The matrix elements are obtained with the use of the relations of Eqs. (16). The letter i without subscripts is $\sqrt{-1}$. For the particular case of HD we set $i_1 = \frac{1}{2}$, $i_2 = 1$, and $J = 1$. The spin orbit interactions of the form $I \cdot J$ are obtained in the usual manner by setting

$$
I \cdot J = I_z J_z + \frac{1}{2} (I_x + iI_y) (J_x + iJ_y) + \frac{1}{2} (I_x - iI_y) (J_x + iJ_y)
$$

together with Eqs. (16).

The perturbations of the energy levels of Eqs. (5) and (8) are obtained from the matrix elements by the usual second-order perturbation theory.

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Secondary Emission from Films of Silver on Platinum*

A. E. HASTINGS[†] Brown University, Providence, Rhode Island (Received February 1, 1940)

Total secondary emission and energy distribution of secondary electrons have been measured for films of known thickness of silver on platinum. The depth of origin of the total secondary emission in silver as a function of primary energy, and the depth of origin of secondaries having a given energy were determined. Practically all the secondaries from primaries of 20 ev energy originate at a depth

INTRODUCTION

 $M^{\rm HILE}$ the general characteristics of secondary emission from pure metals have been well established, there is lack of agreement among investigations as to the depth at which the secondary electrons originate and as to the relative effects of the work function and the characteristic production of secondaries within the metal. Secondary emission is generally assumed to be dependent on the surface work function through which the electrons must escape and on the production and absorption of electrons within the metal, these two effects being independent and characteristic of the particular meta1.

Treloar¹ concludes that a sufficiently thin film of a foreign material on a metal acts chiefly to alter the work function, the emission from the film itself being important only at greater film thickness. Plotting secondary emission against

of less than 15 atomic layers, and those from primaries of 50 ev energy originate at a depth of less than 30 atomic layers. For higher primary energies, it was found that an appreciable amount of emission comes from a depth greater than 150 atomic layers. Secondaries with energies close to that of the primaries originate at a depth small compared to that of the low energy secondaries.

thickness of barium deposited on tungsten, he found an increase in the secondary emission as the work function was 1owered to that of barium, the production of secondaries still occurring mostly in the tungsten. At greater thickness of barium fi1m more of the secondaries originated in the film, which has a smaller production than that of tungsten, and the emission decreased, resulting in a maximum in the curve. The thickness at which half the emission came from the film and half from the base metal he estimated as 1.4 atomic layers, the mean depth of origin of secondaries from 300-volt primaries.

Coomes' has not observed this maximum for thorium on tungsten, but Bruining' has observed it for barium on molybdenum. He found that the photoelectric emission also reached a maximum for the same thickness of barium, indicating that these changes were due in part to the decreasing work function. From experimental work with rough surfaces and from an experimental value of the absorption coefficient,

[~] Part of the dissertation presented for the Degree of Doctor of Philosophy at Brown University.

f Now at Naval Research Laboratory, Washington, D. C. '

 $1 L$, R, G, Treloar, Proc, Phys. Soc. 49, 392 (1937).

² E. A. Coomes, Phys. Rev. 55, 519 (1939).
³ H. Bruining and J. H. DeBoer, Physica **6**, 941 (1939).

FiG. 1. Diagram of apparatus.

Bruining4 has calculated the mean depth of origin for secondaries from primaries of 500 ev energy to be about 14 atomic layers. He has $also^{5-8}$ investigated the mechanism of secondary emission in detail.

In the present work, measurements were carried out to determine the depth of origin of the total secondary emission in silver as a function of primary energy, and the depth of origin of secondaries having a given energy. Total emission and energy distribution of secondary electrons were measured for films of silver on platinum. Energy distributions were obtained by the retarding potential method. Silver films were obtained from a calibrated source, so that the film thickness was determined absolutely from the time of evaporation. While the measurements were affected by changes in work function, resulting in the maximum in the curves described, no means for measuring the work function directly were included in the apparatus.

APPARATUS AND PROCEDURE

The electron gun is based on the one described by Farnsworth,⁹ and is shown in Fig. 1. F is an oxide-coated filament, surrounded by a guard ring. Electrons from F are accelerated through a circular disk and cylinder A , and again to B , where the beam is defined by the 1.5-mm holes. C is a disk connected at filament potential to repel any electrons leaking around the gun. The beam is so defined that all the electrons pass through the hole in the disk D and strike the platinum target T . The secondaries coming from T are collected by D , and the current to D is measured by a galvanometer. The current to T and D is the primary current, and the ratio of secondary to primary current is called R.

