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D. W. Juenker

INTRODUCTION

With this report we conclude eleven years of research in photoelectric emission under AEC sponsorship. We shall attempt to select for mention here those novel findings, technical advances, and conclusions which seem to us the most significant output of this program, leaving elaboration of those points as well as less significant developments to the various publications and closed-circulation accounts which have emanated from it.

In the first of the following sections, a brief history of our research group and its activities is reprinted from the Ten-Year Summary of May 20, 1963. The second section consists of correlated and sparsely illustrated abstracts of the major theoretical and experimental undertakings. The third lists those techniques of experimentation or analysis which have been uncovered or refined in the course of our work and which may have more general usefulness. These are described briefly if no suitable formal references exist or are in prospect. In the second and third sections, numerical references are used for AEC-sponsored publications or reports, while alphabetic superscripts refer to work done elsewhere. The latter are identified in an appendix to Section III, and the former are included in a comprehensive listing of publications, dissertations, papers delivered at professional meetings, and other formal reports, which comprises Section IV.

I. BRIEF HISTORY OF THE PROGRAM

This program of fundamental research in photoemission had its beginnings in a group of investigations carried on in the late 1940's and early 1950's by the Physical Electronics section of the Notre Dame Physics Department. There was, first of all, a semi-applied research project underway, stemming from wartime interest and involving the oxide cathode, and hence active electron emitters in general. This inevitably led to more fundamental problems in electron emission, culminating in a thorough exploration of such emission - particularly thermionic - in the Schottky field region and from clean metal surfaces. Since the periodic deviation from the normal Schottky emission behavior showed great promise of yielding information on the important issue of the barrier shape at the metal surface, it was decided to explore this effect both thermionically and photoelectrically. The early parallel efforts in this area were carried on as thesis projects under the direction of Coomes. The pre-doctoral investigators were Juenker and Carroll, and the systems they studied were barium-on-tantalum and practical barium oxide cathodes, respectively.

It must be pointed out that, at this stage, the photoelectric effect was used merely as a tool for ejecting electrons out of an emitter over a potential barrier whose shape was to be elucidated. While this was so, there was a recurrent confrontation with the fact that the "well-known"

and widely exploited phenomenon of the external photoeffect had, for metals at least, little solid foundation in theory beyond the Einstein equation. It became for this group a research interest in its own right, albeit a minor one. There were, therefore, three quite separate areas of interest in the group, namely active thermionic emitters, metallic surface barriers, and photoemission from metals. Pertinent elements of all of these areas were combined in the AEC-supported program commencing in 1953 under the principal investigatorship of E. A. Coomes.

The first line of activity under AEC sponsorship was a follow-up on work which had been started before the contract's inception, namely the photoelectric Schottky investigation. The photo-Schottky behavior of tantalum and molybdenum were studied by Juenker, Gumnick, and Jaklevic, who showed that the ad hoc photoelectric theory of Fowler is adequate to account for the gross features of the emission, and that non-uniformity of the emitter work function is an important consideration in photoelectric measurements. The electron interference effect presumably responsible for the periodic Schottky deviation was either absent altogether or of too small a magnitude to be observed. A by-product of this series of studies was a method of photoelectric threshold determination using collecting field as the variable, analogous to the wavelength- and temperature-variable methods of Fowler and DuBridge.

In the same period, some useful technical advances were made by Gifford, who developed a crystal-growing technique for highly refractory metal wires, by R. LeBlanc and P. Dickerman, who carried out sub-incandescent temperature calibrations for such metals, and by Parsons and Juenker, who refined the procedure for depositing transparent conducting coatings on phototube walls. Toward the end of this period (in 1959) the roles of principal investigator and associate investigator were exchanged by Coomes and D. W. Juenker.

Throughout the work on the photoelectric Schottky effect, what had been surmised earlier became increasingly apparent, that there was a sad lack of knowledge about the photoexcitation process in a metal. The shape of the potential near the metal surface and in its interior, the effective state of freedom of the electrons and their transport in the excited state, and even the very optical performance of the metal were all such dubious matters that the usual theoretical assumptions concerning them would combine to predict no photoemission at all or else an emission totally unlike that which is observed in practice. An attempt to elucidate these points has comprised our program in the past five years, with the rationale that such problems are the most fundamental part of "fundamental research in photoemission."

