

by Sproull<sup>8</sup> for a tungsten crystal. With a (112) surface plane of tungsten and the azimuth perpendicular to the cube diagonals, beams which obeyed a depth grating formula corresponding to rows of atoms in the (011) plane were found by Sproull at every primary voltage tried. We<sup>9</sup> have previously pointed out that these observations can be explained by assuming the presence of etched facets parallel to (011) planes resulting from evaporation during heat treatment of the crystal. G. P. Thomson<sup>10</sup> has also suggested a similar interpretation. The above observations from a silver crystal are seen to be of just this type. We have further verified this interpretation by checking the positions of the diffraction beams shown in Set 5 of Fig. 5 when using a silver crystal cut and etched parallel to a (111) set of planes, and set at the

proper angle of incidence in the (111) azimuth to correspond to these observations.

The fact that no beams characteristic of the (100) or (111) facets were obtained with the silver crystal which was chemically etched parallel to a (110) set of planes proves the effectiveness of the method in etching parallel to only one set of crystal planes. It may also be noted that it was found possible to heat the silver crystal for many hours at temperatures up to about 650° or 700°C without the appearance of diffraction beams characteristic of (100) or (111) facets, thus indicating that there was no appreciable evaporation at this temperature.

The sensitivity of this method of detecting what crystal facets are present should be of value in any experiment which is concerned with the surface properties of particular crystal facets such as the photoelectric characteristics.

Messrs. E. C. Bray, C. R. Lewis, A. E. Hastings, J. C. Turnbull, and Dr. B. A. Rose have aided at various times in taking the numerous observations.

<sup>8</sup> W. T. Sproull, Phys. Rev. **42**, 904 (1932); **43**, 516 (1933).

<sup>9</sup> H. E. Farnsworth, Phys. Rev. **43**, 906 (1933); **44**, 417 (1933).

<sup>10</sup> G. P. Thomson, Phys. Rev. **44**, 417 (1933).

## Penetration of Low Speed Diffracted Electrons

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A known number of atomic layers of one metal was deposited on the surface of a single crystal of another metal by evaporation in a high vacuum. Direct results on depth of penetration were obtained from measurements on electron diffraction as a function of the thickness of the surface layer. A silver film having a thickness up to 15 atoms does not form in a single crystal when deposited on the (100) face of a copper crystal. A monatomic layer reduces the maxima of the beams from the copper lattice by at least 70 percent for energies up to 300 ev. A number of foreign

silver atoms equal to a few hundredths of that contained in a monatomic layer can be detected by this method. A silver film forms in a single crystal when deposited on the (100) face of a gold crystal. At least 50 percent of the maximum of each diffraction beam from a thick silver crystal is contributed by the surface atomic layer of silver, for energies as high as 300 ev, while at least 90 percent is contributed by a surface layer two atoms thick. A possible selective effect was observed for low voltage reflection from a film 2 atoms thick.

### INTRODUCTION

ALTHOUGH it is known that low speed electrons are diffracted by only a small number of atomic planes at the surface of a metal crystal, there have been no direct quantitative data on the exact number which is effective in special cases.

Davisson and Germer<sup>1</sup> calculated a rate of extinction for 54-volt electrons in a direction perpendicular to a (111) surface of a nickel crystal. In making the computation, use was made of the intensity-voltage relation which was assumed to be determined entirely by the

<sup>1</sup> Davisson and Germer, Phys. Rev. **30**, 705 (1927).

rate of extinction in the crystal. As they state, this assumption appears justified since the product  $V^{\frac{1}{2}} \sin \varphi$  ( $\varphi$  = colatitude angle) is nearly constant for the 54-volt beam. However, since this product is not constant for most diffraction beams, and since observations by the writer<sup>2</sup> have shown that changing certain factors such as the angle of incidence by small amounts may greatly affect the variation of this product, it follows that this method of computation cannot be used in general.

Mention has already been made in the previous paper of the computations of v. Laue, based on wave mechanics, which estimate the contribution of the surface atomic layer to the intensity of the diffracted beam for the case of hydrogen atoms, and of the uncertainty of making accurate corrections which apply to heavier atoms when using low speed electrons.