The energy analyzer is shown below the gun. Part of the secondary emission from T passes through a hole in D and through a small shielding tube through the hole in E . The beam of secondaries is defined by the target and the hole in E , and can pass through the disk H , without striking the sides of the hole, and into the shielded collector G. A retarding field is applied between the cylinder E , and H and G . The current to G is measured with a d.c. amplifier, using an FP-54 in a DuBridge and Brown circuit and a sensitivity of about 5×10^{-14} ampere per mm. Only those secondaries from T will reach the collector whose energy in electron volts is numerically greater than the retarding potential applied between the collector and target. Curve 1, Fig. 2, shows a typical curve of secondary emission obtained with this analyzer. The retarding potential must be corrected for the contact potential of the collector. This analyzer does not give a true distribution curve in energy, but actually gives the integral of the distribution curve between the energy at the point in question and the maximum energy which is the primary energy. The slope of this curve gives the true energy distribution curve, the number of electrons dn having energy between E and $E+dE$. Instead of plotting the complete distribution curves and taking slopes at certain energies, these slopes were determined directly by measuring the collector current at two retarding potentials, one either side of the point in question, and by dividing the difference in currents by the difference in potentials. In this manner, a quantity called R_{e} , which is proportional to the true number of secondaries having a given energy, was determined. The primary current was of course held constant throughout these readings.

The analyzer was tested by placing it in front

⁴ H. Bruining, Physica 3, 1046 (1936).
⁵ H. Bruining and J. H. DeBoer, Physica 4, 473 (1937).
⁶ H. Bruining, Physica 5, 17 (1938).

⁷ H. Bruining, Physica 5, 901, 913 (1938). H. Bruining and J. H. DeBoer, Physica 6, 823, 834 (1930)

 $H.E. Farnsworth, Rev. Sci. Inst. 15, 290 (1927).$

of the electron gun, so that their axes coincided. Then electrons from the gun could enter the analyzer and their energy distribution could be determined. Curve 2, Fig. 2, shows this distribution. The lack of a very sharp drop at the right is due to the inhomogeneity in energy in the beam from the gun and to scattering in the analyzer. Curve 3 was taken with a small magnetic field along the axis of the analyzer, and the resulting sharper drop indicates that there is a slight amount of scattering in the analyzer.

The evaporator is built similar to one used by The evaporator is built similar to one used b
Farnsworth.¹⁰ A block of silver is completel enclosed in a molybdenum container except for a 1-mm hole in the upper face through which silver can evaporate. The silver is heated by radiation from a flat spiral filament beneath it and enclosed in a molybdenum radiation shield. A Chromel-Alumel thermocouple imbedded in the side of the silver, in conjunction with a type K potentiometer, indicates the temperature, which is held so that the evaporation rate is constant within one percent.

The silver source was calibrated in a separate tube by depositing on clean microscope cover glasses, which could be moved into the path of the vapor stream for known lengths of time with the source at 900 degrees centigrade. The source was thoroughly outgassed in a high vacuum until the pressure was about 2×10^{-7} mm of mercury with the evaporator running, so that the rate of deposition would become constant before calibrating. In weighing on a microbalance, sensitive to about 10^{-6} g, the glass with the deposit was counterbalanced by a glass similarly treated but not exposed to silver. The film was removed either by rubbing the glass with lens paper, or by washing in 50 percent $HNO₃$, or both, all methods giving substantially the same result. The glass counterpoise was similarly treated. A maximum error of 5 percent was estimated for this determination. It was found that 4.65×10^{-6} gram of silver was deposited on a square cm in one hour, with the source 12.2 cm from the plates. For a (100) face, this corresponds to 21.6 atomic layers per hour, and for a (111) face, 30.6 atomic layers per hour. All data here are expressed in (100) units.

The electron gun is placed in the main tube, and the analyzer in a side tube sealed at 45 degrees from the axis of the main tube. The evaporator is built in a small side tube and sealed to the experimental tube. The vacuum system consists of two Apiezon vapor pumps backed by a Cenco Hyvac pump. No grease or wax seals were used in the high vacuum side. The condensing traps between the experimental tube and pumps and between the fore pump and the vapor pumps were cooled with $CO₂$ snow in acetone. The experimental tube was kept sealed to the pumps throughout the experiments and the vapor pumps were run continuously. Helmholtz coils were used to compensate the earth's magnetic field. Pressure in the experimental tube was measured by an ionization gauge.

Curves of R vs. film thickness were plotted for several primary energies, and curves of R_e vs. film thickness were plotted for secondary energies with primary energy held at 300 ev. These curves show the effects of the film of varying thickness on the emission characteristics.

RESULTS AND DISCUSSION

Thin films

The curves of Figs. 3 and 4 are typical of the results obtained. All the curves of R vs. film thickness, except that for 20-volt primaries, show a maximum. This is the behavior observed

FIG. 2. Curve 1, for secondary electrons from platinum, shows the variation of collector current with retarding potential on the analyzer. Curve 2 shows the same variation for electrons corning directly from the gun. Curve 3 is similar to Curve 2, but was taken with a small axial magnetic field around the analyzer.