Accordingly, the active projects in the recent past concern:

an extension of the photo-Schottky studies in which the surface barrier was lowered, not by an applied field, but by the superposition of electropositive dipolar adlayers; the optical properties of metals and their relation to the external photoeffect, as exemplified in the vectorial effect; the mechanisms of photoelectron generation and transport, as revealed in photoelectric and optical measurements on thin metal films; and a major phase of the study of the energetics in the high-melting point transition metals, as represented by measurements of their optical properties from the visible through the extreme ultraviolet regions of the spectrum. All of these matters are of course interrelated, and the one kind of evidence which is lacking to gather most of them into a completely conclusive story is the energy analysis of the photoemitted electrons. While it has been our intention to include such analysis with other measurements as a routine matter, there has not been enough time to do so during the tenure of AEC support.

II. SUMMARY OF RESULTS

A. The Effect of the Surface Barrier on Photoelectric Emission

Because the Fowler theory^a has proven so successful in describing the dependence of the photoelectric yield from a metal on the illumination frequency and on a retarding applied field,^b it is naturally to be assumed that it can be invoked with equal success for the description of photoelectric emission from a metal to which an accelerating field is applied. We have found this assumption to be justified.^{36, 48} Figure 1 shows emission data taken from a crystalline molybdenum wire³⁹ as a function of the square root of the applied electric field, for several incident photon energies in the vicinity of the threshold. The curves through the data represent the Fowler theory, in which the threshold energy has been continuously modified by the Schottky mirror-image barrier lowering.^c The fitting parameter in each case is the zero-field threshold energy hence the curve-fitting procedure is a valid and sensitive method of determining that energy.

We have described²⁰ in some detail the two principal kinds of deviation from this first-order effect that might be expected to occur. The more evident of these is patch effect, a well-known complication in thermionic studies.^d This results in a slow approach of the data to the theoretical curve at low fields, as in Fig. 1, and also gives the

Figure 1

effective, or measured, threshold a dependence on the experimental parameters.

The second type of deviation from the Fowler-Schottky theory which was expected in the photoelectric data at high collecting fields is the so-called "periodic Schottky deviation."^d This effect, repeatedly verified in thermionic work, is brought about by interference of the electron wave in its double reflection in the high surface field of the metal and at the peak of the mirror-image barrier. We corrected and refined^{11, 48} the photoelectric version of the theory for that effect,^{e, f} but were unable to detect it experimentally.

The influence of accelerating external fields on photoemission from a metal is relatively minor. If the excitation occurs in the surface field, the small change in that field that can be produced from without is probably a trivial influence on the excitation efficiency. The lowering of the threshold amounts only to a tenth of an electron volt or so, and it would be surprising if the Fowler theory were found to be invalid over this small extension of its useful range. Hence we turned to a more radical treatment of the surface barrier, by the addition of an electropositive dipole layer of an alkaline earth oxide.⁷¹ By this means the threshold could be reduced by more than two volts. The spectral distributions of the yield at various stages in this reduction are shown in Fig. 2 for the case of BaO on Mo in thicknesses from

Figure 2

zero (curve A) to about one monolayer (curve D). There was little departure from purely metallic behavior. Fowler theory was obeyed over a remarkably broad energy range, indicating a deep Fermi-Sommerfeld sea of unexcited electron states and freedom of the excited states from influences of band structure. The arrows in Fig. 2 indicate the yield level one volt above threshold. If the photoelectrons are generated at the emitter surface, the addition of the polar layer apparently changed the shape of the barrier too little to affect the excitation probability in a dramatic way.

