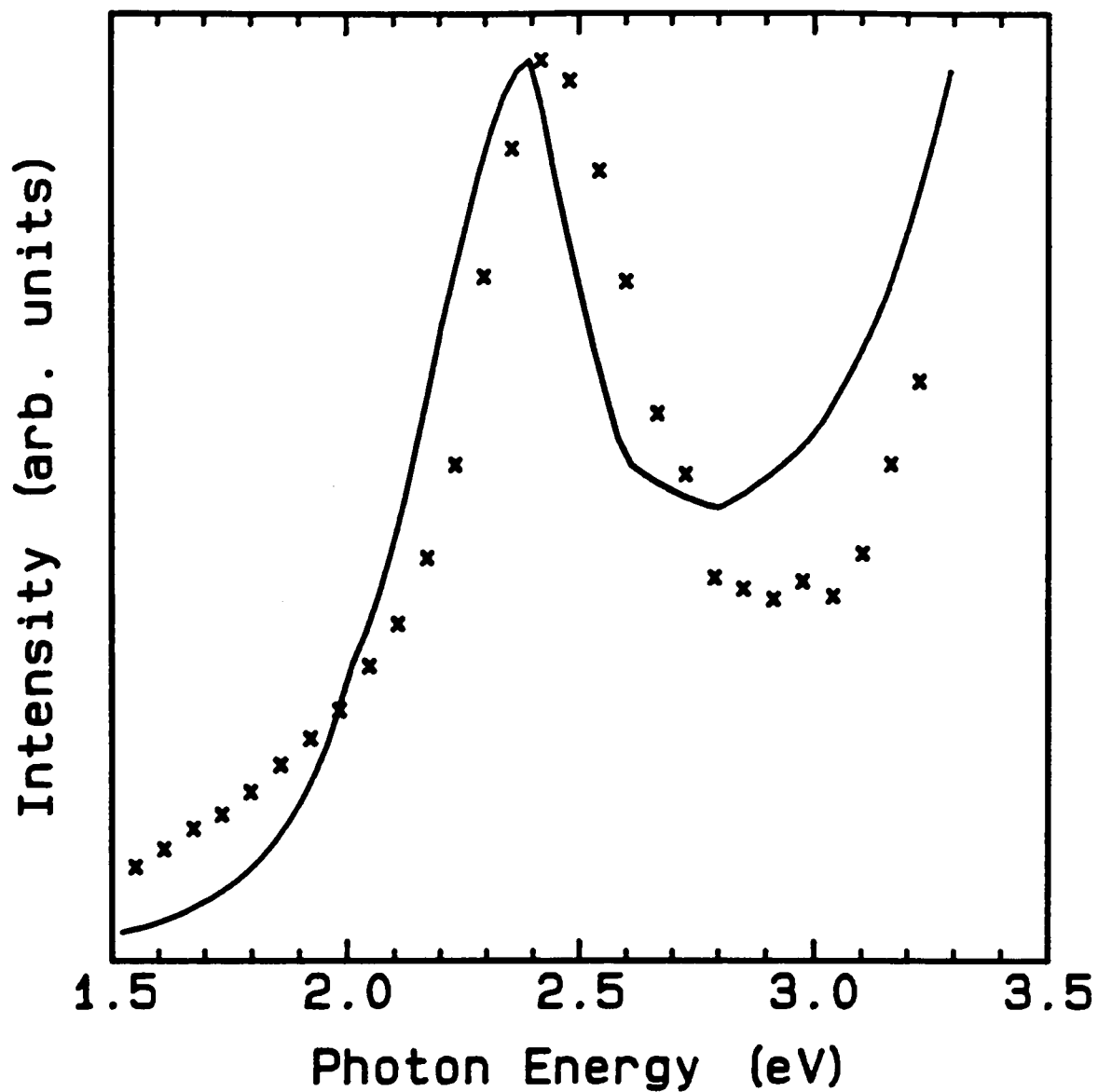


Figure 9. Solid line: calculation of the power radiated from a 3 nm silver-island film on a 6 nm magnesium fluoride spacer above a 10 nm gold foil. Dotted line: experiment for the same structure but on an aluminum-alumina layer.

Figure 10 displays the theoretical power radiated by silver particulates 6 nm above a gold foil. For Figure 10, the electron has kinetic energy equal to 3.8 eV which corresponds to a bias voltage of 3.8 V. For silver particulates there are two peaks for the (1,0) mode. The lower energy peak is strongly driven off resonance and is due to the gold foil while the second peak occurs near the resonant energy of the (1,0) mode for isolated silver particulates.

Figure 11 is a plot of the calculated power radiated by gold particulates above a gold foil. All other parameters are the same as in Figure 10. Gold particulates display only one peak corresponding to the resonant energy of the (1,0) mode. On the basis of this, a large radiative yield would be expected from gold particulates above a tunnel junction with a gold top electrode. This was tested experimentally and only a weak, broad peak at 2.4 eV was detected. This is attributed to the strong internal damping of gold at these frequencies compared to silver. In the calculation, the only losses for the induced moments are radiative. The fast surface plasmon modes in the gold foil are subject to internal damping but a significant portion of the fields associated with these modes lie outside the film and therefore are not strongly damped [31].

For the large particulates of the 9 nm thick annealed silver film, retardation is important and higher order modes may be excited [24]. Retardation effects could be responsible for the difference in the spectra of the 3 nm and 9 nm silver films above 3 eV. The present calculation does not include retardation or modes higher than the

