PHOTO-RESISTANCE EFFECT FOR METALS AT LOW TEMPERATURES

By Russell S. Bartlett

Abstract

Photo-resistance effect for sputtered metallic films at low temperatures.—Waterman's equilibrium theory of resistance predicts an effect for metals, increasing as the temperature is decreased. To test this, thin sputtered films, after aging, were held at liquid air temperature and illuminated with light from a quartz mercury vapor arc, with or without screens. *Bismuth* showed the largest decrease in resistance, 16×10^{-6}, *palladium* 14×10^{-6}, *copper* 1.6×10^{-6}, *platinum* even less and *gold* and *silver* no detectable change. The order of these metals is in agreement with the theory. The effect was not in general instantaneous but increased with time along a saturation curve, and in the dark returned only slowly toward the original value. The effective wave-length was found to be beyond 3000A for fresh Bi films, but the threshold seemed to move to longer wave-lengths with age. Some older Bi films showed a reverse positive effect of even larger magnitude which apparently is due to longer wave-lengths, but the exact circumstances were not definitely fixed. The magnitude of the negative effect for Bi decreased rapidly with increasing temperature, to 3×10^{-6} at $-110°$. *Tellurium*, sensitive at room temperature, showed a 70 percent greater effect at $-185°$C.

Temperature coefficient of resistance of sputtered films.—For Bi the coefficient decreased from .0014 at 0°C to practically zero at $-185°$C. In general, the coefficients were smaller for the sputtered films than for the same metals in bulk.

Introduction

IT APPEARS to be well established that metals, under the influence of light, show no change in electrical conductivity other than that due to the heating effect of the radiation absorbed.[1] As we pass from good conductors to the poorly conducting metalloids and non-metals, we find an increasing photo-resistance effect. Waterman[2] has suggested a theory which accounts for this variation and at the same time indicates that metals should show a photo-resistance effect at very low temperatures.

Theory

From theoretical considerations, Waterman derived an expression for the electrical resistance of the form

$$\rho = A\,T^{a}e^{b/T-cT}$$

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[1] L. Ancel (Zeits. Elektrochemie, **9**, 695, 1903) makes a reference of uncertain significance to light sensitivity of metal plates. Since, however, nothing further on the subject can be found in the scientific journals of that time, it would seem that he was merely speculating on the possibility of such an effect.

[2] Waterman, Phys. Rev. **22**, 259, 1923.

where A is a constant characteristic of the element, and a is a constant having the value 5/4 for most metals. For such metals

$$b=(\phi_0-\psi_0)/2R$$

where ϕ_0 is the photo-electric and ψ_0 the thermionic work function; c involves the specific heat of electricity.[3] The effect of incident light should be to reduce ϕ_0 and thus diminish the energy $(\phi_0-\psi_0)$ necessary to create a free electron. This disturbs the equilibrium condition and leads to an increase in the number of free electrons in the metal.

If b is calculated from specific resistance data at different temperatures, it is found to be small for all metals, so that the factor $e^{b/T}$ is nearly unity except at low temperatures. But when T is sufficiently small this factor becomes effective, and a change in b, due to incident light, should alter the resistance. Assuming, as seems reasonable, that when b is large its change under the influence of light will also be large, it is possible to predict the metals most favorable for the result sought.

Such calculations were made, indicating that Pd, Cu, Pt, Rh, in that order, are particularly suited for this work. Following them are Na, Cd, Sn, Te, Ag, Au, etc.

Bismuth is peculiar in many of its properties, and as such might not follow the simple theory outlined. But considerations similar to those applied to other metals indicate a sensitivity larger than that for palladium. Further favorable indications are found in the fact that bismuth has a high specific resistance and is a border substance between metals and non-metals.

Iron and nickel were uncertain because of transition points and the effect of impurities.

