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Effect of the Type of Support on the Photoelectric Work Function of Silver Films

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Silver was doubly and fractionally distilled with the middle fraction deposited on previously outgassed bulk silver, on smooth fused quartz, and on outgassed molybdenum sheet in a sealed-off, gettered tube. Photoelectric measurements were made using the Fowler method. Deposit of a film of silver on bulk silver caused φ to decrease by varying amounts as great as 0.25 ev to 4.50±0.02 ev. Subsequent heating estimated at below 100°C caused ϕ to increase to the original value. φ for a silver film on smooth fused quartz and on outgassed molybdenum sheet is 4.41 ev. The results are unaffected by residual gas pressure in the tube. The low values of φ for the film appear to be due to a surface structure composed of microcrystals which are much smaller than those of the bulk silver. The variations in the observed values of φ for films on different supports is attributed to a dependence of the sizes of the microcrystals on the structure of the support. Information is given regarding the effect of the equilibrium conditions between volume and surface gas on the value of φ during the outgassing period of bulk silver.

INTRODUCTION

PREVIOUS experiments on thin films deposited on various bases have been carried out by means of electron diffraction,[1–3] contact potential,[4–6] and photoelectric[6] measurements. This interest in metal films is largely due to the fact that a specimen properly prepared by deposition from the vapor state in a high vacuum should present a surface nearly free of gas. The results obtained have led various experimenters[6, 7] to suggest that the work function of such a metal film is greatly influenced by the underlying structure, although no detailed study of the problem has been made. Such an influence is expected if a particular crystal face predominates at the surface and is related to the support on which the film is deposited, since the work function of a single crystal is known to be a function of the crystal face which forms the surface. Observations by Farnsworth[1] on low speed electron diffraction indicate that a film which is deposited by evaporation at a low rate forms in a single lattice on the surface of a crystal of the same metal with an orientation which is the same as that of the underlying crystal face. Furthermore, it seems probable that any preferred orientation of a lattice in the film may also depend on the roughness[8] and temperature[3, 9] of the condensing surface.

The primary purpose of this investigation was to determine the effect of the type of support and of its condition prior to deposition on the photoelectric work function of silver films deposited from the vapor state in high vacuum. Observations were also made on the effect of elapsed time after deposition, of heat treatment of the film after deposition, and of exposure to gas pressure.

APPARATUS AND PROCEDURE

A double evaporation procedure was employed in order to obtain films as nearly gas free as possible. The experimental arrangement was such that the silver source A, Fig. 1, could be heated by electron bombardment from the filament F_2 while the supports B were withdrawn into the side tube T_1. The U-shaped molydenum filament F_1, which received some silver from A, could in turn be heated by conduction to deposit silver on the supports after they had been moved into the proper forward positions. Before making deposits, the source A and filament F_1 were outgassed at red heat for several hundred hours. The first few deposits on F_1 were driven off before exposing the supports, and it was thereafter kept coated with a heavy layer of silver. Usually one support was placed directly in front of the opening in F_1 during the evaporation from F_1 so that readings could be taken on the film immediately after deposition.

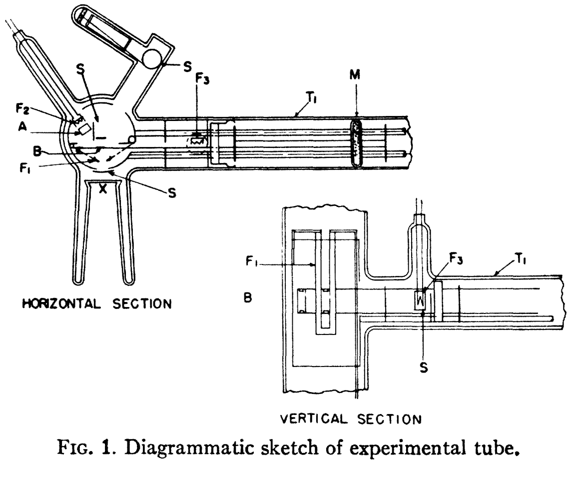

FIG. 1. Diagrammatic sketch of experimental tube.

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* The experimental results presented here are taken from a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Brown University.

** Now with Eastman Kodak Company, Rochester, New York.

[1] H. E. Farnsworth, Phys. Rev. **43**, 904 (1933).

[2] H. E. Farnsworth, Phys. Rev. **49**, 605 (1936).

[3] O. Goche and H. Wilman, Proc. Phys. Soc. London **51**, 625 (1939).

[4] P. A. Anderson, Phys. Rev. **56**, 850A (1939); **49**, 320 (1936).

