

## ELECTRICAL CONDUCTIVITY AND THE STRUCTURE OF THIN ANTIMONY FILMS

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*Abstract:* Measurements of the electrical conductivity and the observations of the accompanying changes of structural properties of antimony films of different thicknesses were carried out at room temperature. The electrical conduction mechanism was correlated with the structural changes occurring during growth of the films. Carbon and cleaved rock salt were used as substrates.

### 1. Introduction

Measurements of the electrical properties of thin films could offer a suitable means for characterising structural changes, if sufficient data relating the film structure to the electrical properties were available. Several investigators<sup>1-4)</sup> have pointed out that changes in the electrical properties may arise from scattering of the conduction electrons at the surfaces of the crystallites. These effects are ascribed to the structural changes occurring during growth or annealing processes.

The structure of the deposited films depends on physical parameters which could significantly affect the electrical conduction<sup>5)</sup>;

- the material and the state of the substrate,
- the pressure and composition of residual gases,
- the rate of deposition, and
- the thickness of the layer.

It has been proved<sup>6,7)</sup> that in a pressure interval of  $10^{-5}$ — $10^{-9}$  torr inclusions due to residual gases do not influence the structure of the layer essentially.

The aim of the present contribution is to investigate the electrical conductivity, the mechanism of growth and the microstructure of antimony films of different thicknesses prepared by vacuum evaporation.

The films were prepared by vacuum evaporation of highly pure antimony (99.999 %) simultaneously onto copper supported thin carbon film and quartz substrate at room temperature in a vacuum of  $10^{-6}$  torr at an evaporation rate of about 30–40 Å/s. Samples were also deposited onto thin cleaved rock salt. Electrical resistance measurements were carried out on samples deposited on quartz. Silver paste contact areas and elastic clamps secured in a frame were used. A small current passed along the film and the potential difference was measured by a potentiometer circuit. Film thickness was measured by Tolansky interference method<sup>8</sup>.

## 2. Results and discussion

The dependence of film resistance on thickness is shown in Fig. 1 (for quartz substrate) deposited at four different temperatures. The curves can be separated into four regions which are determined wholly by those structural changes which occur when the film thickness increases.

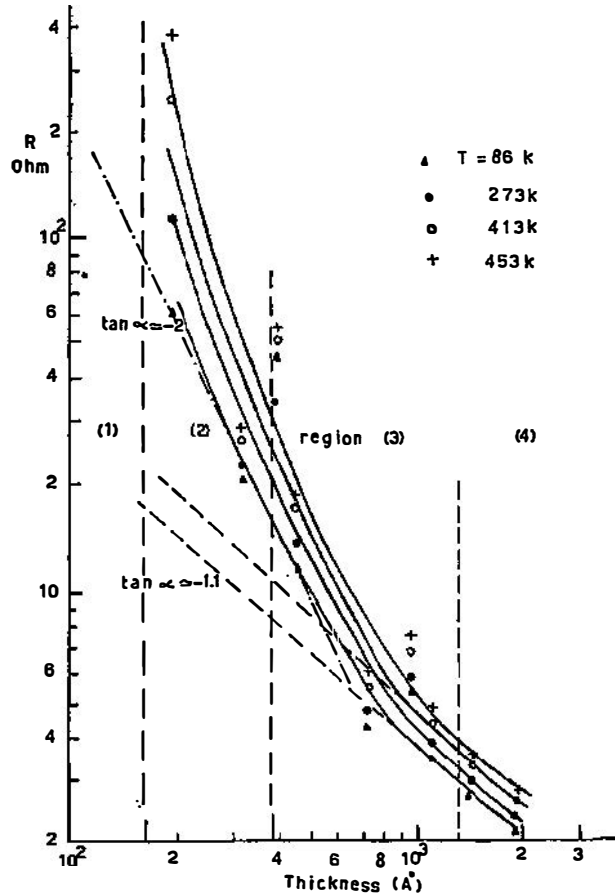


Fig. 1. The dependence of the film resistance on the film thickness at temperatures 86, 273, 413 and 453 K.

When the atoms are condensed in vacuum on the substrate they are captured by crystallization centers such as point defects, cleavage steps etc. The resistance in this case is that of the dielectric substrate, Fig. 1, region 1.