Experimental Problem

Preparation of thin films. A preliminary trial was made with thin metallic foils and fine wires at liquid air temperature, but no change in resistance was noted under the influence of light. It appeared that thin films of a wide variety of metals were necessary, and the method of cathode sputtering was selected as the means for obtaining these. The apparatus used was similar to that described by Richtmyer and Curtiss[4] and by Perkins.[5] Au, Ag, Pt, and Pd sputtered readily in residual air with a 2 to 4 cm cathode dark space. Bi and Te required a dark space of

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[3] This term, which is in general small except at high temperatures, has been added by Waterman in a supplementary paper: Waterman, Phys. Rev. **23**, 781, 1924.

[4] Richtmyer and Curtiss, Phys. Rev. **15**, 465 (1920).

[5] Perkins, Jour. de Phys. et le Radium (IV), **4**, 246 (1923).

6 cm or more for most rapid deposition. For copper, to avoid oxidation, the discharge tube was filled with hydrogen at a pressure just sufficient to support the discharge at 10,000 volts.

The thickness of the films was obtained by weighing, assuming the density to be the same as that for bulk metals. The thickness, below a certain critical value, seemed to have no effect upon the results.

It was found that the resistance of freshly sputtered films varied considerably with time, so that it was necessary to age all the films either naturally or artificially before taking resistance measurements. The degree or method of this aging appeared to have no effect upon the behavior of the film under the influence of light. An exception to this in the case of bismuth is discussed later. Of all the metals used bismuth alone showed an increase of resistance with aging, the others all showing a very marked decrease.

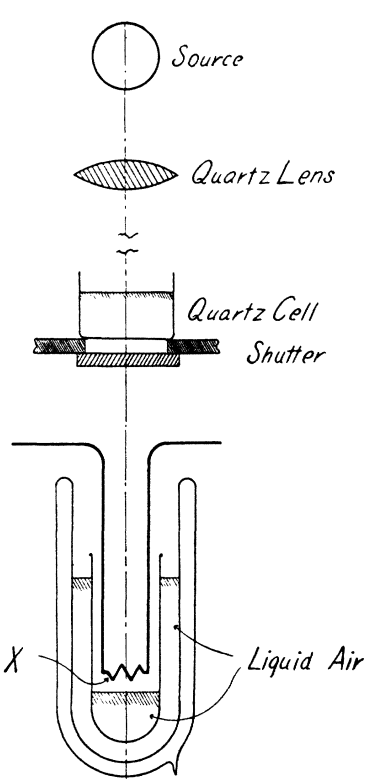

Fig. 1. General arrangement of apparatus.

Contacts which maintained a constant resistance over the range of temperatures investigated were made by sputtering the ends of the films heavily with gold, and attaching permanent leads by means of brass clamps. For higher resistance films, "clamping paste," furnished through the kindness of the General Electric Company, was used with similar clamps, and proved satisfactory. The connections to the resistance measuring apparatus were made by dipping the leads into mercury cups.

Source of radiation. As a source of radiation a quartz mercury vapor lamp was used. A quartz lens, quartz cell, and shutter were arranged as shown in Fig. 1. This gave a limit on the short wave-length side of about 2000 A. Absorbing filters, as described by Williamson,[6] were used in the cell to limit further the wave-length range, to fix the region of

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[6] Williamson, Phys. Rev. **21**, 107 (1923).

effective wave-lengths, and to eliminate as far as possible the inactive heat radiation.

Temperature control. The temperature of liquid air, taken as about −185°C, was the lowest available. For this temperature the metal films were placed in actual contact with the liquid air. By means of films sputtered on quartz and inverted with the metal just touching the liquid air, the absorption of light in the liquid air was avoided, and by comparison it appeared that the absorption in a thin film was negligible. Slightly higher temperatures could be obtained with sufficient constancy by means similar to that shown in Fig. 1, the metal foil being suspended above the liquid air and surrounded by it, though not in actual contact. For still higher temperatures a bath of petroleum ether was used. Temperature measurements were made with a pentane thermometer, calibrated in liquid air and in freezing ether, acetone, chloroform, and distilled water. Sufficient time was always given before taking measurements to allow the temperature to become constant.

