A RENEWAL PROPOSAL FOR RESEARCH ON

The Study of Electrons Photoemitted from Field-Emission Tips

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Photo-induced field emission is a technique which studies electrons that have been photoemitted from a field emission tip. This experimental method promises to combine the proven utility of both field emission and photoemission for investigating the electronic states near a metal surface. The primary objective of the research described in this proposal is to measure photo-induced field emitted electrons as a function of both their final state energy and the applied electric field. An Argon-ion laser in conjunction with a tuneable cw dye laser will be used to photo-excite the electrons. A differential energy analyzer will allow energy resolved measurements of the photo-field emitted electrons. Other experiments, directly related to the unique effects associated with the illumination of metallic tips by laser light, are also proposed. Experiments that exploit the large temperature rise of a field emission tip when illuminated by a focussed laser beam are proposed to study thermally activated surface diffusion of alkali adatoms on a field emission tip. These experiments may eventually provide information about thermally-induced or laser-induced chemical reactions on small metallic surfaces.
I. INTRODUCTION

The following report is a proposal to continue work on photo-induced field emission experiments. The advances in implementing experiments in this new and interesting area of solid state physics have been outlined in the Progress Report and that report should be read in conjunction with this Renewal Proposal. Section II of this proposal provides a brief review of pertinent background material. Section III describes in summary form three experiments that have been started and will be continued during the year 1982-1983. Section IV contains a list of University-wide facilities which are available to implement the proposed experiments while Section V contains a brief description of the principal investigator's background and scientific qualifications. Finally, in Section VI, a proposed budget for the fiscal year 1982-83 is presented.
II. BACKGROUND SURVEY

The dielectric response of a metal surface to an external charge distribution is of much importance to a number of surface related phenomena. A key aspect of the metal surface-external charge interaction is the image potential which has been used extensively to discuss such things as the Schottky effect, the tunnelling between two metal electrodes separated by an insulating barrier, field evaporation, field absorption, field emission and low energy electron scattering problems.

As is well known from classical electrostatics, the image potential between a static point charge of strength q located in vacuum and a perfect conducting surface is given by

\[ V(x) = -\frac{1}{4\pi \varepsilon_0} \frac{q^2}{4x_0} \]

where \( x_0 \) is the distance of the charge from the metal surface and \( \varepsilon_0 \) is the permittivity of free space. For an ideal conductor, the screening charge induced in the metal is located entirely at the surface.

The above expression is valid only for distances \( x_0 \) large compared with the actual screening length \( \lambda_s \) (\( \lambda_s = 0 \) for a perfect conductor) of the metal electron gas. For quantitative purposes it is important to know how the singularity of Eq. 1 at \( x_0 = 0 \) is removed by the effect of finite screening. Also, for \( \lambda_s \neq 0 \), the charge induced on the surface extends over a layer of finite thickness, a feature which may lead to further modification of Eq. 1. Lastly, in the case of a moving external charge, one might expect
the existence of dynamical corrections to the image potential in addition to the static corrections mentioned above. These dynamical corrections are likely to occur in two different ways. First, if the velocity v of the external charge is comparable to the velocities of metallic electrons; the screening response of the electrons can no longer be treated adiabatically. Secondly, sufficiently fast charged particles may excite surface and bulk plasmon oscillations in the electron gas that will manifest themselves through additional corrections to the quasi static image potential.

Because of these general considerations, there has been a long term interest, dating back to the 1940's, in an experimental determination of the shape of the surface potential barrier by measuring the flux of electrons which have been thermally excited or photoemitted from a metal. The literature provides a long list of investigators who have studied the periodic deviations which occur in photoelectric and thermionic emission of electrons from metal surfaces as a function of an applied electric field. Such studies in principle reveal effects which are related to the shape of the surface potential barrier; however, no unambiguous experimental determination of the shape of this barrier as a function of distance from the metal-vacuum interface has been obtained. This situation seems to be a result of the complicated approximations necessary in order to describe the thermionic and photoemission data which were obtained in this early work. With the advent of high intensity monochromatic light sources and with the increasing sophistication of computer calculations, it seems likely that a better understanding of this problem of long term interest to solid state physicists is now possible.