For higher film thickness (120 Å), on amorphous carbon substrate, very small and thin nuclei are formed, Fig. 2 a. The electron diffraction pattern recorded is consisted of continuous rings which indicates that the film has a polycrystalline structure and consists of aggregates of antimony crystals randomly oriented on the carbon substrate.

When the nuclei coalesce, Fig. 2 b (230 Å) the resistance falls sharply and the effective cross section of the current conducting films increases with the average thickness. With increase in film thickness the nuclei tend to become small crystallites of different shapes (Fig. 2b). Some islands are formed from several nuclei (dark areas), which either represent thicker parts of the film or due to group of crystals in the reflecting position, while others consist of a few nuclei (transparent areas). The continuous increase in the effective cross section of the current conducting film explains why the resistance continued to fall rapidly. In double logarithmic coordinates this part of the dependence  $R(d)$  is given by a straight line whose slope is  $\sim -2$  ( $R \sim d^{-2}$ ), region 2 in Fig. 1.

Larger crystals of sharp geometrical shape are formed with the deposition of further metal atoms, Fig. 2c. Small irregular holes are observed for thicker films (405 Å), Andrew et al<sup>9)</sup> have attributed these holes to bubbles of residual gases in deposited thin films of gold.

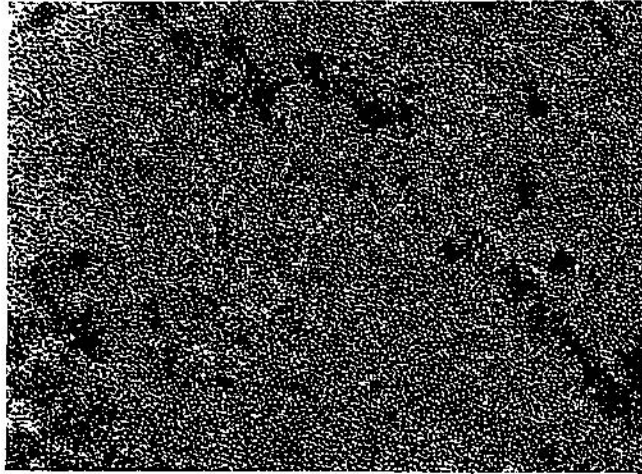
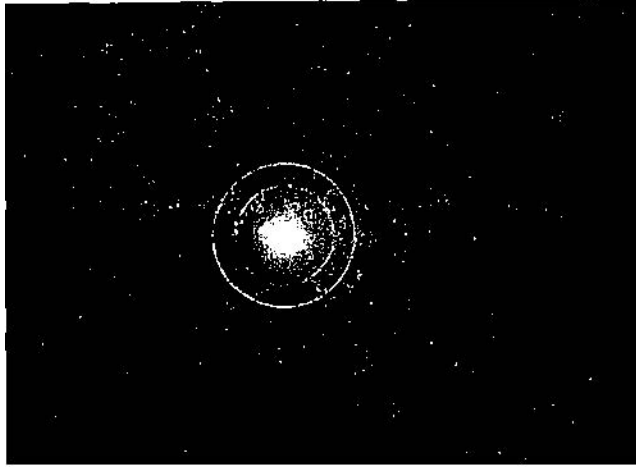
Increasing the film thickness, ( $d \sim 600-650$  Å), Fig. 2d, the film contains transparent areas, dark grains and grain boundaries. It appears that transparent areas are grains or portions of grains out of Bragg condition, dark grains are grains or portions of grains in the Bragg condition for diffraction. Subgrains are not seen in Fig. 2d, which may be confused with bend contours (narrow black lines). Black elongated features in Fig. 2d represent bend contours and diffracting grains. Continuous paths are formed from coalesced islands having a low electrical impedance which control the conduction in the film and lead to further decrease of film resistance. The gaps in the quasi continuous structure are filled to give a continuous film. The slope of the  $R(d)$  curve decreases with increasing thickness and for  $d \sim 1000$  Å the slope is about  $-1.1$  and a relation  $R \sim d^{-1.1}$  holds for film thickness  $> 1000$  Å.