Resistance measurements. A potentiometer method was found to be the most satisfactory for measuring small changes of resistance and at the same time eliminating extraneous disturbing factors. A Leeds and Northrup type H.S. galvanometer was used in connection with a Wolff potentiometer of 15,000 ohms internal resistance. Lead storage cells furnished a constant potential difference. Since the resistance of the film was small compared to the resistance in series with it, after the bridge had been balanced and the key closed, the change in resistance on illumination could be measured by the galvanometer deflection. The current through the metal strips was kept at as large a value as possible without appreciable heating. With this arrangement it was possible to measure changes of resistance of one part in three million, or slightly better. By taking a large number of readings under identical conditions, errors due to slight fluctuations were largely eliminated. The arrangement of the apparatus was such that the flow of heat between the warm and cold parts would have a very small disturbing influence, so that after a short time a very good balance could be obtained. By measurements made on a film sputtered completely except for a slight break in the middle, it was shown that the changes in conductivity of glass and liquid air under the influence of light, were of such an order as to have no appreciable effect on the result, and that conduction due to emission electrons could be neglected.

Elimination of temperature effects. The most serious problem was that of distinguishing changes in resistance due to a slight rise in temperature upon illumination from the true photo-resistance effect looked for. Careful measurements were made to determine the nature of the temperature coefficient of resistance, in sign and magnitude, and its variation with temperature. Special care was taken with bismuth and palladium because of their negative coefficients. A typical curve of the resistance temperature relation, given in Fig. 2 (A), shows that the coefficient for Bi is continuously negative down to −185°C,[7] but that the value decreases rapidly towards this limiting temperature, so that the possible effect of heating would be very small for liquid air temperature. A smaller and generally similar coefficient was obtained for palladium. Tellurium showed a much larger negative coefficient. The other metals used all showed positive temperature coefficients of resistance, though much smaller than for the same metals in bulk.[8]

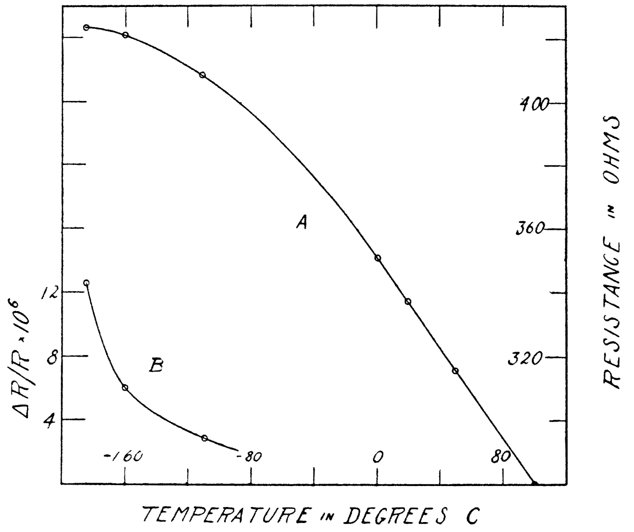

Fig. 2. Bismuth films. Curve A. Resistance as a function of temperature. Curve B. Photo-resistance effect as a function of temperature.

From these data and from the results of investigations on screening by distilled water and on constant temperature baths, it was concluded that the effect due to heating by incident radiation was in all cases small, and entirely negligible if a distilled water screen was used. Since this

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[7] Becker and Curtiss (Phys. Rev. **15**, 457, 1920) have remarked this negative temperature coefficient for bismuth for the range 0° to 150°C. The results check very well for the region common to both investigations.

[8] Longden (Phys. Rev. **11**, 40 and 80, 1900) and Patterson (Phil. Mag. 4, 652, 1902) have both noted this low temperature coefficient of resistance for sputtered films.

screen cut off somewhat on the short wave-length side, it was thought advisable also to take some measurements without it.