[5] P. A. Anderson, Phys. Rev. **59**, 1034 (1941).

[6] H. E. Farnsworth and R. P. Winch, Phys. Rev. **58**, 812 (1940).

[7] R. S. Cashman, Phys. Rev. **57**, 971 (1938).

[8] P. A. Anderson, Phys. Rev. **54**, 753 (1938).

[9] O. Rudiger, Ann. d. Physik **30**, 6 (1937).

Three supports for the films were used, one of polycrystalline silver 1.5 mm thick, one of smooth fused quartz, and one of molybdenum sheet. The silver support was cut from the same sample as the primary source used for the deposited films. It was of the same purity as that used by Farnsworth and Winch[6] in their determination of the work functions of silver crystal faces. Each support presented a surface 5×12 mm, and was mounted in a molybdenum frame held between molybdenum rods which were fastened to a sliding mechanism.

The specimens could be withdrawn into the side tube T_1 opposite the filament F_3 by an external electromagnet acting on the iron armature M. Magnetically controlled shutters S were provided to prevent condensation of metal on the windows, and other shields were placed at appropriate places. The bombarding filaments were surrounded by molybdenum shields on all sides except that facing the element to be heated. All iron armatures were enclosed in Pyrex glass. The collector of photo-electrons consisted of a molybdenum cylinder with suitable apertures to permit entrance of filaments. Ultraviolet light entered through the fused quartz window X, attached to the Pyrex envelope by a graded seal.

Before final assembly all parts were cleaned chemically. The assembly was made in a dust-free, dry room and parts were touched only with clean tools. Immediately thereafter, the tube was sealed directly to a vacuum system with two large traps in series separating the tube from the oil diffusion pumps, and a third trap separating the diffusion and backing pumps. The traps were cooled by solid carbon dioxide in acetone.

The gas pressure in the tube was measured with an ionization gauge. After the second baking of the experimental tube in an electric furnace, outgassing of the elements was conducted at a rate such that the pressure did not exceed 5×10^{-7} mm Hg. After the third baking, outgassing was continued until all elements could be heated to the desired temperatures at a pressure not in excess of 5×10^{-8} mm Hg. At this point the tube was gettered by two sets of six RCA getters[10] in series and sealed from the vacuum system. The getters were located in a side tube to prevent contamination of the surfaces under investigation. During the deposition process the pressure was below 5×10^{-8} mm Hg.

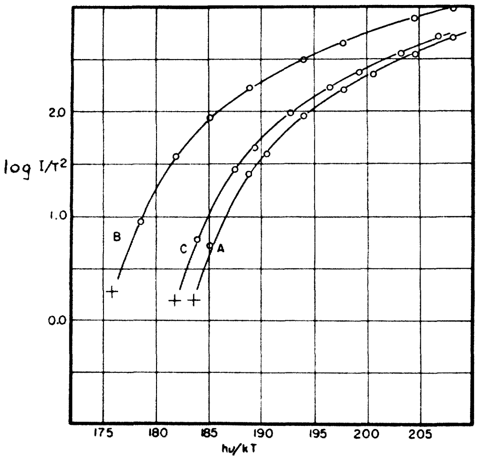

FIG. 2. Typical Fowler plots. Curve A is for a freshly heated surface, curve B is for the same surface some time after heating, curve C is for this surface subsequent to low temperature heating.

TABLE I. Values of the work function after depositions and at various stages of outgassing of the bulk sample.

Total time of outgassing after seal-off	φ immediately after heating	φ prior to deposit	Time between heating and deposition	φ after deposition	$\Delta\varphi$
27 hr.	4.60				
30	4.61	4.55	7 hr.	4.46	0.09
30+	4.62	4.58	3	4.44	0.14
	4.62	4.55	7	4.47	0.08
	4.62	4.56	3.5	4.50	0.06
	4.61	4.46	19.5	4.39	0.07
	4.62		0.25	4.50	0.12
	4.65		0.25	4.51	0.14
	4.64		0.25	4.50	0.14
	4.64		0.25	4.52	0.12
31	4.69				
47	4.66				
57	4.76				
159	4.76			4.64	0.12
198	4.74		0.25	4.49	0.25
222	4.76		0.25	4.51	0.25
232	4.68				
247	4.67				
265	4.68				

The monochromator, light source for photoelectric readings, and procedure have been described in a previous paper.[6] The Fowler method of analysis was used to determine work functions.