B. Optical Influence on Photoemission from Bulk Metal Samples

We measured the photoelectric emission from clean molybdenum surfaces⁵⁷ as a function of the angle of incidence and state of polarization of monochromatic irradiation. For polarization perpendicular to the plane of incidence, the photocurrent decreased monotonically with increasing angle of incidence. For parallel polarization, the photocurrent increased with increasing angle to values at 75° that were as much as 40 times that at normal incidence (Fig. 3). No spectral dependence of the effect was detected within the narrow range of ultraviolet wavelengths which were used. It is apparent that we were observing the same vectorial effect studied by Ives⁸ in more complex emitting systems. It could not be related directly to the power absorbed from the incident beam (the dashed

Figure 3

line in Fig. 3);⁵⁸ its variation resembled that of the energy stored in the radiation field within the metal and near its surface.

We have considered the implications of these results in some detail.⁶¹ They would follow from (a) excitation outside the surface optical discontinuity, but with an isotropic probability and a subsequent randomization of the directions of the hot electrons; (b) oriented excitation near the surface but inside the optical discontinuity, or (c) isotropic excitation in the volume, with the hot electrons arriving at the surface without intermediate scattering. The last of these is thought to be an improbable explanation of the observed result, since it would also cause a dependence of the spectral characteristic of the yield on angle; such a dependence was found to be absent. Had the vectorial effect been absent, the possibility of either type of surface excitation (a or b) being an appreciable contributor to the emission could be ruled out, and only hypothesis (c), modified to include randomization of electron directions would be feasible.

C. Optical Properties of Molybdenum, Tantalum, Tungsten, and Rhenium

Having constructed a vacuum monochromator for use in the extreme ultraviolet,⁶⁹ we made a survey of the reflectances of four transition metals of the high-melting point group.⁶² The results are shown in Fig. 4. This was followed by a more comprehensive study

Figure 4

of the optical and dielectric constants of the same metals.⁷⁰ A sample of the results is shown for the case of molybdenum in Fig. 5, which is a plot of the real (K_1) and imaginary (K_2) parts of the complex dielectric constant. In the visible and near ultraviolet, a solid curve denotes the behavior of a coarser-grained, better annealed specimen than that from which the point data were obtained.

The resonant absorptions evident particularly at the low-energy end of the spectrum are doubtless connected with interband photoelectric transitions. The measurement of photoelectric yield necessary to ascertain which of these result in externally emitted electrons had not yet been carried out at this writing, although the high quantum yield of the metals in question throughout the far ultraviolet was utilized for photon detection in the optical experiments. The absorption near 4.0 ev in molybdenum is particularly interesting. It is energetically similar, but not to be hastily related, to the photoemission threshold in that metal. Although it could conceivably correspond to a transition from the Fermi level to one near the barrier edge, such a terminal state did not show up in the photoelectric survey illustrated in Fig. 2. However, a band edge near the top of the barrier could account for the otherwise inexplicably high electron reflection coefficients¹¹ in molybdenum and similar metals. Unfortunately, the negative photoelectric evidence could indicate either that such a band does not exist, or that its contribution to emission is masked completely by a preponderant surface

Figure 5

excitation.

The reflecting properties of the refractory metals in the far ultraviolet, while not directly pertinent to the ends of this program, are interesting in their own right. They point to a high free-electron density in these metals and suggest the possibility of devising efficient optical systems for short wavelength applications.

D. Excitation and Transport of Electrons in Vapor-deposited Films

An extensive study of the optical constants of bulk and film samples of molybdenum was carried out⁶⁷ in the visible and near uv. It was found that the absorption structure noted in the previous subsection was prominent in well-annealed bulk specimens and in films deposited at quasi-adiabatic rates, but that the structure became less and less well-defined as the crystalline state of the sample was more and more disordered. This is shown in Fig. 6, where the curves for the imaginary part of the dielectric constant of a variety of specimens are arranged, from top to bottom, in order of their decreasing crystalline perfection.

