Conduction Processes in Thin Deposits of Antimony

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Sublimed antimony deposits having a resistivity 1.35 times massive resistivity have been prepared. Assuming two conduction processes in antimony, the mean free paths for the conducting processes in thin sublimed deposits of antimony were found to be 1725A and 666A. $\Delta\rho/\Delta T$ measurements for thin antimony deposits indicate that the trapping of electrons in the surface becomes important for thicknesses less than 1000A, and lend support to the concept of surface electronic states in metals.

ACCORDING to modern theories of the behavior of electrons in metals, the conductivity, σ, of a comparatively simple metal, such as sodium, can be expressed to the first approximation as

$$\sigma = ne^2l/m^*v = 1/\rho,$$

where n is the number of charge carriers per unit volume; e, the electronic charge; v, the velocity of the charge carriers; l, the mean free path of the charge carriers; and m^*, the effective mass of the charge carriers. The mean free path of the charge carriers in most metals is believed to be in the range from 200 to 2000A. It is apparent that the specific resistivity, ρ, of a thin film of a metal should increase rapidly with decreasing thickness when the thickness is less than the normal mean free path and should change much more slowly when the thickness is greater than the normal mean free path. The mean free path of the charge carriers can therefore be estimated from the variation of specific resistivity with thickness.

The outer electrons in arsenic, antimony, and bismuth are distributed between two overlapping energy bands. The unfilled energy levels in the lower band behave as positively charged carriers, n_+, while the electrons overlapping into the upper band behave as negatively charged carriers, n_-. The conductivity equation for these metals should be rewritten

$$\sigma = (ne^2l/m^*v)_+ + (ne^2l/m^*v)_-,$$

where the + and − signs refer to the holes in the lower band and the electrons in the upper band, respectively. In these metals, when pure, n_+ equals n_- and n is a small number compared to the total number of atoms. The distribution of charge carriers can be changed significantly by adding traces of impurities which may act as electron donors or acceptors. Mott and Jones[1] have estimated n_+ and n_- in bismuth from the sudden change in the magnetic anisotropy of this material when all n_- are removed by the addition of small amounts of tin and lead. In addition, the temperature dependence of the specific resistivity of bismuth was found to change sharply when all n_- are removed. In a similar manner Brown and Lane[2] have estimated n_- for antimony from measurements of the magnetic anisotropy of tin-antimony alloys. Lane and Dodd[3] have measured the temperature dependence of the specific resistivity of tin-antimony alloys and a plot of $\Delta\rho/\Delta T$ from their data shows a sharp break at one atomic percent of tin, where all n_- have been removed by the addition of this electron acceptor.

Surface energy levels[4] may have the same effect as electron acceptors in metals which have nearly filled conduction bands. Thin metal deposits offer a means of studying the effects due to the trapping of electrons in surface energy states because of the large ratio of surface to volume. The removal of conduction electrons by increasing the ratio of surface to volume should have the same effect on the properties of a metal as that produced by alloying small traces of electron acceptors. A plot of $\Delta\rho/\Delta T$ against reciprocal thickness of thin films of antimony should show a discontinuity similar to that observed for tin antimony alloys when the films are thin enough for surface electronic states to become important.

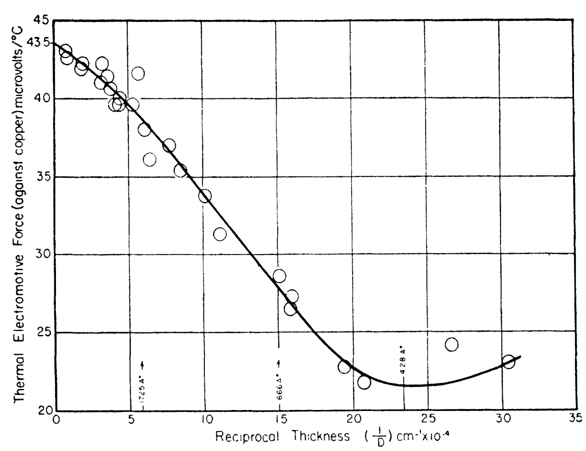

FIG. 1. Thermal e.m.f. of sublimed antimony deposits against copper between 14 and 26°C as a function of the reciprocal thickness of the antimony deposits.

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[2] S. H. Brown and C. T. Lane, Phys. Rev. **60**, 895 (1942).
[3] C. T. Lane and W. A. Dodd, Phys. Rev. **61**, 183 (1942).
[4] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 320–326, has discussed the work that has been done on the theory of surface energy states.