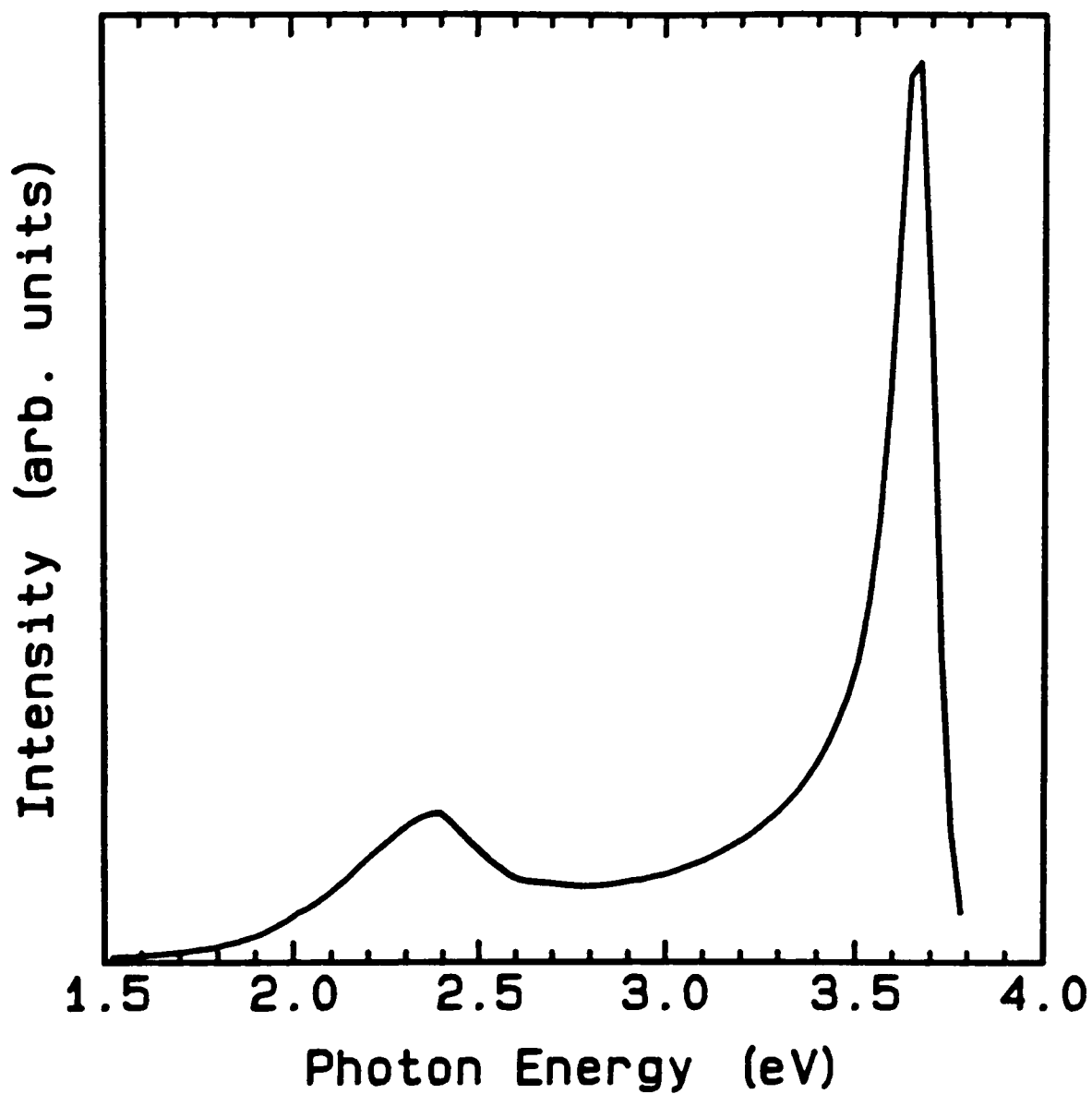


Figure 10. Calculation of the power radiated from a silver spheroid whose minor-to-major axis length ratio is 0.4 and whose major axis length is 35 nm.

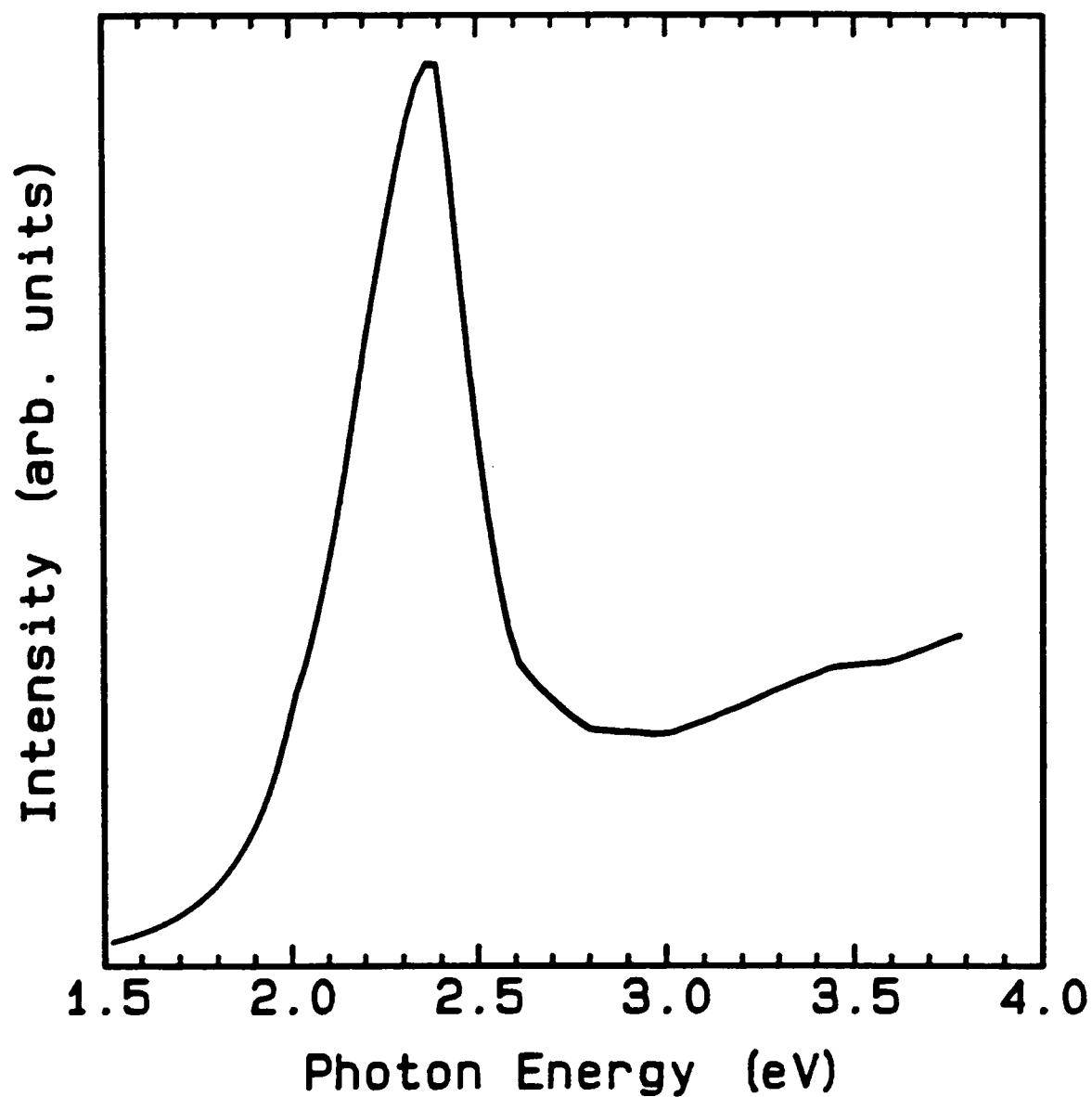


Figure 11. Calculation of the power radiated from a gold spheroid whose minor-to-major axis length ratio is 0.4 and whose major axis length is 35 nm.

electric dipole and quadrupole moments. Moreover, particulates of this size are not well-modeled as oblate spheroids.