Films of molybdenum, tantalum, and rhenium, in the general category of sample 11 in Fig. 6, were subjected to photoelectric examination.⁶⁸ It was found that for such a state the photoemission arises principally in the volume, as opposed to the surface, and that

Figure 6

the hot electrons experience considerable scattering before their escape from the metal. As a result, these films exhibit no vectorial effect. In view of the optical evidence, the volume excitation which does exist probably is not related to band-to-band transitions at all, but rather occurs in the neighborhood of imperfections. Presumably, these are near the grain surfaces, so that the emission actually is due to an internal surface effect.

(In the same study,⁶⁸ certain deficiencies were uncovered in the usual approach^h to the analysis of photoelectric data in terms of hot electron range. For all three metals we investigated, the attenuation length for electrons 4.5 to 5.0 ev above the Fermi level was about 50 Å. This number had to be interpreted as a diffusion length or random walk range, rather than as a mean free path.)

While there is no necessary difference between the properties of bulk and film specimens of metals, there is a usual difference, and much of the past evidence for a volume origin of photoelectrons near the long wave limit has been obtainedⁱ from films which were, in all probability, in as poorly annealed, highly disordered states as those discussed here. The only common conclusion satisfying all of the evidence we have accumulated over the years is that the near-threshold photoemission from a typical annealed metal emitter originates primarily near the surface where the band structure is deformed.

The thickness of this sensitive region must be small compared with the optical wavelength, but sufficiently large to inhibit the passage of the abundant photoelectrons excited beyond it.

III. TECHNICAL ADVANCES

In the course of the photoelectric research program, a variety of techniques, pieces of apparatus, and calibration experiments were evolved which are more or less generally useful. Some of them are listed below.

A. Techniques for Determining Fundamental Emitter Properties

A method for determining the photoelectric threshold of a metal, in which illumination wavelength and temperature are held fixed and the variation of the photoemission with applied accelerating field is observed. ^{36, 48}

A retarding potential technique, applicable to photoelectron energy analysis, which employs plane parallel geometry and magnetic collimation of the slow electrons. The method is similar to, but a much simplified version of that used by Shelton^j and by Kisliuk for thermionic work.

A method for evaluating the optical constants of an absorbing material, in either bulk or film form, from measured values of the reflectance. ^{65, 67}

A procedure for determining the hot electron range in thin tapered films by a comparison of the photocurrents and optical transmission for illumination incident from vacuum and substrate sides of the film. ⁶⁸

B. Apparatus and Laboratory Methods

A technique for growing long single crystals in wires of molybdenum and tungsten. ³⁹

A novel vacuum monochromator for use in the extreme ultraviolet. The unique features of this device are its simple wavelength scanning mechanism, and the achievement of vacuum less than 10^{-8} torr in the working space outside the exit slit without the use of intermediate windows between that space and the gaseous discharge lamp. ⁶⁹

The application of direct photoelectric detection methods to extreme ultraviolet investigations, in place of the conventional, cumbersome, and unreliable phosphor-photomultiplier arrangement. ^{62, 70}

An automated apparatus for the continuous recording of reflectance vs angle of incidence. ⁶⁷

C. Calibration Measurements

A temperature scale (resistivity and heating current vs temperature) for tantalum from 300° to 1000°K . ⁷³

Ultraviolet transmission properties of stannic chloride conducting coatings on Corning #9741 glass.²⁵

D. Computer Programs

Data analysis of reflectance vs angle of incidence or degree of polarization in terms of the complex refractive index of film or bulk specimens.⁶⁵

Calculation of plotting points for iso-reflectance curves on the optical $n-k$ plane using arbitrary sets of parameters.⁶⁵

Evaluation of electromagnetic energy density at any point in a film, for arbitrary angle of incidence, degree of polarization, wavelength, film thickness, and incident and substrate regions.

Evaluation of the thickness contour of a film condensed on a plane substrate from a rectangular evaporator of arbitrary dimensions, position, and orientation.

Data analysis of vectorial photoemission for the relative influences of the electric field components parallel and perpendicular to the surface, according to various models for the photoelectron excitation.

Appendix: External References from Sections II and III

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IV. REPORTS AND PUBLICATIONS

A. Dissertations

Following is a list of magisterial and doctoral theses presented to the Graduate School of the University of Notre Dame and describing work partially supported under this contract.