In the present experiments, direct quantitative data on the penetration of low speed electrons in a silver lattice were obtained because of their bearing on other results of electron diffraction discussed in the previous paper. In addition, it is shown that, because of the low penetration, such data are also of value in any work on surface characteristics which requires a knowledge of the number of foreign atoms present.

#### APPARATUS AND PROCEDURE

The method consisted in depositing a known number of atomic layers of one metal on the surface of a single crystal of another metal, and then obtaining measurements on electron diffraction as a function of the thickness of the surface layer. Silver atoms were deposited on the (100) faces of both copper and gold single crystals. The deposition was made by evaporating from a hot solid silver source in a high vacuum, the rate of evaporation of the source at a known temperature having been determined previously. Information on the rate of extinction was obtained by observing the intensities of the diffraction beams from the underlying crystal as a function of the thickness of the surface layer. In the case of silver on gold, for which the surface layer forms in a regular crystal lattice,

the intensities of the beams from this layer were obtained as a function of the thickness.

The arrangement of the source is indicated in Fig. 1. A slab of silver was completely enclosed in a tight cylindrical molybdenum container except for a 1-mm circular opening in the center of the upper end through which the vapor passed. The silver was heated by radiation from a flat spiral tungsten filament which was placed directly beneath it, and was enclosed in a molybdenum radiation shield. A chromel-alumel thermocouple imbedded in the side of the silver, when used with a Leeds and Northrup type K potentiometer and sensitive galvanometer, indicated the temperature and was sensitive to a change of temperature of 0.01°C.

The silver source was calibrated by depositing on clean microscope cover glasses, which could be moved alternately into the path of the vapor stream, for known lengths of time with the source at 850°C, the weight of the deposit being determined with a sensitive micro-balance. The rate of deposit was such that 0.000113 g of silver was deposited on 1.37 sq. cm at a distance of 11.4 cm from the source in 54 hours. At this rate a layer one atom in thickness was deposited in approximately 8 min., assuming the number of atoms per unit area to be that of a (100) plane of the normal silver lattice. It was noted that the silver film became visible when the thickness was between 10 and 15 atomic layers. The deposit was weighed as soon as possible after coming in contact with the air. The silver

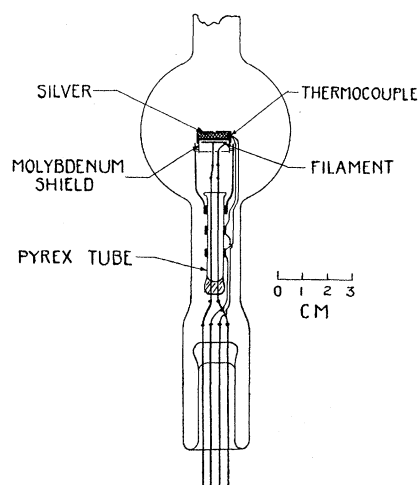


FIG. 1. Source of silver vapor.

<sup>2</sup> H. E. Farnsworth, Phys. Rev. **40**, 684 (1932); **43**, 900 (1933).

film was then removed with a sharp razor blade without touching the cover glass with the hands and the weight of the glass determined. The whole assembly was thoroughly outgassed before making the deposits so that the rate of evaporation at a given temperature would remain constant in time. The Pyrex tube containing the silver source was then sealed directly to the experimental tube with no ground or wax joints so that when the crystal was withdrawn into a side tube for bombardment it was also in approximate position for receiving a deposit. The crystal could be rotated so as to deposit at normal incidence.