Several investigators<sup>3,10,11)</sup> have shown, that the electrical resistance of thin films should in some way depend on the film thickness ( $d$ ). From their studies it follows that if the electron scattering at the film boundaries is mainly of the diffuse type and if  $d < L$ , where  $L$  is the electron mean free path in a bulk sample at a given temperature, the resistivity — thickness dependence should be

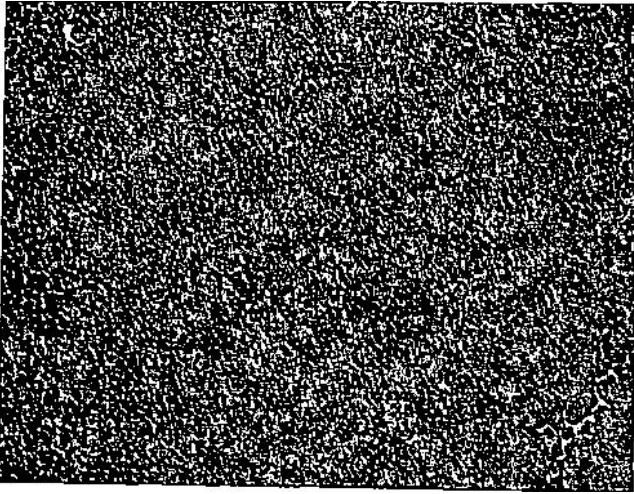
$$\rho(d)/\rho_0 \approx \frac{4L}{3d} \left( \frac{1-p}{1+p} \right) / \left( \ln \frac{L}{d} \right), \quad (1)$$

where  $\rho_0$  is the resistivity of the bulk crystal,  $p$  is the specularity parameter. For  $d \gtrsim L$ , according to Sondheimer<sup>3)</sup>, the  $\rho(d)$  dependence is given by

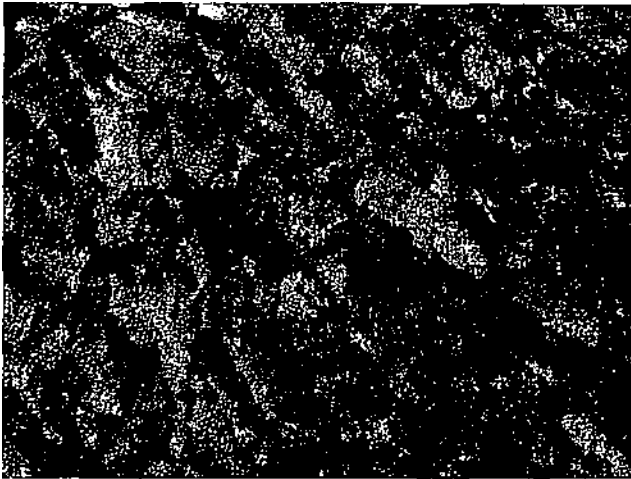
$$\rho(d)/\rho_0 = 1 + \frac{3L}{8d} (1-p). \quad (2)$$



2 a).  $\text{\AA}$  film, 24000 X,



2 b). 230 Å film, 18000,



2 c). 405 Å film, 18000 X,

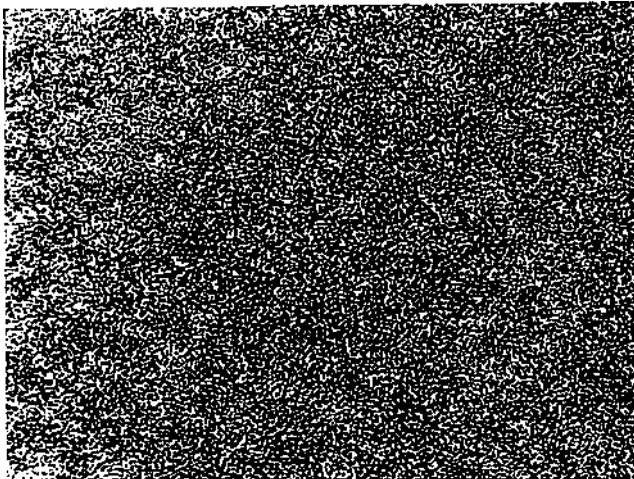


2 d). 650 Å film, 6000 X.