In a quite different context than the above discussion, it has recently been emphasized that information about the electronic states of a metal
which lie in the usually inaccessible energy range between the Fermi energy and the vacuum level might also be obtained from studies similar to those listed above. Such information would be useful in further checks of the validity of various band structure calculations. An important aspect of these particular electronic states is that they can be populated by thermal excitation. Thus it seems likely that any information about these states should in principle provide a more detailed understanding of the chemical and physical properties of hot metallic surfaces.

It is apparently for these reasons discussed above that there has been an increasing interest in the study of a relatively new surface-sensitive technique called photo-induced field emission. Photo-induced field emission is an experimental technique which studies electrons that have been photo-excited from a field emission tip. The primary motivation for studying photo-field emitted electrons can be understood by discussing the effect which a strong electric field has on the potential barrier at the surface of a metal. As is known from the theory of field emission, the strong electric field which can be applied to a field emission tip causes the surface barrier at a metal-vacuum interface to assume a triangular shape. This distortion in the surface barrier is of crucial importance for the experiments to be proposed because it allows photoexcited electrons to quantum mechanically tunnel out of the metal even when the incident photon energy is less than \( \phi \), the work function of the metallic surface. The triangular surface barrier is further modified by the interaction of an escaping electron with its image charge. This interaction rounds the peak in the surface barrier and lowers it from the work function by an amount proportional to \( F^{1/2} \) where \( F \) is the applied electric field strength.
The resulting shape of the surface barrier due to these two effects is shown in Fig. 1. A general feature of this potential barrier is the presence of a maximum which is displaced from the surface of the metal and which lies in energy below the work function of the metallic surface. By photo-exciting electrons to final states which lie in energy below the vacuum level, it is possible to probe the surface potential barrier in the vicinity of this maximum. This very important feature can be further elucidated by considering the electric field dependence of this surface barrier as shown in Fig. 1. For electric field strengths sufficiently small, the photoexcited electrons escape from the metal by tunnelling through the top of the surface barrier (field emission regime). By contrast, in sufficiently strong electric fields, the photoexcited electrons pass over the peak of the surface barrier before escaping into the vacuum (photoemission regime). As can be seen from Fig. 1, one of the primary interests in studying the photo-induced field emission process lies in the new information which will be obtained about the shape and structure of the surface barrier at a metal-vacuum interface.

A significant aspect of the photo-field emission process which is of interest in areas of applied physics is the capability of studying the interaction of intense laser light with small metallic particles in the presence of intense electric fields. Using the photo-field emission configuration, such studies can be performed in a controlled way by varying the wavelength of the laser light, the size of the field emission tip and the strength of the applied electric field. In addition, by permitting monolayers of adsorbed gas to accumulate on the field emission tip, it is also possible in principle to study the influence of intense light and strong electric fields on these adsorbed gases. Although such aspects of photo-field emission are not the main thrust of the experiments discussed in this proposal,
Figure 1. An illustration of the electric field dependence of the surface potential barrier at a metal-vacuum interface. The photo-induced field emission process is schematically indicated and the low field (field emission) and high field (photoemission) regimes are indicated.
their perceived applicability to such areas as solar energy, electro-chemistry and laser chemistry should not be summarily overlooked. It can be anticipated that when the important physical processes in the photo-field emission process are well understood, the techniques and information gained will be of use in the more applied areas of the physical sciences.

III. PROPOSED RESEARCH TOPICS

Three experiments will be continued during the year July 1982 - June 1983. The three experiments are essentially the same as those found in the previous renewal proposal and for this reason, the proposed experiments and the motivation for performing them are discussed below in summary form only.