RESULTS AND DISCUSSION[11]

A. Polycrystalline Bulk Silver

φ for polycrystalline bulk silver, following a total heating of 250 hours after seal-off with frequent flashing to the evaporation point, was found to increase to 4.68±0.01 ev. Before this value was reached, numerous deposits were made. However, the sample was heated at temperatures high enough to evaporate deposited layers, and later heating at still higher temperatures produced no change from the above value.

No change of φ with time was observed during intervals of less than one hour after heating was discontinued. Over longer periods, φ decreased with time after heating. In the early stages of outgassing a decrease of 0.25 ev was observed in 700 hours. There is evidence that the rate of decrease is less after more outgassing, although the data on this point are not complete. At the end of the experiment the pressure was

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[10] E. A. Lederer, RCA Rev. 4, 310 (1939).

[11] The constants h and k used in determining the experimental values of φ reported here are those given by Raymond T. Birge, Rev. Mod. Phys. **13**, 233 (1941). Use of these constants results in a φ which is about 0.05 ev greater than that obtained with the constants accepted previously. No corrections have been applied to published results determined with the old constants.

increased to 10^{-6} mm Hg for five minutes by heating one of the side tubes. After this treatment the pressure dropped rapidly to 10^{-7} mm Hg and then continued to fall more slowly. Within the experimental error no change in φ for the freshly heated surface was observed within one hour. Subsequent to a decrease of φ with time after heating, it was found that only a small increase of temperature (to a value estimated to be considerably less than 100°C) for times as short as one minute was required to cause φ to return to the higher value obtained by high temperature heating.

B. Deposition of Silver on Polycrystalline Silver

Deposition of silver on the bulk sample soon after heating and at various stages of outgassing of the bulk sample[12] caused a sharp decrease in φ as shown in Table I. The results of six runs indicate a value for φ of 4.50±0.02 ev for the film. Prior to seal-off, deposits were made on the freshly heated surface without taking intermediate readings and φ was 4.48 ev. The film thickness is not known, but it must have been of the order of several hundred atoms. Readings were taken as a function of time, starting within 30 seconds after deposition, but in no case was there a rapid increase such as that observed by Farnsworth and Winch[6] for a single crystal face. Even after periods as long as 18 hours no change in φ greater than 0.05 ev was observed and this was always a decrease.

When the time between end of heating of bulk metal and beginning of deposition of the film was several hours, the observed value of φ following deposition was lower than that given above. In some cases the difference between the two values is very nearly the decrease in φ for the bulk silver which occurred following heating and prior to deposition. However, the data are too limited to draw a definite conclusion on this point.

As in the case of the bulk silver subsequent to remaining at room temperature for some time after heating, a small rise in temperature caused an increase in φ for the film to nearly the same high value obtained for the freshly heated surface. Typical Fowler plots for this cycle are given in Fig. 2. As indicated by the data in Table I, the value of φ, which is obtained when deposition is made on the freshly heated surface, is independent of the outgassing time and of the value of φ before deposit.

The decrease of 0.12 to 0.25 ev brought about by deposition may be compared to a decrease of 0.09 ev observed by Farnsworth and Winch[6] in the case of the (100) crystal face of silver and a decrease of several tenths of a volt in the case of the (111) face of the same metal.

C. Deposition of Silver on Clear Fused Quartz

In the early stages of the investigation, before seal-off of tube from the vacuum system, deposition resulted from heating the adjacent bulk silver specimen. The film thus formed was clearly visible, but transparent. At this time φ was 4.68 ev. After subsequent heatings of the adjacent bulk silver, φ decreased to 4.52. Deposits, using the doubly distilled source, resulted in further decreases of φ to the equilibrium value of 4.41 ev after the fourth deposit. At the time of seal-off the surface was opaque. Later depositions in the gettered tube caused no further change in φ.

Raising the temperature of the film on quartz by heating the adjacent bulk silver to a temperature just below red heat caused an increase of φ to 4.48 ev. There was no change of this value with time, but deposition always decreased φ to 4.41±0.01 ev. This value may be compared with 4.47 ev obtained by Anderson[5] for a silver film on glass.

The precision of the observations was not sufficient to make an accurate comparison of the minimum temperature required to increase φ for bulk silver with the minimum temperature required to increase φ for a silver film on bulk silver. However, it was estimated that they are approximately the same.

D. Deposition of Silver on Molybdenum Sheet

Deposition of silver on polycrystalline molybdenum caused φ to decrease from the value of 4.78 ev, obtained after outgassing at red heat for 150 hours. After the fourth deposit the value of φ was 4.41 ev, the same as that for silver or quartz, and did not change with further deposition. No noticeable change of φ for the silver film occurred with time after deposit when the molybdenum had been thoroughly outgassed. A low temperature heating (less than 100°C) of the silver film on molybdenum caused an increase in φ of 0.1 to 0.2 ev.