The calculation does show that as the particulate size increases, the power radiated by the quadrupole mode approaches that of the dipole and yet it peaks in the vicinity of 2.4 eV. The quadrupole mode is also driven far from its resonant energy by the surface plasmon modes of the gold foil.

B. EFFECTS OF SHIFTING THE RESONANT ENERGY

Red shifting the resonant energy of the (1,0) mode in silver should cause the power radiated at 2.4 eV to increase, as the resonance would then lie closer to the driving frequency. Retardation effects red shift the (1,0) mode which would agree with the increased power radiated for thick versus thin annealed silver film. The increase may also be due in part to stimulation of higher order modes. If a calculation could be accomplished which included retardation effects, then such speculation might be better quantified. Also, a prolate spheroidal model might be better suited to the 9 nm films.

Another method of red shifting the mode is to change the shape of the spheroid [22]. The resonant energy of the (1,0) mode decreases as the particulate becomes more spherical. In order to test this, a 6 nm thick silver film was evaporated on the spacer. A peak near 2.4 eV was detected for this unheated silver film when the junction was biased. The sample was then removed from the liquid nitrogen and annealed in the manner prescribed above. Emission measurements on

the annealed sample revealed an increase in the peak height by 15%. No shift in the peak position was observed. The electrical properties were not altered by the annealing, and the slight increase in emission intensity for the sample without silver particulates was subtracted from the peak height. Absorbance measurements in air for a 6 nm annealed silver film on quartz showed a red shift in the absorbance peak of 6 nm for the (1,0) mode compared to the unheated film.

Covering the islands with a dielectric medium was also seen to red shift the modes. Absorbance measurements indicated a red shift of 20 nm for the (1,0) mode when overcoating the annealed silver film with 75 nm of magnesium fluoride. Emission spectra from tunnel junctions with the particle layer embedded in magnesium fluoride revealed a decrease in the peak height by 30% compared to the uncoated particulate layer. This is contrary to the above argument, but fields in a dielectric media are reduced by the square of the index of refraction, n . The fields driving the (1,0) modes were reduced in the magnesium fluoride compared to liquid nitrogen by a factor of 22%. The radiative yield is also reduced for spheroids in a dielectric media by a factor of n^4 [21]. This further reduces the yield by another 39%. These losses are partially offset by the red shift of the (1,0) resonance of particulate in magnesium fluoride compared to liquid nitrogen, but are in reasonable agreement with our observations.

The power emitted from the type of junction used in this paper is weak. The dipole mode along the particle's major axis has a resonant energy near the peak energy of the driving field of the gold foil. A large increase in radiative yield can be expected if the spheroids are oriented with their major axes along the junction normal.

C. THE RADIATION PATTERN

Figure 12 is the radiation pattern measured near the peak in the spectra for the 9 nm thick annealed silver film. The pattern is similar to that of tunnel junctions on rough substrates [32]. For these statistically rough junctions, fast mode surface plasmons associated with the top electrode are scattered by roughness features on the electrode itself. The simple theoretical model developed here furnishes information on peak positions but not on the radiation pattern. The expressions for the radiated power neglects interparticle interactions and the dielectric effect of the multiple thin film system on which the particles reside. It is possible that other modes contribute to the radiation, especially for large particles where retardation is important.

The emission of S-polarized light by the junctions is not accounted for in our calculation. However, it may be shown that an electron traveling in the z-direction, but along a grazing-incidence trajectory with respect to an oblate spheroid, engenders a strong (1,1) dipole mode [33]. This would produce both additional

ORNL-DWG 86-15896

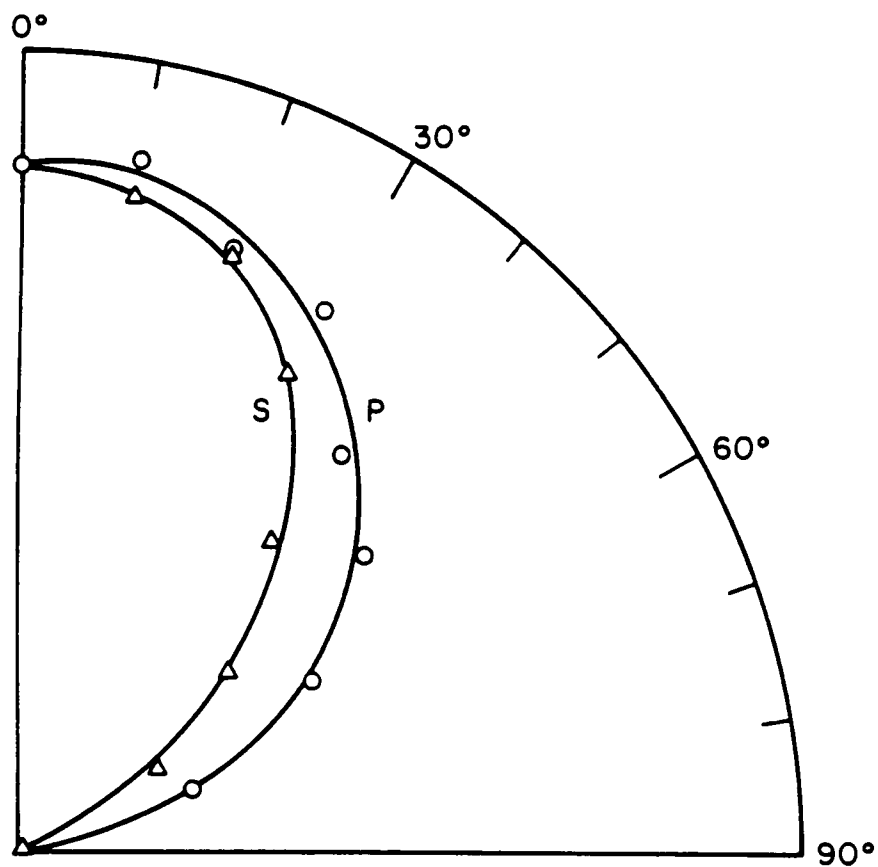


Figure 12. Radiation pattern for a 9 nm silver-island film on a 6 nm magnesium fluoride spacer (0 degrees lies along the junction normal).