Results

Sputtered films of gold and silver showed no measurable change in resistance under the influence of light. Platinum showed a probable decrease in resistance, but so small as to be barely discernible, less than one part in 10^6. This appeared only for the thinnest films used, about 10^{-6} cm in thickness, and for the shortest wave-lengths, below 2500A.

Copper showed a very definite and instantaneous decrease in resistance under the influence of light for the thinnest films used, 1.5×10^{-6} cm in thickness. The decrease was found to be between 1.1 and 1.6 parts in 10^6 for different films, the corresponding increase on darkening being about half. It is probable that the original value was reached after a slight lapse of time.

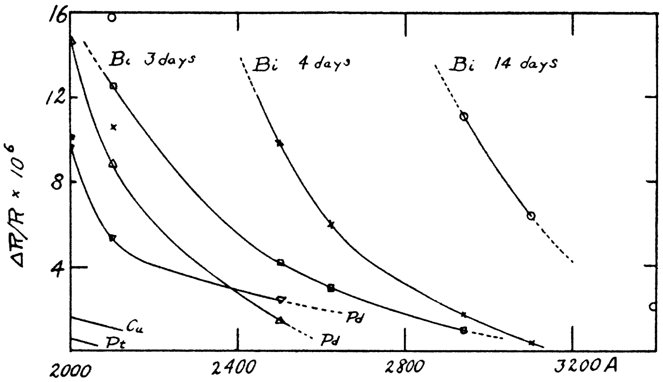

Fig. 3. Photo-resistance effect as a function of wave-length.

Palladium and bismuth showed much larger changes, amounting to 14 and 16 parts in 10^6 respectively. For both of these metals various absorbing screens were used, the decrease in sensitivity with longer wave-lengths being indicated in Fig. 3. For bismuth the decrease in sensitivity for increasing temperature was investigated, the results appearing in Fig. 2 (B).

It would be expected that any effect would depend directly on the intensity of incident light, and this was roughly confirmed. For the observations noted above or indicated in curves, the same intensity was used in all, excepting that the use of an absorbing screen to cut out certain wave-lengths slightly diminished the intensity of others.

Tellurium films, sensitive at room temperature, showed a considerable increase in sensitivity at liquid air temperature, in agreement with the prediction of theory. The sensitivity decreased with increasing wavelength, the effective limit being near 4500A at 20°C, and slightly longer at −185°C. A curve showing the decrease of resistance with time of illumination at 20°C and at −185°C is given in Fig. 4 and will prove useful for comparison with others to be discussed later.

These results conform rather well with predictions. Bismuth might be expected, from resistance data, to show the largest light sensitivity, and such was the case. Palladium, copper and platinum follow in that order, from observation, and from theoretical considerations. The evidence appears, then, to support Waterman's prediction of a light sensitivity for metals at low temperatures, and to justify the general form of his equation as far as the term $e^{b/T}$ is concerned. Quantitative deductions are not possible with the data available at present.

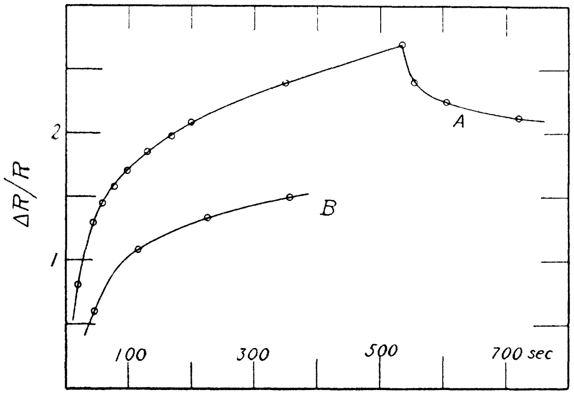

Fig. 4. Tellurium films. Photo-resistance effect as a function of time. Curve A. At −185°C; Curve B. At 20°C. Break in A is at the point where illumination was shut off.

