THE CRYSTALLINE STRUCTURES OF SPUTTERED AND EVAPORATED METALLIC FILMS.[1]

By H. Kahler.

SYNOPSIS.

Crystalline structures of evaporated films of bismuth and silver, condensed on a cool surface, were determined by the X-ray powder method. The films were found to contain no pure metal in the crystalline state, but to consist of amorphous metal and of metallic compounds. Optical evidence indicates that *selenium* also condenses on a cool surface in the amorphous form, although on a heated surface crystals are deposited whose size and color depend on the temperature.

Crystalline structures of sputtered films of bismuth, cobalt, gold, platinum and silver, as determined by X-ray analysis, were in each case the same as that of the unsputtered metal. The crystal grains had a random distribution of axial direction. Evidently in sputtering crystalline grains are knocked off the cathode and are transported and deposited grain by grain, whereas evaporation takes place atom by atom.

Relative sputtering of hexagonal and cubic forms of cobalt. The hexagonal form is easily sputtered whereas the other form is not.

Crystalline structure of bismuth, determined by X-ray analysis of the powdered metal and sputtered film, is rhombohedral trigonal, with elementary triangular prism of side 4.54 Å and height 5.91 Å.

INTRODUCTION.

THE optical and electrical constants of thin metallic sputtered and evaporated films have been the subject of investigation for many workers since the pioneer experiments of Plücker. The crystallographic study of such films, however, has never been undertaken. As a result of the conductivity experiments[2] by Professor Richtmyer, Mr. J. A. Becker and Mr. L. F. Curtiss on sputtered films of bismuth it was questioned by the latter whether their films were crystalline. It was in part to answer this question that the writer's experiments were originally undertaken.

Method.

The x-ray powder method as developed in Germany by Debye and Scherrer[3] and in America by Hull[4] was used in this study. As a source of Rontgen radiation a small General Electric molybdenum-target x-ray

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[1] An abstract of this paper was read before the Chicago section of the American Physical Society, Dec., 1920. PHYS. RÉV., 17, p. 230, 1921.

[2] J. Becker and L. Curtiss, PHYS. REV., 15, p. 457, 1920. F. Richtmyer and L. Curtiss, PHYS. REV., 15, p. 465, 1920.

[3] P. Debye and P. Scherrer, Phys. Zeits., 17, p. 277, 1916; 18, p. 291, 1917.

[4] A. Hull, PHYS. REV., 10, p. 661, 1917.

tube which normally operates on two milliamperes current and 30 kilovolts potential was used. The photographic films consisted of two thicknesses of duplitized material which were clamped half way around two rigidly fastened metal rings turned on a lathe to an exact circle of 17 cm. diameter. One ring was supported about two centimeters vertically above the other by means of iron straps. The powdered material to be examined was in the form of a flat sheet and was put at the center of the circular films. A filter of zirconium oxide of thickness four tenths of a millimeter was inserted in the path of the x-rays between the tube and the lead slits used in defining the beam. The slits were each about a half millimeter wide. The slits, powder and circular photographic films were enclosed in a heavy lead box to screen off stray radiations.

Intensifying screens were discarded after a few tests as they were found of little value for a tube of low power output.

Bijl[1] has pointed out that under some conditions a large correction must be applied to the calculation of the planar spacings. This correction was avoided in the present work by using a layer of crystalline powder of such small thickness that it was easily penetrated by the x-rays.

Structure of Bismuth Metal.

Filings from a rod of bismuth were sifted through a screen 100 mesh to the centimeter, mixed with a small amount of soft wax, pressed into a flat sheet and put at the center of the circular photographic films. Exposures of 150 milliampere hours were made.

Knowing the crystal system and axial ratio from the standard crystallographic works, tables of planar spacings could be computed. It was found that the lattice may be considered as being made up of three interpenetrating sets of unit equilateral-triangular prisms, the atoms of the second set being raised one third the prism height vertically above the first and placed so that their vertical projections center alternate triangles of the basal plane. The third set are raised two thirds of the prism height above the first set, and center the remaining alternate triangles. The experimental values were in agreement with the theoretical values for the rhombohedral trigonal structure with elementary triangular prism of side 4.54 A and height 5.91 A with an axial ratio of $C = 1.303$.