The present pumping system consists of two *n*-butyl phthalate vapor pumps in series which are backed by a Cenco Hyvac pump. The condensing traps between the experimental tube and vapor pumps, and between the Hyvac pump and vapor pumps were cooled with CO<sub>2</sub> snow in acetone. The experimental tube was kept sealed to the pumping system throughout the experiments, and the vapor pumps were run continuously. The pressure under best conditions as measured with an ionization gauge was approximately 10<sup>-8</sup> mm Hg. During the deposits it was less than 5 × 10<sup>-8</sup> mm Hg. Check readings taken after heating the silver source at 850°C, but with the crystal *not* exposed for a deposit, showed no observable change in the intensities of the diffraction beams so that the observed changes resulting from deposit are due to silver, and not to gas atoms. Although the source was calibrated only at the beginning, check readings on beam intensities taken under the same conditions, over a period of time during which considerable evaporation took place, indicated that there was no appreciable change. We believe the error in the computed value for thickness of deposit should not exceed ten percent. In computing the thickness of the silver film the number of atoms per unit area was assumed to be that of a (100) plane of the normal silver lattice. At no time was there any indication of a tendency of the film to form in patches on either crystal when left for days at room temperature.

## RESULTS

Fig. 2 shows colatitude curves for two beams of different voltages taken at normal incidence

on the (100) face of a copper crystal after depositing different thicknesses of silver.

It is seen that a layer of silver two atoms thick is sufficient to absorb almost completely both the 60- and 296-volt beams, and that the intensities are greatly reduced by a layer containing one-fourth as many atoms. A layer one atom thick reduces the maxima of the beams by at least 70 percent for energies up to 300 ev. From this it is seen that a number of silver atoms equal to a few hundredths of that in one atomic layer can be easily detected.

Since the lattice constant of silver is larger than that of copper, we anticipated that the first layer of silver would form in a double spaced, face-centered or a single spaced, simple cubic structure as is the case for a surface gas lattice.<sup>3</sup> However, no diffraction beams corresponding to these structures could be found, except one very weak beam corresponding approximately to the first beam, first order, (100) azimuth. But this beam did not increase in intensity as the thickness of the layer was increased up to 15 atomic layers. It thus appears that a thin silver film deposited by evaporation on a copper crystal is not in the form of a single crystal.<sup>4</sup>

<sup>3</sup> H. E. Farnsworth, *Phys. Rev.* **35**, 1131 (1930).

<sup>4</sup> There may be some question whether this film is amorphous or microcrystalline. The distinction obviously becomes trivial for films which are only one or two atoms thick. But for thicker films there is a difference of opinion about the existence of amorphous films. See, e.g., J. Kramer, *Ann. d. Physik* **19**, 37 (1934); E. Perucca, *Zeits. f. Physik* **91**, 660 (1934); Lassing and Brück **22**, 65 (1935); L. Hamburger, *Ann. d. Physik* **10**, 905, 789 (1931); Zelmanoff and Schalnikoff, *Physik. Zeits. Sowjetunion* **4**, 825 (1933). Part of the difference of opinion appears to result from lack of uniformity of experimental conditions. Some of the factors which must be considered are: Type and condition of the backing of the film, film thickness, temperature of the backing during deposition, and subsequent temperature history of the film. In view of these factors, evidence for the crystalline structure of thin films obtained by the high speed electron diffraction method does not exclude the possibility of amorphous films because this method requires relatively thick films in terms of atom layers, and in addition the film may become heated locally, by the high speed electrons used for observation, above the relatively low temperature which may be required for crystallization.

During the present experiments, as noted above, it was found possible to form a semi-lattice from the film by heating at approximately 200°C, but further deposition failed to build up this lattice. This seems to favor the amorphous condition, since if many microcrystals were oriented somewhat similarly by the low temperature heating, a further deposit should build up the lattices of these microcrystals as it does for a silver single crystal so that the diffraction beam would have the same intensity before and after deposition. On the other hand if the film were