A. Final State Effects in Photo-Induced Field Emission

Ever since the paper by Lundqvist, et al.\textsuperscript{19} proposed the photo-induced field emission process as a probe of final states which lie between $E_F$ and $E_F + \phi$, there has been considerable interest in searching for final state effects within this energy range. Pioneering experiments by M. J. G. Lee\textsuperscript{33} on photo-induced field emission from tungsten revealed a broad, featureless energy distribution of photoexcited electrons from which structure, attributable to final state effects, was noticeably absent. A similar conclusion can be drawn from a more detailed study of the photo distribution performed by Reifenberger, Goldberg, and Lee.\textsuperscript{40} An important question is thus raised about the apparent lack of direct transitions which can potentially give information about the bulk band structure of the metal tip under investigation. For this reason, a careful study of the photo-field distributions from two different metals (molybdenum and rhodium) is proposed.

Two materials, Mo and Rh, are chosen for investigation because of the widely different characteristics of their calculated energy band structures.
between $E_F$ and $E_F + \phi$. Although a detailed spectroscopy of the final states within this energy range in these two metals is in principle possible, it is emphasized that this is not the main thrust of the initial work under progress. Rather, we are more interested in measuring the total number of electrons per incident photon which are photo-field emitted from a certain symmetry direction and at a given energy. The rationale for this type of experiment is that the density of final states for energies between $E_F$ and $E_F + \phi$ are quite different for the two metals. This result is a general one and is due to the different types of crystallographic structure for the two metals, BCC for Mo and FCC for Rh.\textsuperscript{42}

B. Electric Field Dependence of the Photo-Field Current

Experiments are planned to measure the electric field dependence of photo-field current originating from field emission tips constructed from a number of different materials. The interest in these experiments are two-fold. First, it should be possible to obtain information about the transmission probability of electrons which are photoexcited above the peak in the surface barrier (see Fig. 1) from such measurements. Secondly, the large amplitude oscillations in the photo-field current reported by Lee and Reifenberger\textsuperscript{34} have not yet been fully explained and more data is needed in order to define the theoretical context necessary to understand this data. For these two reasons, experiments designed to measure the photo-field current using a differential energy analyzer will be performed.

An assumption which has been made in all previous discussion of photo-field emission is that the static image charge potential adequately describes the interaction of an electron traveling away from the metal surface. As discussed in the introduction of this proposal, this assumption seems questionable because of the short times ($\sim 10^{-16}$ sec.) involved in photo-field emission.
Experiments which measure the photo-field current as a function of the electric field will be performed in order to check the validity of the model recently proposed by Reifenberger, Haavig, and Egert. A particularly simple prediction of the model is that the oscillatory photo-field current measured from a single facet of a field emission tip will exhibit a frequency which can be determined from the characteristic surface plasmon energy of the material from which the tip is constructed. This prediction, as illustrated in Fig. 2, will be tested by searching for and measuring the frequency of the photo-field oscillations from field emission tips constructed from the more refractory elements listed in Figure 2. If these measurements prove conclusive, it will strongly support the suggestion made above that photo-induced field emission experiments are capable of probing the dynamics of the image charge formation.

C. Laser-Induced Diffusion of Alkali Metal Atoms on Field Emission Tips

Recent results have shown that the temperature rise of a field emission tip is of order 5000°K per watt of incident power when it is illuminated by a focused laser beam. This large temperature rise is accompanied by a short thermal time constant which insures that the tip heats up and cools off very quickly. It seems clear that the large temperature rise of the field emission tip along with the short (<< 1 sec) thermal relaxation time of the tip may well open the way for more applied investigations which involve field emission or field ion tips at elevated temperatures.

As a first step in exploiting the temperature rise of the tip, an experiment is planned in which monolayer coverage of alkali atoms are deposited on one side of a tungsten field emitter. Because of the lower work function of the tungsten-alkali metal composite, the extent of the alkali atom coverage of the tip should be clearly visible by observation of the resulting field
Figure 2. A plot of the predicted frequency of the oscillatory photo-field current vs. the surface plasmon energy for a number of different elements. This predicted correlation is a major feature of a model which we have proposed to explain the oscillatory photo-field effect.
emission pattern. Furthermore, if the tip is held at liquid nitrogen temperatures, little if any diffusion of the alkali metal atoms will occur. The tip can then be illuminated by the focused beam of an argon laser and any resulting diffusion of the alkali metal atoms will be measured. These experiments can be performed in two configurations -- when the electric field is applied to the metal tip and when the field is turned off.