Beyond the first eight lines the intensities were too faint to place with certainty the weaker experimental lines.

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[1] A. Bijl and N. Kolkmeyer, Proc. Amst. Acad., 21, 1, p. 495, 1918–1919.

TABLE I.

Indices.	Theor. Spacing.	Exp. Spacing.	Intens.	No. of Planes.
$10\bar{1}1$	3.27	3.28	V. Strong	3
$10\bar{1}2$	2.36	2.38	V. Strong	3
$11\bar{2}0$	2.27	2.25	V. Strong	3
0001	1.97	1.96	V. Weak	1
$20\bar{2}1$	1.84	1.83	Weak	3
$10\bar{1}1$	1.64	1.64	Medium	3
$11\bar{2}3$	1.49	1.50	Strong	6
$21\bar{3}1$	1.44	1.44	Strong	6
$10\bar{1}4$	1.38	——	——	3
$12\bar{3}2$	1.33	1.33	Strong	6
$10\bar{1}0$	1.31	——	——	3
$10\bar{1}2$	1.18	——	——	3
$10\bar{1}5$	1.14	1.15	V. Weak	3

For a check the number of atoms for the three interpenetrating unit prisms, in this case 1.5 may be computed;[1]

$$n = \frac{52.8 \times 9.7}{1.663 \times 208} = 1.49.$$

SPUTTERED BISMUTH.

Pure cast bismuth was used as a cathode in the sputtering jar. The current used was about one milliampere, the jar being in series with a kenetron rectifying-tube. The time of sputtering was about four hours. The bismuth was sputtered on several thin cover glass slides. When these slides with their metallic films, were superposed and put at the center of the photographic films the result was striking. The positions and intensities of the lines were nearly identical with those obtained with the bismuth rod filings, the only difference being a greater fogging of the lines. This fogging and lack of definiteness is due to the presence of small amounts of oxides of bismuth and to amorphous material.

The conclusion to be drawn from this comparison is that sputtered bismuth is crystalline, the crystal axes being turned in all possible directions, and the structure being the same as the ordinary metal. Although compounds of bismuth with the gases in the sputtering jar were undoubtedly present in small quantities, the pure metal was so predominant as to mask the spectra of the impurities.

EVAPORATED BISMUTH.

A piece of bismuth was put in the bottom of a long pyrex tube and the tube evacuated to approximately the same pressure as was used in sput-

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[1] A. Hull, PHYS. REV., 10, p. 661, 1917.

tering the bismuth. On heating the bottom of the tube till the bismuth came to a low red heat a heavy opaque film was deposited on the cooler parts of the tube. This film was examined by the method previously described. The photograph showed four widely spaced lines on a heavily fogged background indicating the absence of bismuth crystals but probably the presence of amorphous bismuth and a bismuth compound which however could not be identified.

A second sample of evaporated bismuth was prepared. The film was scraped from the glass, mixed with wax as in previous experiments and pressed into a flat sheet. When this was exposed to the x-rays in the usual manner the result was the same as that described above.

This would indicate that sputtering and evaporation are essentially different processes from the crystallographic standpoint.

The Structure of Sputtered Gold, Silver and Platinum.

In a similar manner the structures of sputtered films[1] of gold, silver and platinum were determined. In each case the sputtered film was crystalline and of the same fundamental crystal structure as the ordinary metal. The three metals have the face-centered cubic lattice with the length of the elementary cube 4.08, 4.06 and 4.02 Å respectively. The crystals are very minute and have a random distribution of axial directions.

Evaporated Silver.

Several opaque layers of silver were prepared by evaporation from an electrically heated silver wire in an evacuated vessel. These films were deposited on strips of lime glass. On examination they were found to be without the typical silver structure. The photographs were taken within one day after making the silver film.

In this connection it is interesting to note that Hull has found that distilled sodium and potassium are amorphous.[2] It is obvious beforehand that rapid evaporation in vacuo to a cold surface offers a favorable opportunity for the formation of a metal in the amorphous state.