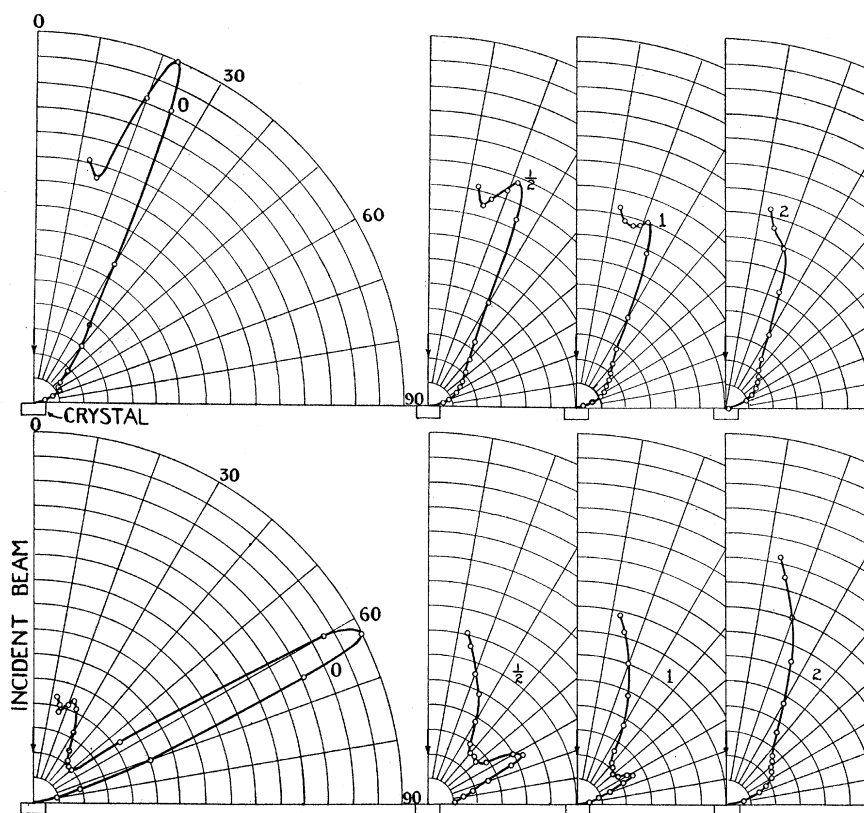


FIG. 2. Colatitude curves for a copper crystal covered with different thicknesses of silver atoms. The numbers 0, 1/2, 1, 2 refer to the number of atomic layers of silver. The voltage of the upper set of beams is 296; that of the lower set is 60.

We have attempted with some success to recrystallize the silver film by heating at a temperature too low to cause the silver to diffuse appreciably into the copper. The silver readily diffuses into the copper crystal at temperatures estimated from the power input to be between 300° and 400°C. By heating at temperatures somewhat lower than this for a few minutes it was found possible to form a semi-lattice of silver but it never became comparable to that of a silver crystal. Deposition on this semi-lattice failed to build it up further; the surface layer again assumed the state originally obtained by deposition directly on the copper. Hence, with this arrangement it was not possible to determine the rate of extinction in a silver single crystal.

In order to obtain results for a silver film in semicrystalline and semi-amorphous, a further deposit might not follow the distorted lattice.

the form of a single crystal, we have deposited silver on the (100) face of a gold crystal. Previous experiments<sup>5</sup> have shown that silver which is deposited by evaporation on a gold crystal is in the form of a single crystal, and has the same orientation as the underlying gold crystal. Although silver and gold have the same lattice constants to within 0.4 percent, some of the experimental beams differ sufficiently in voltage to be separable. In the present case it was possible to observe the intensities of the diffraction beams from the silver as a function of its thickness, and thus determine directly the number of atomic layers making an observable contribution to the intensity. Fig. 3 shows the maxima for two beams as a function of thickness. Because there is some overlapping in voltage of the 56-volt beam from silver with a beam from

<sup>5</sup> H. E. Farnsworth, Phys. Rev. **43**, 900 (1933).