The main interest in this work lies in providing more information on how the diffusion of adatoms proceeds under illumination of a metallic (or semiconducting) surface by intense light in the visible and near UV regions of the electromagnetic spectrum. This seems to be a particularly timely problem of current interest in a variety of different scientific disciplines. The recent interest in laser annealing of semiconducting surfaces to produce a surface of enhanced purity is explained by the hypothesis that rapid diffusion of impurities into the bulk is produced when the surface is subjected to illumination by a high powered laser. It has also been suggested, as far back as the late 1960's, that illumination of a surface by light causes a larger increase in the surface temperature than would be expected from classical heat flow arguments. This situation apparently results because of mean free path limitations in the conduction of heat away from the solid-vacuum interface. With these observations in mind, it is worthwhile to note that one of the main objectives of this particular research problem is to determine the major differences between equilibrium thermal diffusion and laser-induced diffusion of adatoms on a field emission tip.

D. Synopsis

It seems worthwhile to emphasize in a general fashion the guiding thrust and future prospects of the proposed research that has been discussed in Section III of this report. As is already well known, field emission and
field ionization experiments are capable of providing detailed information on a microscopically scale about the surface geometry, structure and electronic properties of metals. By illuminating a field emission tip with intense laser radiation, it is clear that a new experimental variable has been introduced which potentially has much to offer in both very basic and also very applied scientific disciplines.

As is suggested in Section III. B of this report, there is some evidence that the field emission geometry when combined with intense beam of a focussed laser may routinely allow a probe of events at metal-vacuum interfaces which occur in time intervals extending down to $\sim 10^{-16}$ sec. This suggestion has also been made previously within a somewhat different context (see for example the discussion in Ref. 43 concerning the operation of MOM diodes). It should be realized that the present discussion about the importance of the dynamic image charge effects in photo-induced field emission (see Sec. III. B), if they are verified by experiment would have a number of interesting and far reaching consequences, among which are:

a) The possibility of a detailed study of the dynamic formation of the image charge potential.

b) The possibility of measuring the effective relative dielectric constant $\varepsilon$ of monolayer and submonolayer coverages of adsorbed atoms on field emitters by exploiting the well known relationship between the surface plasmon frequency $\omega_{sp}$ and the bulk plasmon frequency $\omega_p$

$$\omega_{sp} = \frac{\omega_p}{(1+\varepsilon)^{1/2}}.$$
c) The possibility of routinely obtaining an independent and accurate (better than ~ 1%) calibration of the field constant which relates the applied voltage to the resulting electric field at a particular facet of a field emission or field ion tip.

Clearly there are many extensions of this simple experiment which may allow new information to be obtained about adparticle-substrate interactions. An immediate extension of the above experiment would involve the use of a field ion rather than a field emission tip for the imaging of foreign atoms. Under these conditions, the movement of a single atom could be recorded as it undergoes thermally activated motion over the surface of the tip. The most obvious advantage of performing this experiment using a laser to heat the field ion tip is that the heating and cooling cycles can be much shorter than conventional methods, thereby allowing greater control of experimental parameters.

An interesting extension of this proposed laser technique for the rapid heating of a sharp metallic tip is to investigate the effects of thermally activated or photon-induced chemical reactions on the surface of a tip fashioned from a catalytically important metal. Because the chemical reaction would take place on a sharp tip of ~ 1000 Å radius, any selectivity of a specific crystallographic plane in promoting the chemical reaction is likely to be observed in subsequent field ionization micrographs of the tip surface. By visual examination of these micrographs, information about the importance of the surface structure (flat, stepped, kinked, etc.) in enhancing the chemical reaction might also be obtained. Such a technique may also elucidate any rearrangement of surface atoms on a tip fashioned from a catalytically active metal. Although such interesting experiments
are not specifically discussed in this proposal, they could be pursued if a particularly promising prototype of a metal-gas system is found.