E. Interpretations

The residual gas pressures maintained in the experimental tube appear to have had no influence on the observed values of φ for the following reasons: (1) An intentional increase of gas pressure produced no observed decrease in φ of bulk silver. (2) The value of φ for a film of silver deposited on quartz or on outgassed molybdenum did not decrease with time after deposit. A slight decrease with time after deposit was observed for a film of silver on bulk silver. (3) Although φ for a silver film on quartz and on outgassed molybdenum was increased by low temperature heating, there was no subsequent decrease of this value with time after heating as in the case for a silver film on bulk silver.

Two other possible causes for the decrease of φ of bulk silver and of a silver film on bulk silver, with time after heating or after deposit may be considered: (1)

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[12] In each case φ was measured immediately after heating was discontinued. This procedure usually required about fifteen minutes. A deposit was then made and a set of readings to determine φ of the film was taken immediately.

During the heating process gas from the interior of the bulk metal diffuses to the surface and evaporates. Because of the relatively long time required to obtain equilibrium between the surface and volume gas at the elevated temperature, the amount of gas on the surface at any instant at the high temperature is less than the equilibrium value which exists after the metal is later cooled to room temperature. Hence a slow increase in the amount of surface gas is expected later at room temperature as a result of diffusion from the interior. This interpretation requires that this equilibrium condition is disturbed by the low temperature heating and that surface gas is removed to the same extent that existed immediately following the higher temperature heating. (2) At the highest temperature of heating a surface arrangement of atoms occurs which is not the most stable at room temperature. Subsequent to high temperature heating a slow rearrangement would then occur at room temperature. We know of no experimental evidence for this second assumption and therefore tentatively conclude that only the first assumption regarding gas diffusion deserves serious consideration.

We interpret the relatively low values of 4.41 ev for a silver film on quartz and on outgassed molybdenum, and 4.50 ev for a silver film on bulk silver as due to a structure of the film which differs from that of bulk silver. Electron diffraction patterns from evaporated films on fused quartz indicate a micro crystalline structure[9] and we tentatively associate the low value of φ with the minute size of the crystals. The increase of φ for the film caused by low temperature heating is attributed to crystal growth. The fact that the same values of φ were obtained for the film on quartz and on molybdenum suggests that the film structure is the same in these cases. Molybdenum has a body-centered lattice of 3.14A compared to 4.08A for face-centered silver and it is expected that there would be little or no tendency for the silver to conform to the molybdenum lattice. In the case of the silver support, the higher value of φ for the film suggests a partial alignment with the underlying structure under similar conditions of rate and temperature of deposition. This would also be expected with other metal supports having suitable lattice constants. For example, the lattice constant of gold differs from that of silver by less than 0.5 percent.

The decrease of φ with increase of film thickness on quartz may also be associated with a structure change, but before considering this result in detail a repetition of the observation should be made with better control of conditions.

The observations of Farnsworth and Winch[6] now appear to require some changes in interpretations. They found, after depositing a silver film on two bulk silver single crystals with (111) and (100) faces, respectively, that the sudden decrease in φ due to the film deposition was followed by a spontaneous increase extending over a period of an hour or two. In many cases the value of φ after the increase coincided with that for the bulk crystal before the deposit. At that time the increase was attributed to adsorption from the residual gas in the tube. That interpretation requires that the values of φ for the two crystal faces after thorough outgassing are characteristic of gas contaminated faces. On the basis of the present observations, it now appears that the spontaneous increase in φ, following the decrease due to film deposition, corresponds to the increase in the present observations induced by slight heating of the film on bulk silver above room temperature. The reason for the spontaneous increase of φ in the observations of Farnsworth and Winch may be due to a greater mobility on the single crystal surface, a different rate of deposition, or a higher ambient temperature during these observations. This interpretation indicates the values of $\varphi_{100}=4.81$ ev and $\varphi_{111}=4.75$ ev obtained by Farnsworth and Winch for the two crystal faces after thorough outgassing are those for *gas-free faces*.

With the above values of φ for the low index faces which are found to predominate in a polycrystal it is clear that the low value of 4.41 ev cannot result from a random arrangement of low index faces, but must be characteristic of the structure of the film composed of exceedingly minute elementary crystals.

Although some evidence has been obtained previously by Anderson[8] that φ for a microcrystalline film of magnesium is less than that for a surface composed of "equilibrium crystal faces," no observations were made on the dependence of φ (for a film) on the type of support.