1. Masters' theses:

F. Gifford, Torsion-Induced Recrystallization of Highly Refractory Metals (1956).

P. Dickerman, A Temperature Scale for Round Tantalum Filaments in the Range 300°-1000°K, Part I: Resistivity vs Heating Current (1956).

R. LeBlanc, A Temperature Scale, etc., Part II: Resistivity vs Temperature (1957).

2. Doctors' theses:

J. L. Gumnick, Experimental Study of Photoelectric Emission from Tantalum in Accelerating Electric Fields (1957).

R. J. Jaccodine, Experimental Study of the Vectorial Photoelectric Effect in Molybdenum (1957).

R. J. Jaklevic, Experimental Study of Photoelectric Emission from a Molybdenum Single Crystal in Accelerating Fields (1960).

J. P. Waldron, The Vectorial Photoelectric Effect and the Optical Properties of Molybdenum (1961).

J. L. Shilts, Photoemission from Thin Films of SrO and BaO on Molybdenum (1961).

C. T. Raymo, Optical Investigation of Molybdenum Films (1964).

M. J. Brienza, Photoelectric Investigation of Thin Films of Molybdenum, Tantalum, and Rhenium (1964).

L. J. LeBlanc, Optical Properties of Molybdenum, Tantalum, Tungsten, and Rhenium from 537 to 5770A (1964).

B. Oral Presentations at Professional Meetings

1. Before the American Physical Society:

Gumnick and Juenker, Photoelectric Measurements on Tantalum in Accelerating Fields, Bull. Am. Phys. Soc. II2, 261 (1957).

Jaccodine and Juenker, Photoelectric Measurements on Molybdenum as a Function of Angle of Incidence, Bull. Am. Phys. Soc. II2, 261 (1957).

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Jaklevic and Juenker, Field Dependent Photoelectric Emission from Molybdenum, Bull. Am. Phys. Soc. II5, 358 (1960).

Juenker, Gradner, Jaklevic, and Quigley, Electron Emission Characteristics of a Model Cylindrical Crystal, Bull. Am. Phys. Soc. II6, 422 (1961).

Shilts and Juenker, Photoemission from Thin Films of Strontium and Barium Oxides on Molybdenum, Bull. Am. Phys. Soc. 116, 422 (1961).

2. Before the Optical Society of America:

Raymo and Juenker, Optical Investigation of Molybdenum Films, J. Opt. Soc. Am. 53, 1332 (1963).

LeBlanc and Juenker, Reflectance of Refractory Metals in the Extreme Ultraviolet, J. Opt. Soc. Am. 53, 1352 (1963).

C. Publications

The numerical references used in the following list are the terminal digits in the standard report numbers prescribed in the AEC directive of March 12, 1964. That system was applied by us retroactively to the inception of the contract. The reports named below are interspersed with periodic technical reports which are not listed. Reports marked * either have been submitted, or are about to be submitted, for publication. In these cases, the probable journal of their appearance is given. Reports marked ** are, or soon will be, available to the limited group of interested investigators upon request.

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Characteristics of Conducting Coatings on Glass, J. Opt.
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- * 65 D. W. Juenker, Digital Evaluation of the Complex Refractive Index
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- * 69 R. J. Jaklevic, L. J. LeBlanc, and D. W. Juenker, A Monochromator for the Extreme Ultraviolet, Revs. Sci. Instr.
- * 70 L. J. LeBlanc, C. M. Martin, and D. W. Juenker, Optical Properties of Mo, Ta, W, and Re from 537 to 5770A, J. Opt. Soc. Am.
- ** 71 J. L. Shilts and D. W. Juenker, Photoemission from Thin Films of BaO and SrO on Molybdenum.
- ** 72 D. W. Juenker, Table of the Fowler-Schottky Photoelectric Function.
- ** 73 P. Dickerman, R. LeBlanc, and D. W. Juenker, A Temperature Scale for Tantalum in the Range 300^o-1000^oK.