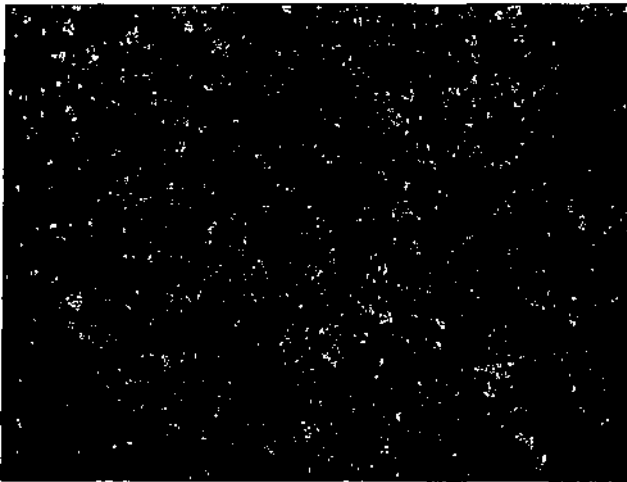
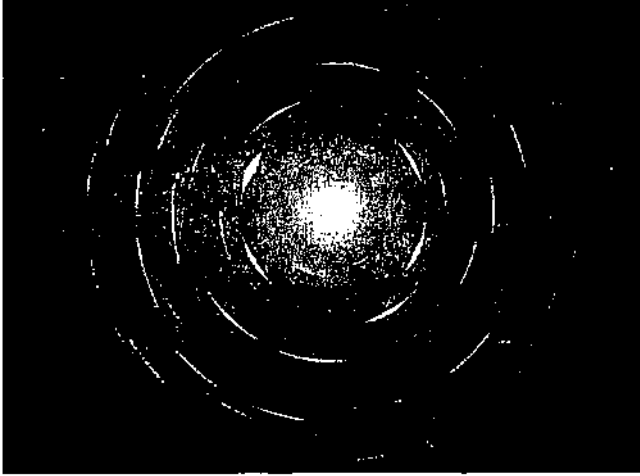
Fig. 2. Electron micrographs of antimony films deposited on amorphous carbon substrates;

For  $d < L$  the resistivity varies as  $\rho(d) \sim \frac{1}{d}$ , therefore,  $R(d) \sim \frac{L}{d^2} \left( \ln \frac{L}{d} \right)^{-1}$ , i. e. the resistance  $R(d)$  should vary and decrease as  $d$  increases, closely in accordance with  $d^{-2}$  (due to the factor  $L/d^2$  which decreases much faster than the factor  $\left( \ln \frac{L}{d} \right)^{-1}$  increases). While for  $d \gtrsim L$ , the resistance should vary as  $R \sim d^{-1}$ .

The structure of thin antimony films deposited on a cleaved rock salt substrate are shown in Fig. 3. For thickness of the film of about 120 Å (Fig. 3a) an-



3 a). 120 Å film, 9000 X,



3 b). 250 Å film, 18000 X,

timony nucleii are small crystallites which predominantly coalesced to worm-like islands. This indicates that the stage of coalescence between nucleii is more pronounced than in the case of carbon substrate.

For thicker films 250 Å coalescence of nucleii and formation of grains is observed (Fig. 3b). At this stage, the electron diffraction pattern consists of arcs having the most intense blackening in the center. This shows that the film consists of many crystals which are preferentially oriented in respect to the electron beam (this is manifested as arcy appearance of the rings in the diffraction pattern), due to the influence of the rock salt substrate (an effect close to epitaxy). By indexing the pattern, the orientation of the crystals is found to be close to [221].



3 c). 405 Å film, 9000 X,



3 d). 700 Å film, 6000 X.

Fig. 3. Electron micrographs of antimony films deposited on a cleaved rock salt substrate;

Large crystals with sharp geometrical shapes produced by coalescence are formed with further increase of the film thickness, Fig. 3c.

For thicker films  $d > 700 \text{ \AA}$  nearly continuous film appears (Fig. 3d) (700 Å), with aggregates of thick particles superimposed on the transparent thin film. Black areas in Fig. 3d may represent grains and/or parts of grains in reflecting position. It appears that hole formation is observed at thicknesses higher than that in the case of amorphous carbon substrate.



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