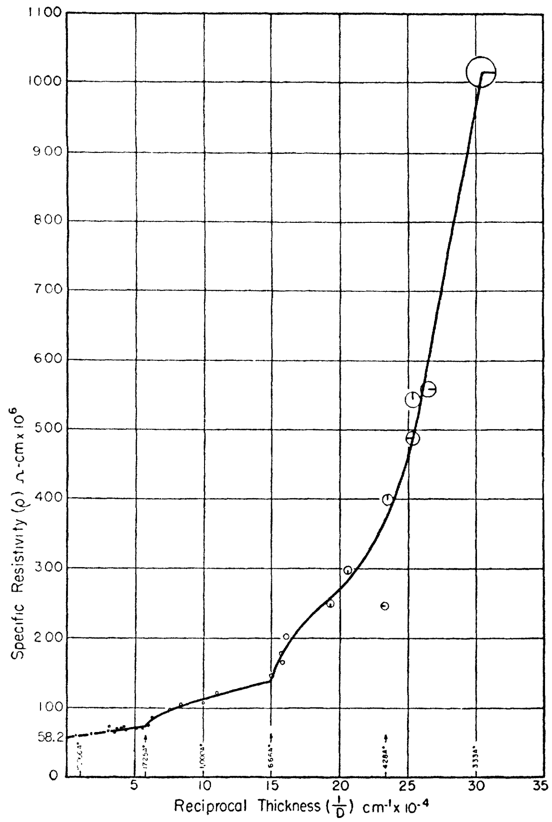

FIG. 2. Specific resistivity (at 25°C) of sublimed deposits of antimony as a function of reciprocal thickness.

EXPERIMENTAL PROCEDURE

Antimony of 99.5 percent purity was sublimed at 400°C from a folded molybdenum strip onto cellulose nitrate films weighing 130×10^{-6} g/cm². The conditions for obtaining deposits of the highest electrical conductivity were found to be:

1. pressure in the subliming chamber less than 10^{-5} mm of mercury;
2. rate of condensation less than 2×10^{-6} g/cm²/min.;
3. temperature of substrate greater than 95°C.

The amount of antimony per unit area was determined in each case either by weighing with a microbalance (to 1 microgram) or for deposits thinner than 50×10^{-6} g/cm² by an amperometric titration with potassium bromate. The nominal thicknesses of the films were obtained from the mass of antimony per unit area divided by the density of massive antimony.

Several of the thin films prepared were examined under a microscope. Except for an occasional pinhole, no flaws were found in the deposits. Lotmar[5] has published excellent photographs of thin evaporated films of antimony and the microstructure of our films was in general similar to that of the films prepared by Lotmar except that the individual crystallites, 0.1 to 0.2 mm across, were much more regular due to the method of preparation. Each crystallite observed extended through the thickness of the film.

[5] W. Lotmar, Helv. Phys. Acta 18, 369 (1945).

The specific resistivity at 25°C, the change of resistivity with temperature from −78°C to 25°C and the thermal e.m.f. in the room temperature range were measured all for nominal thicknesses of antimony from 10000A to 300A.

The resistance of a deposit was first measured at 25°C. After cooling and measuring the resistance at −78°C and intermediate temperatures, the resistance at 25°C was then found to be within 0.5 percent of the original value.

The results are given in Figs. 1–4. The uncertainty in the measurements is shown by the size of the circles.

DISCUSSION OF RESULTS

1. Change of Resistivity with Thickness at 25°C

Electron diffraction studies[6,7] have shown that evaporated antimony deposits are oriented with the principal axis perpendicular to the substrate. Further confirmation of this orientation is afforded by the thermal e.m.f. measurements given in Fig. 1. The extrapolated thermal e.m.f. of thick deposits of sublimed antimony is 43.5 $\times10^{-6}$ volt/°C. This value is to be compared with the measurements on massive antimony. Bridgman[8] obtained 46.2×10^{-6} volt/°C for single crystals measured perpendicular to the principal axis (and parallel to the principal cleavage plane), and 19.5×10^{-6} volt/°C for the thermal e.m.f. parallel to the principal axis.

From Fig. 2, the extrapolated resistivity of thick deposits of sublimed antimony measured parallel to

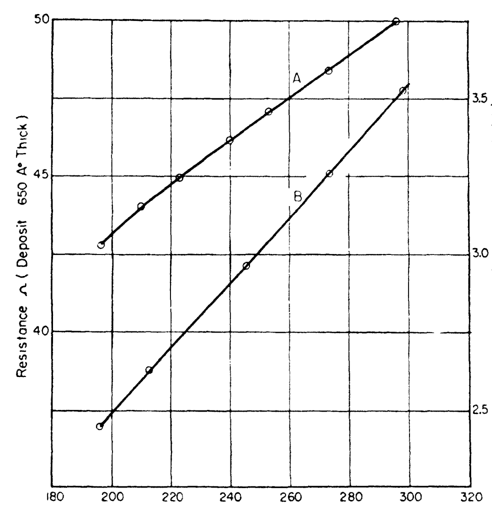

FIG. 3. The resistence of thin evaporated deposits of antimony as a function of temperature. *A*—deposits 650A thick; *B*—deposits 3500A thick.