Further applications of this technique, although somewhat speculative, also deserve mention. It is presently thought that quantitative information about the diffusion of hydrogen out of a metal may be possible by studying the effects of laser heating of a field emission tip made from a metal which absorbs hydrogen gas. Both the number of hydrogen atoms and the direction from which they emerge from the metal might be measured by application of a strong electric field with a polarity so as to cause field ionization of the hydrogen atoms as they diffuse out from the bulk of the metal. Such experiments may give quantitative microscopic information about the amount of hydrogen emerging from a metal and may be a useful tool to compliment other studies of metal-hydrogen systems.\textsuperscript{48} Although the details of such an experiment are still in a preliminary stage, a proposal to fund this work has been proposed and submitted to the Exploratory Research Program sponsored by Procter and Gamble Co.

E. Justification for Capital Requests in Budget.

It is particularly important to note that the subject of photo-induced field emission which forms the core of this proposal has proved to be an area of expanding interest throughout the course of this research and there is every indication that the area will continue to be of continued interest as a better understanding of the important fundamental processes are elucidated. It is partly with this in mind, in addition to the vacuum limitations of our chamber discussed in the Progress Report, that a request is made in the proposed budget to purchase an 8" gate valve and small ion-pump with controller which will be incorporated into our UHV system. With the addition of these two accessories to our system, we hope to lower
the pressure in our chamber below $\sim 1 \times 10^{-10}$ Torr and thereby provide more reproducible data which is truly characteristic of a clean metal surface. Approximately 30% of the price of these items will be cost shared by the Department of Physics at Purdue University.
REFERENCES

10. C. Herring and M. H. Nichols, Rev. Mod. Phys. 21, 185 (1949).
47. See entire issue of Physics Today, November 1980.
IV. FACILITIES AVAILABLE

A. Laser Facility

The Central Laser Facility at Purdue University, established under the NSF-MRL program, consists of a Coherent Radiation Cr-10-U Ar⁺ ion laser, a Coherent Radiation 490 Dye Laser and a Coherent Radiation CR 599 Dye Laser (actively stabilized and capable of single frequency operation). In addition a suitable Kr⁺ ion laser for use as an additional pump laser has been recently obtained. This will allow the entire range of the electromagnetic spectrum between ~ 400 nm and ~ 900 nm to become accessible.

The Ar⁺ laser is installed on a convenient table with suitable optical benches for accessories. The Ar⁺ laser puts out 18 watts in "all lines" and 8.6 watts at $\lambda = 514.5$ nm and 6.6 watts at $\lambda = 488.0$ nm. With appropriate mirrors, a line at $\lambda \approx 350$ nm in the UV is available with a total power of 1.5 watts.

A new dye laser, dedicated to the proposed experiments, has been purchased. With the purchase of appropriate dye laser mirrors and suitable dyes, a tuneable light source which spans the entire visible spectrum with a typical power of ~ $\frac{1}{2}$ watt will result.

Professors W. M. Becker and A. K. Ramdas are in charge of this facility and have already indicated that the high power pump lasers can be used in conjunction with the dye laser purchased for this research. With the exception of possible scheduling conflicts with other users of this facility, it is anticipated that the pump lasers will be available for use with the experiments proposed in Section III of this report on a once-a-week basis.

3. Microstructural Analysis Facility

This facility provides a wide range of services in optical microscopy, scanning electron microscopy, and transmission electron microscopy. Three
staff members provide technical assistance to the users. A full time technician maintains the equipment and either provides full services to the user or trains the user to become self-sufficient in the operation of the equipment. The limited use of this facility is anticipated whenever measurements of the shape and geometry of the field emission tips are made.

C. Liquid Helium and Liquid Nitrogen

The Department of Physics at Purdue University has helium liquifying and liquid nitrogen facilities. The use of this facility is anticipated when using the roughing pump which is attached to the UHV vacuum chamber.

D. Shop Facilities

Modern equipment is available in two machine shops. In addition, a glass shop and an electronics shop are available.

E. Computer Facilities

There are available at Purdue University two high speed CDC 6500 computers complete with interactive programming terminals located conveniently throughout the campus, including the principal investigator's laboratory.
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