P-polarized and S-polarized light in the theoretical radiation pattern. The only difficulty in comparing the pattern with our experimental results is that the theory would show emission of S-polarized light along the direction tangential to the top electrode as well as other directions. This is not observed. It should be noted that the cross section for scattering and absorption of S-polarized light encountering the large number of particles presented tangentially is large compared to that for P-polarized light. For instance, if the minor-to-major axis ratio is 0.4, the S-polarization cross section is at least an order of magnitude greater for each particulate than that for P-polarization. Thus, the radiation observed by Little et al. [20], which presented P-polarized light emission tangential to the surface does not preclude the possibility that S-polarized light would be greatly reduced in the tangential direction due to scattering by other particulates.

D. SUMMARY

Thin film tunnel junctions of Al-Al₂O₃-Au have been fabricated with silver particulates situated above the gold electrode by means of a magnesium fluoride spacer. Thin aluminum electrodes had the advantage of smooth junction interfaces and better junction stability at high bias voltages. This, along with metal island microstructures of known optical properties had the benefit of optimum sample characterization.

If a dc bias voltage is applied, these junctions emit broadband visible light with a peak in the spectrum near 2.4 eV. A crude model

has been developed to identify the significant feature of the light emission process. In this model, tunneling electrons excite non-local, thin-film, surface plasmon modes in the gold electrode. The fields associated with these modes stimulate surface plasmons localized in the metal particulates. The light emission results from the radiative decay of surface plasmon modes in the metal islands. It is found that the resonant modes of the silver particulates are driven off-resonance by the thin-film, surface plasmon fields of the gold electrode. The calculation neglects retardation but gives reasonable agreement with the experimental results.

REFERENCES

REFERENCES

1. T. Hwang, S. E. Schwarz, and R. K. Jain, Phys. Rev. Lett. 36, 379 (1976).
2. T. L. Ferrell, T. A. Callcott, and R. J. Warmack, American Scientist 73, 344 (1985).
3. E. T. Arakawa, N. O. Davis, and R. D. Birkhoff, Phys. Rev. 135, A224 (1964).
4. E. T. Arakawa, N. O. Davis, R. C. Emerson, and R. D. Birkhoff, Le Journal De Physique 25, 9 (1964).
5. H. Boersch, P. Dobberstein, D. Fritsche, and G. Sauerbrey, Z. Physik 187, 97 (1965).
6. M. S. Chung, T. A. Callcott, E. Kretschmann, and E. T. Arakawa, Surface Sci. 91, 245 (1980).
7. E. Kretschmann, T. A. Callcott, and E. T. Arakawa, Surface Sci. 91, 237 (1980).
8. R. H. Ritchie, Phys. Rev. 106, 874 (1957).
9. R. H. Ritchie, Surface Sci. 4, 497 (1965).
10. R. H. Ritchie, Surface Sci. 34, 1 (1973).
11. J. Lambe and S. L. McCarthy, Phys. Rev. Lett. 37, 923 (1976).
12. D. Hone, B. Muhlschlegel, and D. J. Scalapino, Appl. Phys. Lett. 33, 203 (1978).
13. S. L. McCarthy and J. Lambe, Appl. Phys. Lett. 30, 427 (1977).
14. A. Adams and P. K. Hansma, Phys. Rev. B 23, 3597 (1981).
15. A. Adams, J. C. Wyss, and P. K. Hansma, Phys. Rev. Lett. 42, 912 (1979).
16. P. K. Hansma and H. P. Broida, Appl. Phys. Lett. 32, 545 (1978).
17. R. W. Rendell, D. J. Scalapino, and B. Muhlschlegel, Phys. Rev. Lett. 41, 746 (1978).

18. R. W. Rendell and D. J. Scalapino, *Phys. Rev. B* 24, 3276 (1981).
19. J. W. Little, T. L. Ferrell, T. A. Callcott, and E. T. Arakawa, in *The Physics of Submicron Structures*, H. L. Grubin, Ed. (Plenum Press, New York, 1984).
20. J. W. Little, T. A. Callcott, T. L. Ferrell, and E. T. Arakawa, *Phys. Rev. B* 29, 1606 (1984).
21. J. W. Little, T. L. Ferrell, T. A. Callcott, and E. T. Arakawa, *Phys. Rev. B* 26, 5953 (1982).
22. S. W. Kennerly, J. W. Little, R. J. Warmack, and T. L. Ferrell, *Phys. Rev. B* 29, 2926 (1984).
23. R. J. Warmack and S. L. Humphrey, *Phys. Rev. B* 34, 2246 (1986).
24. B. K. Russell, J. G. Mantovani, V. E. Anderson, R. J. Warmack, and T. L. Ferrell (unpublished).
25. P. Royer, J. P. Goudonnet, R. J. Warmack, and T. L. Ferrell (unpublished).
26. A. Gras-Marti, P. M. Echenique, and R. H. Ritchie, *Surface Sci.* 173, 310 (1986).
27. W. R. Smythe, *Static and Dynamic Electricity* (McGraw-Hill, New York, 1968).
28. J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1975).
29. Hummer V, manufactured by Technics, Alexandria, VA.
30. H. J. Hageman, W. Gudat, and C. Kunz (Deutsches Elektronen-Synchrotron Hamburg), Report No. DESY-Sr-74/7, 1974 (unpublished).
31. B. N. Kurdi and D. G. Hall, *Phys. Rev. B* 34, 3980 (1986).
32. P. Dawson, D. G. Walmsley, H. A. Quinn, and A. J. Ferguson, *Phys. Rev. B* 30, 3164 (1984).
33. B. L. Illman, V. E. Anderson, R. J. Warmack, and T. L. Ferrell (unpublished).
34. R. K. Jain, C. W. Slayman, M. G. Farrier, and T. K. Gustafson, *J. Appl. Phys.* 48, 1543 (1977).
35. P. K. Hansma, *Tunneling Spectroscopy* (Plenum Press, New York, 1982).