Sputtered Cobalt.

This metal[3] occurs in two systems, the face centered cubic and the close-packed hexagonal, the former of which is made by annealing in a hydrogen furnace while the latter is made by rapid electrolysis.

The electrolytic cobalt sputtered readily and the structure of the film obtained from it was hexagonal.

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[1] The films of gold and silver were sputtered by Mr. L. Koller.

[2] A. Hull, Phys. Rev., 10, p. 688, 1917.

[3] A. Hull, Trans. Am. Inst. El. Eng., 38, p. 1189, 1919; Phys. Rev., 17, p. 571, 1921.

On the other hand, samples of cobalt consisting largely of the cubic variety did not sputter at all under the same conditions as obtained in the case of the hexagonal variety.

This indicates that rapidity of sputtering is determined in some cases by the crystal structure of the cathode. In the case of cobalt the less stable hexagonal arrangement seems to sputter better than the stable cubic variety. However as films of oxide exert very great influences upon the rate of sputtering and as the cubic variety may have been coated by more oxide than the hexagonal sample these results should be considered as preliminary only.

SPUTTERED SELENIUM.

Longden,[1] Pfund[2] and Nicholson[3] have found that metallic cathodes of gray selenium when sputtered give films of amorphous material. On continued sputtering these films become black and granular.

In the present experiments a cathode of the metallic variety when sputtered at a very low current density over a period of several hours gave a film of the same character as the cathode, namely, the gray metallic modification. When the current density was increased so that the surface of the cathode became molten the sputtered sample turned to the vitreous modification which appears red by transmitted light. The thinnest parts of the gray sputtered film did not transmit red light.

Other cathodes made of the red vitreous selenium were sputtered at several current densities and in all cases gave the red vitreous variety as the sputtered film.

Attempts made to obtain x-ray photographs of the various kinds of selenium proved futile. This may be ascribed to the fact that the characteristic fluorescent radiation predominates over the scattered beams. By suitably choosing a filter to stop the selenium characteristic radiation and prolonging the exposure by the order of ten times it may be possible to obtain suitable photographs.

OPTICAL COMPARISON OF EVAPORATED AND SPUTTERED SELENIUM.

Selenium crystals were formed by using the method of evaporation described by Brown.[4] If selenium is put in a long tube heated at one end and having a uniform temperature gradient, a great variety of crystals form along the tube. These crystals have characteristic colors and structures. In the hotter portions of the tube the crystals are

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[1] Longden, Am. Jour. of Sci., 10, p. 55, 1900.

[2] Pfund, PHYS. REV., 28, p. 324, 1909.

[3] Nicholson, PHYS. REV., 3, p. 1, 1914.

[4] F. Brown, PHYS. REV., 4, p. 85, 1914; 5, p. 236, 1915.

largest in size and are of metallic luster, their colors being blue-black, gray and white. At the cold edge, the amorphous red variety collects. On continued heating the red kind is transformed into the gray modification.

It is obvious that when sputtering with a high voltage and current density the temperature will be sufficiently elevated to cause rapid evaporation simultaneously with the sputtering as selenium melts at 220° C. On the other hand at low current densities the gray metallic crystals were sputtered intact, indicating that sputtering took place without appreciable evaporation of the selenium cathode. If the selenium had evaporated, the red modification would have formed, on condensing at the cold glass slide. Evidently when selenium is sputtered, under suitable conditions, no alteration of crystal structure takes place, the crystals leaving the cathode in grains.

General Discussion of Data.

Reinders and Hamburger[1] examined with the ultramicroscope films of sputtered silver and tungsten. The grains making up the silver films were found to range from 6 μ to 8 μ in diameter while those making up the films of tungsten varied from 2 μ to 5 μ. These comparatively large grains were found to be imbedded in a thin layer of amorphous metal. When sputtered at high temperatures the particles were of larger size than when sputtered at low temperatures.

In the present work it has been shown that the sputtered films are crystalline and that the crystalline particles making up the film are arranged at random orientations with respect to each other.