It seems probable that the magnitude of this light sensitivity could be greatly increased through the use of thinner films, shorter wave-lengths, and lower temperatures. With sufficient refinements in these particular it should be possible to find a light sensitivity for many more metals.

In addition to the results given above, *another peculiarity of bismuth films* was noted, an *increase* of resistance under the influence of light for certain conditions. Thus a single film would at one time show a decrease in resistance and at another an increase.

A film soon after sputtering showed only the normal and expected decrease in resistance. With continued aging the reverse effect increased. At a certain time in this aging process it was possible to obtain a decrease in resistance by using a distilled water screen, and an increase without the screen. With further aging the increase of resistance alone could be noted, though the distilled water screen always decreased this greatly. A screen of glass had a similar and somewhat greater effect, while paraffin transmitting in the long infrared did not entirely eliminate the change. It appears probable that this increase in resistance is due to long wavelengths.

The reaction to light appeared to be practically instantaneous, reaching a nearly steady value after a short time. The increase in resistance was in some cases as large as 8 parts in 10,000 or about 50 times as great as the maximum decrease noted. Upon shutting off the light, there was no instantaneous change but a gradual and very slow decrease, indicating that the original resistance would be reached only after a very long time if at all. A graphical representation of these results is given in Fig. 5. It is interesting to compare these curves with those of Fig. 4.

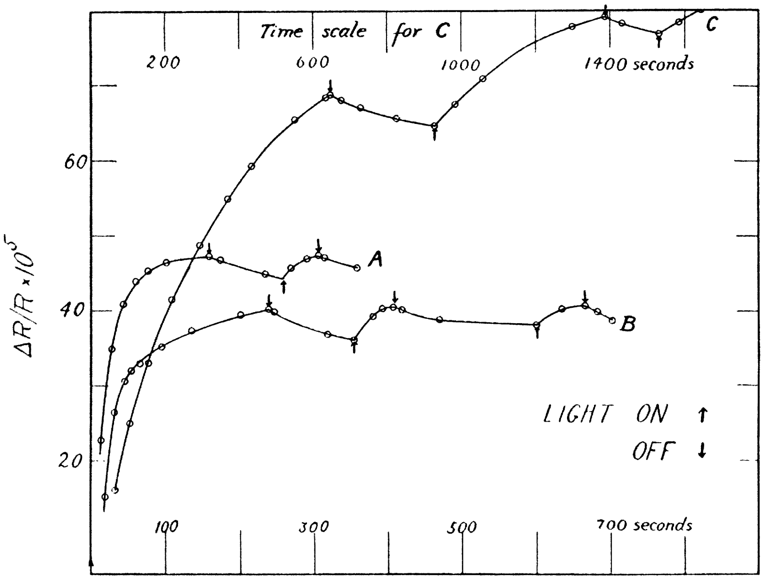

Fig. 5. Bismuth films. Negative photo-resistance effect as a function of time.
Curve A. Age 14 days, thickness 3×10^{-6} cm (lower scale of abscissas).
Curve B. Age 20 days, thickness 10×10^{-6} cm (lower scale).
Curve C. Age 30 days, thickness 6×10^{-6} cm (upper scale).

The temperature appeared to have little effect upon the magnitude of this change.

Further investigation of this phenomenon is being carried on at this time in the hope of obtaining enough additional data to determine to what this effect is due. Perkins has called my attention to the fact that radiation has an effect upon the aging of bismuth films. He found that screening greatly reduced the rate of increase of resistance. This was confirmed, a slight decrease in resistance being noted in one or two cases. These two phenomena may quite possibly be related. We may perhaps postulate a structural change such as that used to explain positive and negative light sensitive selenium; or we may find that this effect is in some way related to the magnetic properties of bismuth.

I wish to express my thanks to Professor A. T. Waterman, who suggested the problem, for continued assistance and interest, and to Professor J. Zeleny for his kindness in placing facilities at my disposal.

SLOANE LABORATORY,
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