36. D. C. Tsui, Phys. Rev. Lett. 22, 293 (1969).
37. E. N. Economou, Phys. Rev. 182, 539 (1969).
38. J. J. Burke, G. I. Stegeman, and T. Tamir, Phys. Rev. B 33, 5186 (1986).
39. L. C. Davis, Phys. Rev. B 16, 2482 (1977).
40. K. Parvin and W. Parker, Solid State Commun. 37, 629 (1981).
41. B. Laks and D. Mills, Phys. Rev. B 20, 4962 (1979).
42. B. Laks and D. Mills, Phys. Rev. B 21, 5175 (1980).
43. J. R. Kirtley, T. N. Theis, and J. C. Tsang, Appl. Phys. Lett. 37, 435 (1980).
44. J. R. Kirtley, T. N. Theis, and J. C. Tsang, Phys. Rev. B 24, 5650 (1981).
45. N. Kroo, Z. Szentirmay, and J. Felszerfalvi, Phys. Lett. 81A, 399 (1981).
46. B. Laks and D. L. Mills, Phys. Rev. B 22, 5723 (1980).
47. J. R. Kirtley, T. N. Theis, J. C. Tsang, and D. J. DiMaria, Phys. Rev. B 27, 4601 (1983).
48. J. Drucker and P. K. Hansma, Phys. Rev. B 30, 4348 (1984).
49. P. Dawson and D. G. Walmsley, Solid State Commun. 50, 383 (1984).
50. B. N. Kurdi and D. G. Hall, Optics Commun. 51, 303 (1984).
51. B. Laks, D. Mills, and M. G. Weber, in Tunneling Spectroscopy, P. K. Hansma, Ed. (Plenum Press, New York, 1982).
52. S. Ushioda, J. E. Rutledge, and R. M. Pierce, Phys. Rev. Lett. 54, 224 (1985).
53. S. R. Brueck, V. Diaduik, T. Jones, and W. Lenth, Appl. Phys. Lett. 46, 915 (1985).
54. M. G. Weber and D. L. Mills, Phys. Rev. B 32, 5057 (1985).
55. R. W. Gruhlke, W. R. Holland, and D. G. Hall, Phys. Rev. Lett. 56, 2838 (1986).

56. S. K. Khanna and J. Lambe, *Science* 220, 1345 (1983).
57. N. F. Mott, *Trans. Faraday Soc.* 35, 1175 (1939).
58. N. F. Mott, *Trans. Faraday Soc.* 43, 429 (1946).
59. G. Hass and M. H. Francombe, *Physics of Thin Films* (Academic, New York, 1978), Vol. 10.
60. J. L. Miles and P. H. Smith, *J. Electrochem. Soc.* 110, 1240 (1963).
61. R. M. Handy, *Phys. Rev.* 126, 1968 (1962).
62. A. L. Geiger, B. S. Chandrasekhar, and J. G. Adler, *Phys. Rev.* 188, 1130 (1969).
63. W. M. Bowser and W. H. Weinberg, *Surface Sci.* 64, 377 (1977).
64. C. C. Chang, T. A. Callcott, and E. T. Arakawa, *Phys. Rev. B* 32, 6138 (1985).
65. R. C. Jaklevic and J. Lambe, *Phys. Rev. B* 12, 4146 (1975).
66. R. C. Jaklevic, in *Tunneling Spectroscopy*, P. K. Hansma, Ed. (Plenum, New York, 1982).

APPENDIXES

APPENDIX A

REVIEW OF TUNNEL JUNCTIONS

Light emitting tunnel junctions have potential for use as flat screen display devices. They operate at low voltages and radiate throughout the visible spectrum. The major disadvantage at present is their low efficiency, one photon out for every million tunneling electrons. Tunnel junctions have proven useful as ultraviolet detectors [34]. In a similar fashion, they may have potential for a new type of solar cell. They also provide an ideal sample for fundamental studies of high-field breakdown at electrode surfaces since they endure field strengths of the order of 10^7 volts/cm at a few volts.

Since the 1960s MIM tunnel junctions have been widely utilized in molecular spectroscopy [35]. For this type of experiment, a monolayer of the molecules of interest is placed on the oxide. The upper electrode is evaporated over the molecules to complete the junction. A slowly ramped bias voltage is applied with the junction held at liquid helium temperatures. When the tunneling electrons have enough energy to excite a molecular vibration, an inelastic channel opens. The small increase ($\sim 1\%$) in conductance can be measured by recording the second derivative of the current with respect to the bias voltage.

In 1969, Tsui [36] applied the second derivative technique to metal-semiconductor tunnel junctions without molecules on the

interface. A noticeable increase in conductance occurred when the tunneling electrons had energy $eV = \hbar\omega_s$, where ω_s is the surface plasmon frequency of the GaAs semiconductor used in the junction. Varying the amount of doping in the semiconductor changed the voltage at which the increase in conductance appeared. This was the first direct evidence of surface plasmon excitation in tunnel junctions.

Researchers took an active interest in surface plasmon modes in MIM tunnel junctions after Lambe and McCarthy's [11] initial report of light emission. The surface plasmon dispersion relation for the planar interface between two semi-infinite media is well known. For a thin film in vacuum another mode appears. Including the effects of retardation alters these modes. For a multiple thin-film tunnel junction, more modes appear and shift the existing modes for a thin film in vacuum. Economou [37] calculated the dispersion relations for a multiple thin-film system appropriate for tunnel junctions with planar interfaces. He included retardation but considered the metals to be a free electron gas without damping.

In general, the number of surface plasmon modes is equal to the number of interfaces in the tunnel junction. (Recently, Burke et al. [38] postulated the existence of new modes for lossy films, but these modes have not been observed experimentally.) For frequencies of visible light, there are two nonradiative modes of interest in a planar junction. In the literature they are referred to as the "fast" and "slow" modes [35]. The dispersion curve for the fast mode is closer to the light line than the slow mode and hence has a higher phase

velocity in that region. The fields and energies associated with the fast mode have a maximum at the top electrode-air interface. For the slow mode this occurs in the region of the insulator. Economou's [37] calculations show that the fast mode is entirely decoupled from the other modes of the junction, i.e., it has the same dispersion relation as the semi-infinite metal-vacuum interface. In light of the above, one might be misled to believe that these modes are highly localized to the interfaces. In a typical tunnel junction, the top electrode is only 15 nm thick. Thus, although the fields and energies peak at the interfaces, they have a finite extent and may have appreciable values at other interfaces. The exact values depend on the material's dielectric function, the film thickness, and the wavenumber of the surface plasmon. Also, Economou's calculation is for a free electron gas without damping; this is clearly not applicable to the metals used for the top electrode.

In 1977 the first paper on the coupling of tunneling electrons in MIM structures to surface plasmons was presented by Davis [39]. He considered coupling only to the slow mode. He calculated the quantum efficiency for excitation of a surface plasmon to be $\sim 10\%$. A large portion of the surface plasmons excited were at high k (wavenumber) values which would not radiate efficiently unless there is extremely small scale roughness. This would account for the low overall efficiency of light output from tunnel junctions.

Light emitted from statistically rough tunnel junctions is unpolarized [32]. The roughness is usually produced by an underlayer

of calcium fluoride. The light is broadband and in most experiments has an energy up to the value of $|eV|$. The radiation is most intense along the junction normal and follows a cosine squared distribution [40]. Since all interfaces are rough, there has been much debate concerning which mode is responsible for the light emission. Initially it was assumed the slow mode is responsible since its fields and energies are strongest in the tunneling region [39]. In this view, the electrons tunnel inelastically by coupling to surface plasmons in the barrier.