The writer's data show that evaporated metallic films do not consist of the pure metal in the crystalline state but of metallic compounds and amorphous metal.

It has been shown by Langmuir[2] that metallic evaporation in a fairly high vacuum takes place atom by atom. (However it appears from the work of Reinders, Hamburger, Kaye and Ewen[3] that the low melting-point elements occasionally eject large particles during the process of sublimation.) The vapor of tungsten was found to be monatomic as long as the gas pressure in the tube was kept below a definite value. At every collision between a nitrogen molecule and a tungsten atom the compound WN_2 was formed. Other gases were found to behave in a similar manner with respect to tungsten.

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[1] W. Reinders and L. Hamburger, K. Akad. Amsterdam Proc., 19, p. 958, 1917.

[2] I. Langmuir, Jour. Am. Ch. Soc., 35, p. 944, 1913; 37, p. 1139, 1915.

[3] Kaye and Ewen, Proc. Roy. Soc., 89, p. 58, 1913.

Using the ultra-microscope, Reinders and Hamburger[1] found that the high melting-point elements W, C, Mo, Pt, Ni and Fe gave evaporated films that were mainly "amorphous." The low-melting metals Au, Ag, Cu and magnesium show a tendency toward a coarser condensation and seemed to form a connected network of ultra-microscopic particles.

The writer's spectrograms of the evaporated films show that the vapor in transit to the film has combined with the gases present in the tube and that if pure metal is present it exists only in the amorphous state. Indeed the conditions are favorable during evaporation in a high vacuum for the formation of an amorphous metal.

Maurain[2] has shown from magnetic deflection tests that the cathodic particles while charged electrically have the ratio e/m of such a value as to indicate that the particles in transit consist of large groups of atoms.

Lack of fluorescence when these particles impinge upon a suitable material is a further indication that the sputtered particles are large and slow moving.

In the present tests the relatively pure condition of the sputtered films indicates that the number of collisions per atom with gas molecules in transit has been small, showing that the particles in transit consist of a large number of atoms.

Concerning the origin of the sputtered particles there has been much difference of opinion in the past. Some have maintained that sputtering is an evaporation phenomenon and others have held that the particles were bodily knocked off from the cathode by the impinging gas ion. The evidence here presented seems to prove that the particles initially leave the cathode in granular crystals rather than by mon-atomic evaporation. In the latter case it would have to be assumed that the large particles in transit had been formed by condensation of the vapor near the surface of the cathode. This appears very improbable as the gas pressure used in sputtering is lower than that for which condensation of metallic vapor occurs.

Worthing and Baker[3] have recently shown that the rate of metallic evaporation is not affected by electrostatic fields of less than 800,000 volts per cm. Hence the comparatively low field strengths used in sputtering would exert no influence on the rate of evaporation or size of particles. This eliminates the hypothesis of large particles being thrown

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[1] W. Reinders and L. Hamburger, K. Akad. Amsterdam, Proc., 19, p. 958, 1917; 20, p. 1135, 1918.

[2] C. Maurain, Compt. Rend., 161, p. 1223, 1905; 162, p. 870, 1906.

[3] A. Worthing and W. Baker, PHYS. REV., 17, p. 239, 1921. A. Worthing, PHYS. REV., 17, p. 418, 1921.

off by evaporation under the influence of an electric field such as that present in sputtering.

In conclusion the writer wishes to thank Mr. L. F. Curtiss for preparing many of the sputtered films and Professor Ernest Merritt for his kindly interest in the work.

Cornell University,
April, 1921.

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After this paper had gone to press articles appeared on the structure of bismuth by Ogg, Phil. Mag., 42, p. 163, 1921, and James, Phil. Mag., 42, p. 233, 1921. They report a more detailed study of bismuth using a large crystal and the original Bragg method, which of course would be impossible with thin films. The dimensions given by Ogg and James agree with those here given when expressed in the same terminology. Instead of the simple rhombohedral lattice as I have stated the structure of bismuth to be they have found it to be best represented by a slightly distorted rhombohedral lattice resolvable into two face centered interpenetrating rhombohedral lattices.