¹⁰ H. E. Farnsworth, Phys. Rev. 49, 605 (1936).

by Treloar for barium on tungsten, and is assumed to be due to the decrease in work function caused by a thin film of silver, since silver has a work function about two volts lower than that of platinum. The maxinum occurs at about one atomic layer, which is close to the optimum thermionic layer observed by Treloar for barium on tungsten. The maximum in R is smaller for curves taken at lower primary energies, which requires some explanation. During deposition of the first few atomic layers, two things are happening, $-R$ is increasing because of the falling work function, and R is decreasing from the value characteristic of platinum to that characteristic of silver because of the emission from the silver film. The latter effect is more marked in the case of low primary energies, since there is smaller penetration of the low energy primaries. The former effect is more marked in the case of high primary energies, since there are many more secondaries with energy near that corresponding to the work function, and these secondaries are free to escape when the work function decreases. These effects tend to produce a greater initial increase in the curves of R at high than at low primary energies, and for 20-volt primaries, there is no maximum at all, but R decreases continually with film thickness.

The maximum does not appear in the curves of R_e vs. film thickness, since a change in work function of the order of two volts affects only electrons with very low energies in the metal, which are always excluded at the retarding potentials used.

FIG. 3. Secondary emission R (ratio of secondary to primary current) is shown as a function of atomic layers of silver on platinum for several primary energies.

 R_e increases with film thickness for secondaries with energy near that of the primaries, and decreases for secondaries with low energies, because of the change in the secondary energy distribution from that characteristic of platinum to that characteristic of silver. However, the increase at high secondary energies is much more sudden than the decrease at low secondary energies, which would mean that most of the secondaries of high energy originate at a smaller depth than those of low energy, and that most of the highenergy secondaries come from only a few atomic layers. This agrees with the results of Farnsworth¹⁰ for electron diffraction. He used secondary electrons with energy very close to that of the primaries, and found that when the conditions for diffraction were established, the diffracted beam was entirely eliminated upon deposition of a few atomic layers of a foreign material. This indicates that secondaries with energy near that of the primaries do not originate at a very great depth as compared with the depth of origin of some of the low energy secondaries. This can be explained by saying that those primaries which penetrate the target to a depth of more than a few atomic layers are, because of the greater probability of scattering with loss of energy, nearly all effective in producing secondaries of low energy, while primaries scattered very near the surface have a greater probability of being returned with small loss of energy.

Thick films

The curves of R in Fig. 3 for thick films give the maximum depth of origin of secondaries as a function of primary energy, since at the film thickness where the curve becomes flat all the secondaries are coming from the film. The curves indicate that practically all the secondaries from primaries of 20 ev energy originate at a depth of less than 15 atomic layers, and those from 50-volt primaries originate at a depth of less than 30 atomic layers. For higher primary energies, the curves do not flatten sufficiently to indicate the maximum depth from which secondaries come. Some data obtained out to 150 atomic layers show that the emission is still changing.

The curves of R_{ϵ} (Fig. 4) at thick films all tend to flatten out at about the same rate with film thickness regardless of secondary energy.

For a primary energy of 300 ev the curves become very nearly flat at less than 20 atomic layers. The following explanation may account for the fact that secondaries with high energies appear to come from depths no greater than those at which secondaries with low energies originate. The number of high energy secondaries, coming partly from the base metal even at large film thicknesses, is still changing at these thicknesses. These secondaries are effective in producing some low energy secondaries in the film, and thus the low energy secondaries continue to change as long as do the high energy ones.

Since the total emission R is the integral of R_{ϵ} over the whole range of secondary energies, R should be affected by changes in R_{ϵ} , and R should change with film thickness as long as any curve of R_e does. Actually R for primary energies above 20 ev changes much longer than does any of the curves of R_c for energies measured, for which there is no explanation.

The slope of the R vs. film thickness curve would give the number of secondaries originating in a layer of thickness dx at depth x . However, because the slope changes so little beyond the first few atomic layers, and because of the experimental errors, it was not possible to determine this slope graphically with sufficient accuracy to be of any value.

Effects of gas

While the pressure in the experimental tube was about 5×10^{-8} mm of mercury during readings, it rose to about 1.5×10^{-7} mm of mercury when the evaporator was running. At this pressure the values of R for the outgassed target dropped as much as 10 percent in a few minutes, as determined by running the evaporator without exposing the target to the silver vapor. This rapid change did not occur with the gun filament, but not the evaporator, running, and was not due to contamination of the target by evaporation

FIG. 4. Secondary emission R_e of electrons having several energies e is shown as a function of atomic layers of silver on platinum. The primary energy is 300 ev.

from the filament. The initial maximum in the curves of R , Fig. 3, was not observed when silver was deposited directly on the outgassed target, without first exposing it to gases from the heated evaporator. The gas condensed on the target lowered R sufficiently to overcome the rise due to the silver film. Since it was not possible to outgas thorough)y the large block of silver in the evaporator, the procedure was to expose the clean target to gas coming from the evaporator until the emission no longer changed with exposure, and to take the value of R so obtained as characteristic of platinum for this work. The fact that with this procedure the maximum in R occurred seems to indicate that the surface layer of gas remains or is constantly formed during deposition, has a constant effect on the work function, and does not affect the interpretation of the results. moreover, readings could be checked closely over long periods after the initial contamination of the target with gas had occurred. Several sets of curves similar to those in Figs. 3 and 4 showed essentially the same behavior.

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