In a series of theoretical papers by Laks and Mills [41,42] the role of the two modes is explored. The coupling of the tunneling electrons to surface plasmons is modeled as being through optical frequency fluctuations in the tunnel current as developed by Hone, Muhlschlegel, and Scalapino [12]. The coupling of surface plasmons to photons is treated by a perturbation approach which is valid for small amplitude roughness. Strong coupling between surface plasmons and photons is found if $ka_0 = 1$, where k is the surface plasmon wavenumber and a_0 is the mean transverse correlation length of the roughness. This is reminiscent of the Bragg law in which waves may interact strongly with the crystal planes.

For statistically rough tunnel junctions, Laks and Mills [41,42] found the light to result from the slow or junction mode. Emission from the fast mode is negligible. They also found that light may result from the direct coupling of the tunnel current fluctuations to the photon field.

A number of discrepancies exist on comparison of theory and experiment. For rough junctions with a gold top electrode, photons have been detected with substantially higher energies than the slow-mode cutoff. Laks and Mills attempt to explain this by direct coupling. However, this is predicted to give only P-polarized radiation whereas experimentally the emission is unpolarized. Direct coupled emission should also be observed from smooth junctions. If the slow mode is responsible for the radiation, roughness on the 3-5 nm scale is required for visible light. Experiments [6,7] for thin films on calcium fluoride give $a_0 = 40\text{-}50$ nm. Laks and Mills suggest that calcium fluoride may have a smaller scale roughness superimposed on these larger profiles.

Tunnel junctions on random rough surfaces are difficult to characterize due to the many Fourier roughness components. This prompted Kirtley et al. [43,44] and later Kroo et al. [45] to fabricate junctions on holographic gratings. The gratings have a well-defined transverse correlation length equal to the groove spacing (~ 800 nm). Enhanced radiative decay of surface plasmons will take place if

$$k_L \sin \theta = k \pm \frac{2\pi n}{a_0} \quad (28)$$

where k_L is the wavenumber of the emitted photon and θ is the angle measured from the junction normal, while k is the surface plasmon wavenumber. The light emitted by tunnel junctions on gratings has narrow, angle-tunable peaks which are P-polarized. From the peak energies and emission angles the authors were able to construct the

dispersion relation and identify it as associated with the fast mode. In addition to the sharp peaks there was found to be a weak unpolarized background. This was attributed by them as being due to the slow mode. This, they argued, resulted from small scale residual roughness and hence both modes are required to fully explain the emission.

Shortly thereafter Laks and Mills [46] reviewed their theory to include large correlation lengths and re-examined the role of the fast mode. They determined that for tunnel junctions on gratings the fast mode is indeed responsible for the light emission but still insisted the slow mode dominates for junctions on calcium fluoride.

In light of their experimental work concerning junctions on gratings, Kirtley et al. [47] proposed a hot-electron model for surface plasmon excitation. In this view, the electrons tunnel elastically through the barrier and coupling to the surface plasmons occurs near the top electrode-air interface. Evidence presented includes a decrease in emission intensity with upper electrode thickness (which does not match the optical screening length). The peak intensities increase dramatically as the temperature decreases, even though the current-voltage characteristics and optical properties are not strongly temperature dependent. They interpret the intensity increase as being due to the longer mean free path of hot-electrons at low temperatures, thereby allowing more electrons to reach the electrode-air interface.

In another test of the hot-electron theory, Drucker and Hansma [48] were able to detect the emission of energetic electrons from the top electrode of a tunnel junction. The work function of the top electrode was reduced by applying a few monolayers of cesium to the surface. They collected 1% of the tunneling electrons but were not able to estimate the actual percentage of hot-electrons in the junction.

If tunnel junctions are operated in reverse bias (top electrode negative) light emission of slightly lower intensity is observed. Kirtley et al. [47] propose that hot-electrons (or holes) are created in both electrodes, and that excitations in the electrodes may be coupled, for a thin barrier, through the slow surface plasmon mode.

In 1984, Dawson et al. [32,49] advocated that light from statistically rough tunnel junctions is mediated by the fast mode. They compare the emission spectra to the volume loss function, $\text{Im}(-1/\epsilon(\omega))$, for the top electrode. The emission intensity mirrors the loss function; as the value of the loss function increases, the emission intensity decreases. Typically the loss function is used in high energy electron loss experiments but here it is applied to the hot-electrons. Other arguments are also offered in favor of light emission being due to the fast mode.

Kurdi and Hall [31,50] calculated the electromagnetic modes for the tunnel junction geometry. Experimental values for the dielectric functions of the materials are utilized in the computation and the lower electrode is not of semi-infinite extent as considered in an

earlier work [51]. They found the fields associated with the slow mode decay rapidly with distance from the barrier region. For a 20 nm thick, Ag top electrode the fields are near zero at the top electrode-air interface. The fast mode has fields which peak at the metal-air interface but retain appreciable values in the barrier region.

Ushioda et al. [52] detected light from a nominally smooth tunnel junction fabricated on a hemispherical prism. In their geometry, only prism coupled light from the fast mode should be observed. Comparison of the peak in the emission with the theory of Laks and Mills [41,42] indicated the light is from the slow mode. This led the authors to assert that the fast mode is excited via the slow mode through the residual roughness in the films.

Cross coupling of surface plasmon modes in gratings had been suggested by Brueck et al. [53], but this was refuted by a calculation of Weber and Mills [54]. They predicted the cross coupling to be unobservable in their reflectivity experiment.

In 1986, cross coupling of surface plasmon modes on a corrugated metal film was reported by Gruhlke et al. [55]. In the experiment, surface plasmons were excited by molecular fluorescence. The grating provided a well defined roughness coupling between the surface plasmon modes. Radiative decay of the cross-coupled modes was detected and compared to the dispersion curves. The different slopes of the two dispersion curves allowed cross coupling in a narrow frequency range for a particular groove spacing which matched the observed spectra.

In brief, light emission from tunnel junctions on calcium fluoride or gratings has been thought to originate from the slow mode through inelastic electron tunneling. The fields and energies associated with this mode are largest in the barrier region and couple strongly to the tunneling electrons. Tunnel junctions on gratings have well defined roughness and demonstrate that light emission is due to the fast mode. This has led to the hot-electron picture in which electrons tunnel elastically and couple to the fast mode in the vicinity of the metal-air interface. A number of results agree with this argument. However, the emission intensity is not strongly dependent on the direction of the tunneling current. There is evidence in recent experiments for cross coupling of the two modes. In this situation, the slow mode is excited by tunneling electrons. Cross coupling stimulates the fast mode which then radiatively decays. The last two steps of this process require roughness to mediate the coupling.