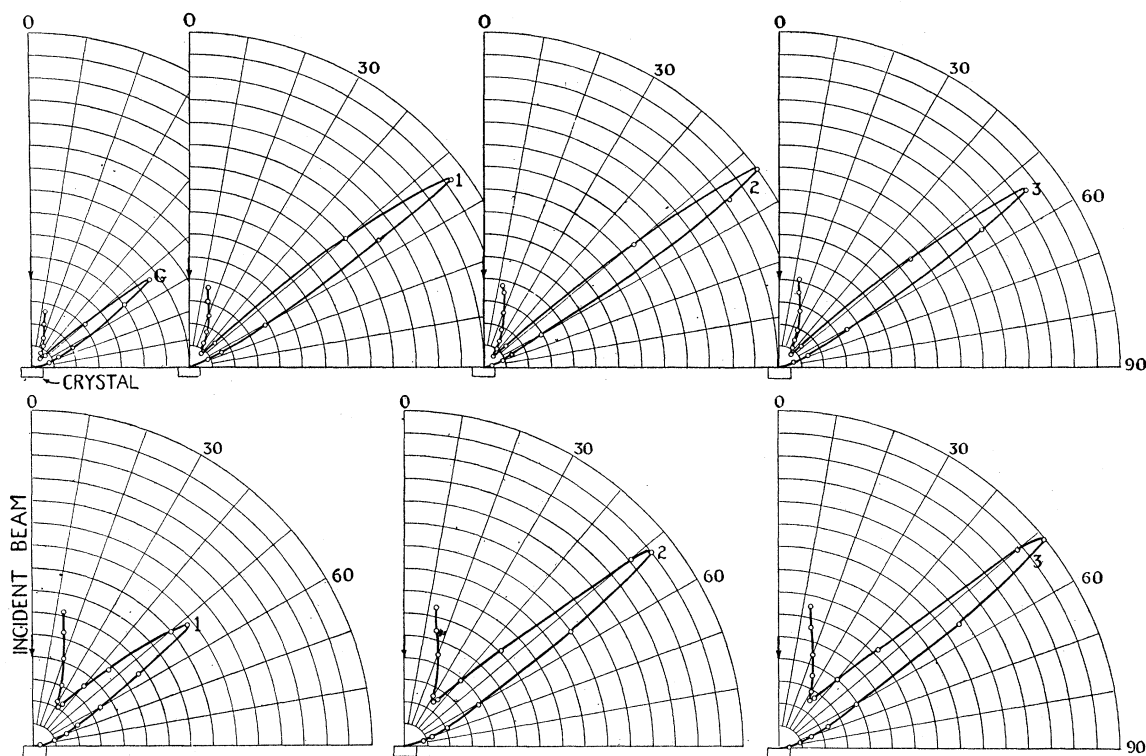


FIG. 3. Colatitude curves for a silver lattice on a gold crystal. Beam *G* is for the gold crystal with no silver. Beams 1, 2 and 3 are for silver lattices of 1, 2 and 3 atomic layers, respectively. The voltage of the upper set of beams is 56; that of the lower set is 206.5.

the underlying gold, the observed maxima should be corrected for the contribution of the underlying gold. However, since the maximum at this voltage for gold is relatively weak and since the absorption of a monatomic layer of silver is very high, this correction should be relatively small for a film of one or more atoms in thickness. After making this correction, it appears that a monatomic silver film contributes more than 75 percent to the 56-volt maximum. It is seen that the 56-volt maximum for a film three atoms thick is slightly weaker than that for a film two atoms thick. This result is apparently due to some selective effect at this voltage. For the 206.5-volt beam, a monatomic film contributes at least 50 percent to the maximum from a thick crystal, while a film two atoms thick contributes at least 90 percent. This is also true for voltages up to 300 volts, the highest value tried.

Because of the very high rate of extinction of the primary radiation, it is impossible to deduce a constant extinction coefficient from the observations. For the (100) face, the atoms in the second layer are directly beneath the positions midway between atoms in the first layer, while in the third layer the atoms are directly below those in the first layer. One might expect, therefore, that the effect of the second layer would be greater than that to be expected with a constant extinction coefficient, and this is found to be the case.

The above results show a very great contribution of the surface atomic layer of silver to the diffraction of electrons up to at least 300 ev. They also indicate that the contribution of this surface atomic layer continues to be appreciable for energies considerably greater than this.

Dr. B. A. Rose and Mr. H. E. Darling have greatly aided in these experiments.