[6] J. A. Prins, Nature 131, 760 (1933).
[7] G. Hass, Kolloid Zeits. 100, 230 (1946).
[8] P. W. Bridgman, Proc. Am. Acad. 63, 351 (1929).

the substrate (and therefore perpendicular to the principal axis) is 58.2×10^{-6} ohm-cm at 25°C (57.3×10^{-6} ohm-cm at 20°C). The specific resistivity of massive antimony perpendicular to the crystal axis is 42.6×10^{-6} ohm-cm at 20°C.[8] We believe that the increased resistivity of thick sublimed deposits is due to additional electron scattering at the mosaic boundaries present in sublimed deposits of antimony. Lotmar[9] estimated the mosaic size in sublimed deposits to be of the order of 300A.

Figure 2, the plot of specific resistivity *vs.* reciprocal thickness, shows two distinct breaks, one at 1725 (±75)A and one at 666A. We believe that the two breaks correspond to the mean free paths of the two conducting processes in thin deposits of antimony. Assuming that both conduction processes contribute significantly to the conductivity of antimony, it is estimated that the mean free paths for the two processes in annealed *massive* antimony are 2500A and 750A, and that the mean free path due to mosaic scattering alone is 5000A. This value was obtained using the extrapolated value of the specific resistivity of the sublimed deposits at 25°C, 58.2×10^{-6} ohm-cm, and the assumption that the mosaic structure alone is the cause of the increased resistivity of the thick sublimed deposits.

Several investigators have attempted to explain the effect of thickness on the mean free path of the conducting electrons.[10–12] The results of those studies lead to the conclusion that $\Delta\rho/\Delta T$ should be temperature dependent for a thin deposit. In Fig. 3 we present the data for the −78° to 25°C temperature range for a sublimed deposit 3500A thick and for a deposit 650A thick. $\Delta\rho/\Delta T$ is temperature independent for both deposits. Those theories are therefore inadequate when applied to antimony.

2. Change of $\Delta\rho/\Delta T$ with Thickness

Figure 4, the plot of $\Delta\rho/\Delta T$ *vs.* $1/D$ shows two breaks, one at 1725A and one at 428A. The break at 1725A is to be correlated with the corresponding break in the specific resistivity plot and so is associated with the effect of thickness on the mean free path of one of the conduction processes. The measurements for Fig. 4 are probably not precise enough to show a small break which may exist at 666A. The leveling-off of the temperature derivative of resistivity for thicknesses less than 1000A and the pronounced break at 428A suggests that the effect of surface energy states become important at these thicknesses. The change in $\Delta\rho/\Delta T$ with thickness can be imagined to be governed by two main processes. The change in mean free path for these thicknesses should cause $\Delta\rho/\Delta T$ to rise as the thickness decreases, while the trapping of conduction electrons on the surface should cause $\Delta\rho/\Delta T$ to fall. The pronounced break and sharp rise in the $\Delta\rho/\Delta T$ *vs.* $1/D$ plot at 428A indicates that at this thickness all the upper zone electrons in antimony are trapped in surface states.

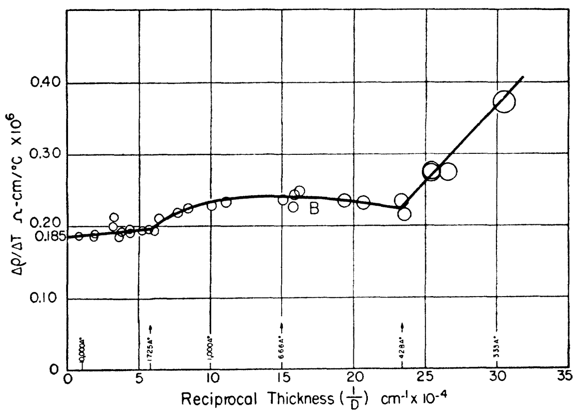

FIG. 4. The change of resistivity per degree centigrade ($\Delta\rho/\Delta T$) of sublimed deposits of antimony as a function of reciprocal thickness.

Assuming that for a layer of antimony 428A thick there is complete removal of the upper zone electrons to the surface states and that the same effect is produced by the addition of one atomic percent tin to antimony, one electron per hundred atoms of antimony are trapped in the surface or there are 1.6×10^{15} electrons trapped per square centimeter of surface.

OTHER EVIDENCE OF SURFACE STATES

In the light of our deductions it is of interest to consider the conduction processes in bismuth. It has been found[13–15] that removal of all upper zone electrons by the addition of electron acceptors to massive bismuth, cause the temperature coefficient of resistivity (at room temperature) to become negative. A negative temperature coefficient of resistivity has also been observed[16] for thin bismuth wires and similar results have been obtained[17,18] for thin evaporated bismuth deposits. By analogy to the results with antimony, negative temperature coefficient of resistivity of thin deposits of bismuth can thus also be explained by the assumption of trapping of electrons in surface states.

ACKNOWLEDGMENT

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