Modern microlithographic techniques permit much better defined microstructures to be placed on tunnel junctions than has previously been possible. Due to the considerable confusion created by the poorly-characterized roughness factor, it appears that a well-controlled roughness is needed. One of the purposes of the present investigation is the study of tunnel junctions in which the microstructures can be better characterized.

The first observation of light emission from tunnel junctions incorporating discrete microstructures was reported by McCarthy and

Lambe [13]. Silver particulates were formed on a thin magnesium fluoride layer which had been evaporated on an aluminum-aluminum oxide-gold ($\text{Al-Al}_2\text{O}_3\text{-Au}$) tunnel junction. Their primary purpose was to increase the light emission intensity of the device by varying the magnesium fluoride spacer thickness. No attempts were made to characterize the emission spectra in terms of the spheroid shapes of dielectric properties. At that time, even simple absorbance experiments for thin annealed films on transparent substrates could not be adequately explained by existing theory.

Properties of metal spheres were better understood and easier to model theoretically. Hansma and Broida [16] fabricated light emitting tunnel junctions with gold spheres directly on the oxide layer. These metal smokes (or spheres) were formed by evaporating gold, in argon at a pressure of 20 torr. The smoke particles were subsequently buried under a gold electrode to complete the junction. Tunnel junctions were also produced with gold smokes overlayed with silver top electrodes [14,15].

For gold particles under a silver or gold electrode the emission spectra is broad. Emission along the junction normal is unpolarized but at higher angles the P-polarization exceeds the S-polarization. The spectra of the excess polarization (P minus S) reveals a peak near 1.9 eV.

A theory, suitable for metal spheres on the oxide layer, was developed in a series of articles [12,17,18]. In this model, surface plasmons localized in the microstructures are excited by a fluctuating

current produced by the tunneling electrons. The dipole moment induced in these miniature antennae radiates the observed light.

As previously mentioned, this model neglects the interaction with the top (noble metal) electrode. Experimentally, the particulates must be connected electrically in order to apply a bias voltage across the oxide. Overcoating the spheres with a metallic electrode would be expected to alter the dipole moments induced in the spheres. Nonetheless, the theory did predict the proper spectra for the excess polarized light. The unpolarized light was attributed to residual roughness in the junction. It could be explained by the theory of Laks and Mills [41,42] for statistically rough tunnel junctions.

To theoretically account for the radiation pattern of the excess polarized light, simple antenna theory was employed. Dipole moments, aligned normal to the surface of the oxide, were situated 3 nm above a semi-infinite aluminum electrode. The effect of the aluminum electrode was to shift the dipole radiation lobe 40 degrees above the plane of the junction.

The present work is an extension of the work of McCarthy and Lambe [13]. By improving the junction in several ways the experiments described in the preceding text offer better possibilities for distinguishing between various models. In particular the works of Scalapino [12,17,18] have tended to give acceptable results in certain cases, as have the works of Laks and Mills [41,42]. However, all models obtained to date are unsatisfactory in one or more aspects, and it is hoped that the experimental improvements described in the

preceding text can form a working basis for continuing the fundamental investigations until a detailed model is complete.

APPENDIX B

THE ALUMINUM OXIDE BARRIER

The critical step in tunnel junction fabrication is the oxidation of the aluminum electrode. An increase in oxide thickness of 0.5 nm will result in a corresponding increase in junction resistance by two orders of magnitude [56]. Any small defect in the oxide could lead to catastrophic failure of the junction.

For good light-emitting junctions the oxide layer is 3-4 nm thick. In this range, the oxides that are grown are superior to evaporated oxides in that they are free of holes and have a more uniform thickness. Pinholes or other irregularities in the oxide may serve as a current sink and will lead to a rapid decline in the junction's performance. Thicker oxides (>4 nm) have negligible tunnel currents and thinner oxides (<3 nm) will not provide the high bias voltages needed for usable tunnel junctions. In view of these considerations a lower electrode of aluminum on which a film of alumina (aluminum oxide, or Al_2O_3) is grown is the preferred choice for tunnel junction fabrication.

The theory of oxidation presented by Mott [57,58] requires the presence of oxygen and an electric field. Adsorbed oxygen ions establish a constant potential which drives the aluminum ions to the surface by diffusion and field drift. The process advances rapidly at first and then slows as the oxide thickness increases and the

electric field strength decreases. For aluminum exposed to air, the oxide will grow to a thickness of 2.5 nm in one to two hours and will be only 3.5 nm thick after one month [59].

Anodization through the use of electrolytic cells follows a similar course to thermal oxidation except an additional electric field is applied by external means. The conducting electrolytic solution provides the necessary oxygen and allows a potential of desired voltage to be established across the oxide. In liquid anodization there is a linear relationship between the applied voltage and oxide thickness [60]. The value of the constant depends on the particular electrolyte but is typically 1.5 nm/V. Electrolytic cells are ideal for forming thick insulating layers but the oxide is porous and rough; therefore they are rarely used in tunnel junction fabrication.

Plasma anodization is another technique for forming metal oxide films [60]. In plasma anodization the aluminum is exposed to pure oxygen at a pressure of 0.05 torr. The sample is mounted between two loops of aluminum wire and a discharge is established. Oxides formed in this manner will grow to a limiting thickness of ~ 2.5 nm in 30 minutes. This process is analogous to thermal oxidation but in this case there is a rich supply of ions which enhances the oxidation rate. The oxide thickness can be increased by applying a small positive bias to the aluminum sample.

Solid-state anodization resembles anodization by an electrolytic cell—the distinction being that oxygen is supplied by a

solid, not a liquid [60]. The first step of this process is to form a thin oxide on the aluminum surface by brief exposure to oxygen. Next, a layer of lead or tin is evaporated onto the oxide. The evaporation takes place in an oxygen environment at a pressure of 0.01 torr. Lead or tin is chosen for the top electrode since large amounts of oxygen will easily dissolve in them. The junction is removed from the evaporator and a bias voltage is applied across the oxide. A current flows and gradually decreases as the oxide grows.

As mentioned earlier, aluminum is employed as the bottom electrode by the majority of investigators because of the uniform oxide that readily forms on its surface. A number of materials are utilized for the upper electrode. Silver and gold are commonly used for light emitting tunnel junctions. Lead is the choice of most workers in inelastic electron tunneling spectroscopy (IETS) owing to its superconducting properties at liquid helium temperatures.

Handy [61] conducted a systematic study of the resistance in $\text{Al-Al}_2\text{O}_3\text{-M}$ tunnel junctions, where M = nickel, copper, aluminum, silver, gold, tin, antimony, or bismuth. It was found that the junctions resistance increased with increasing atomic size up to an atomic radius of 0.16 nm. Above this atomic radius the resistance did not increase but remained constant. The difference in the values of the work function of the upper electrode is not enough to account for the large variation in resistance. Handy suggests the correlation between atomic size and junction resistance is due to the penetration of the atoms into the oxide. The smaller the atoms of the upper

electrode, the farther these atoms will penetrate into the oxide. This results in an overall decrease in oxide thickness.

In a related experiment, Gieger et al. [62] investigated the impurities in the junction by IETS. The upper electrode was formed by plasma anodization and the sample remained inside the belljar until junction fabrication was complete. Two peaks in the tunneling spectra were always present. The peak at 118 mV was ascribed to OH in alumina hydrate and the peak at 450 mV was attributed to free OH. A correlation between the area under the peaks and the ionic radius was found. Junctions with the most impurities had gold as the top electrode. Impurity levels for the various electrodes in descending order were gold, silver, lead, indium, tin, magnesium, and aluminum. The ionic radius of gold is 0.14 nm while that of aluminum is 0.05 nm. The authors propose that for metals of small ionic radius there is considerable penetration of the metal into the oxide, therefore the oxide-metal interface for tunneling is in the interior of the original oxide film. In this case surface impurities are not in the tunneling region and hence will not contribute to the tunneling spectra.

Bowser and Wienburg [63] also investigated impurity levels in tunnel junctions. In their paper, as in Gieger's et al. [62] the impurities are thought to originate from water vapor. Attempts to rid the junctions of these impurities have not been successful.

Another important consequence of the electrode stems from its work function. For an Al-Al₂O₃-Au tunnel junction the difference in the work functions of aluminum and gold is ~1 eV. After the junction

is completed the Fermi levels reach equilibrium. The net result is a one volt potential across the oxide with aluminum being positive. If the oxide is 2 nm thick the electric field strength is $\sim 10^6$ V/cm. Recently, Chang et al. [64] studied the effect of this field in barrier diffusion of Al-Al₂O₃-Au junctions with no external voltage applied. It was found that this field is sufficient to drive aluminum ions through the oxide into the gold. There was no evidence for gold diffusing into aluminum. If oxygen is present at the oxide-gold interface, this diffusion process could increase the oxide thickness.

In Handy's [61] investigation of various electrodes, he tried barium which has a much smaller work function than the other electrodes tested. Although barium has a large atomic radius (0.22 nm) he found these junctions had low resistance indicating the work functions of the electrodes is also influential in oxide growth.

Jaklevic and Lambe [65] have noted that their tunnel junctions have low resistance immediately after fabrication, but the resistance increased by at least an order of magnitude after a few days on the shelf. The effect of aging is not completely understood, but at least two entities appear significant: (1) the work functions of the electrodes; (2) water.

In Handy's [61] paper on the effects of the top electrode he found that for aluminum, tin, copper, nickel, silver, and gold the resistance increased with time by

$$R = A \log(t + t') + B \quad (29)$$

where A, B, and t' are constants. Top electrodes of bismuth and antimony had no consistent aging effects and for lead the resistance actually decreased slightly. The measurements were performed over one week's time. Similarly Chang et al. [64] found that barrier diffusion, which is driven by the difference in work functions, of aluminum into gold proceeded rapidly at first and then slowed. Handy's results for lead may in part be attributed to the degradation of the lead electrode which occurs if water vapor is present [66].

Miles and Smith [60] credit the aging effect to solid-state anodization. The oxygen is either dissolved in the top electrode or diffuses into it. They observe that when the top electrode has a higher work function than aluminum the samples age more rapidly than Al-Al₂O₃-Al junctions. Recall that there is also a field set up by the oxygen ions adsorbed on the oxide which may in part account for aging in junctions with aluminum electrodes.

In IETS the junction is doped with the molecule to be studied. One method of doping is by exposing the oxide to the vapor or simply dipping it into a solution and spinning off the excess. Another method, described in detail by Jaklevic [66], is infusion doping. A thin oxide is first formed by plasma anodization, then the top electrode is evaporated. The dopant is mixed into distilled water and a carrier gas of air or nitrogen is bubbled through it until the relative humidity of the chamber is 50-90%. The junction is exposed for several hours until the resistance rises to the required level. Infusion doping increases the junction resistance one or two orders

of magnitude. No infusion is observed unless water vapor is present. Jaklevic suggests that water penetrates the grain boundaries of the top electrode to carry the dopant to the oxide layer.

To illustrate the importance of water vapor, Jaklevic [66] exposed a fresh aluminum-aluminum oxide-lead ($\text{Al-Al}_2\text{O}_3\text{-Pb}$) junction to an atmosphere of 80% relative humidity. Initially their junction had less than five ohms resistance, but after five minutes exposure the resistance was greater than one hundred ohms. If the relative humidity returns to 0% the resistance decreases to 35 ohms indicating there is some de-infusion taking place. The technique is to overshoot the desired resistance by a factor of two. Lead is known to be porous but Jaklevic [66] has had some success with infusion doping using gold as the top electrode.

The presence of water vapor is also important during the initial oxide formation. It has been noted that water vapor is always present to some extent in the evaporation belljar. In order to reduce the amount of water vapor, Miles and Smith [60] baked out the system overnight. The junctions formed in the "dry" environment had resistances reduced by two to three orders of magnitude compared to those fabricated in an unbaked system.

Jaklevic and Lambe [65] found that plasma anodization in an oxygen atmosphere of 5-10% water yielded good resistance if the junctions were allowed to age a few days. It seems that water vapor, whether present on the oxide initially or infused after junction completion, is important in forming good oxides. It is also noted that water will adsorb readily on many materials including aluminum oxide.

VITA

The author, Mark Joseph Bloemer, was born in Cincinnati, Ohio, on October 22, 1956. He moved to Louisville, Kentucky, in 1968 and graduated from Trinity High School in May 1975. In June of that year he accepted a job at a local foundry as an apprentice machinist. He enrolled at the University of Louisville the following September. In August of 1980 he left his position with the foundry and accepted a teaching assistantship at the University of Louisville. That same year he taught a high school physics course at Louisville Collegiate School. He received a Bachelor of Science degree with Honors in Physics in May of 1981. In August of 1982 he was awarded a Master of Science degree in Physics from the University of Louisville.

He was offered a research assistantship in the Physics Department at The University of Tennessee, Knoxville, and began study in September of 1982. He received his Doctor of Philosophy degree in December of 1986.

The author is a member of Sigma Pi Sigma, Delta Mu Epsilon, and is a past Treasurer of The Society of Physics Students. He received a Science Alliance Scholarship from Oak Ridge National Laboratory and The University of Tennessee for the 1985-86 academic year.