

Influence of Substrate Temperature on Semiconducting Properties of Thin Films *

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The influence of the substrate temperature during deposition on various semiconducting parameters viz. Hall coefficient (R_H), conductivity (σ), Hall mobility (μ_H), carrier concentration (n) and mean free path (l_0) of vacuum deposited films of Tl_2Se and Tl_2Te compounds has been studied. Increasing values of R_H , σ , μ_H and l_0 with increasing substrate temperature are explained by a decrease of growth defects of the films with rising substrate temperature.

In our previous communications on the semiconducting properties of thin films¹⁻⁴ it has been shown that many of the semiconducting parameters are considerably affected by deposition conditions, such as rate of evaporation, substrate temperature and the nature of the substrate. It was also observed that the deposits formed at higher substrate temperatures contained fewer charge carriers but at the same time showed higher conductivities⁵. In this paper this has been investigated in more detail for thin films of Tl_2Te and Tl_2Se .

Experimental

Thallium selenide and thallium telluride were prepared by melting the respective elements in atomic proportion (2 : 1) in vacuum sealed silica tubes. X-ray powder photographs were taken to identify these compounds.

The thin films, used in the present investigation, were obtained by evaporating small quantities of these compounds in a vacuum unit. The ultimate vacuum was of the order of $\cong 10^{-4}$ mm of Hg. Glass substrates (4.5×1.1 cm²) were used for the deposition. For the higher substrate temperature depositions a heater was placed over the substrate and the temperature was noted with a chromel-alumel thermocouple. The rate of evaporation for thallium telluride and thallium selenide was 95 Å/min and 70 Å/min respectively. The specimens thus prepared

were annealed in vacuo at 90 °C and 130 °C and cooled to room temperature, for the subsequent measurements. The thickness of the films was estimated from the difference in weight of the samples before and after the deposition and from the knowledge of the significant area of the film, assuming, that the film had the same density as the bulk material. The measurements of Hall coefficient (R_H) and conductivity (σ) were carried out at room temperature in the same way as described earlier².

Results

All samples of thallium selenide were 'n' type and those of thallium telluride were 'p' type. Figs. 1 and 2 show the variation of the Hall coefficient (R_H) with thickness and substrate temperature for thallium selenide and thallium telluride films respectively. It is clear from these graphs that the Hall coefficient increases with increasing film thickness and ultimately has a tendency to become constant. At higher substrate temperatures R_H was much greater than at the lower temperatures. The large increase in R_H with rising substrate temperature and the comparatively smaller increase with rising film thickness obtained for the same material under more or less the same evaporating conditions is, no doubt, due to a corresponding decrease in carrier concentration. As is well known, the presence of defects in films has same effect as that of impurities in bulk

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¹ A. GOSWAMI and S. S. KOLI, Proceedings of the International Symposium on Basic Problems in Thin Film Physics, Clausthal, West Germany (Academy of Sciences, Göttingen). Edited by R. NIEDERMAYER and H. MAYER, p. 646, 1966.

² V. D. DEOKAR and A. GOSWAMI, *ibid.*, p. 653 [1966].

³ A. GOSWAMI and S. S. KOLI, Z. Naturforsch. **21 a**, 1462 [1966].

⁴ A. GOSWAMI and R. H. JOG, Indian J. Pure Appl. Phys. **2**, 407 [1964].

⁵ V. D. DEOKAR and A. GOSWAMI, Indian J. Pure Appl. Phys. **4**, 288 [1966].



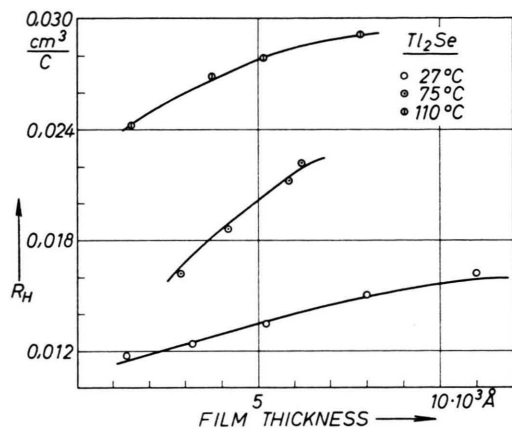


Fig. 1. R_H vs film thickness for Tl_2Se . Substrate Temperature
 \circ 27 °C; \odot 75 °C; $(|)$ 110 °C.

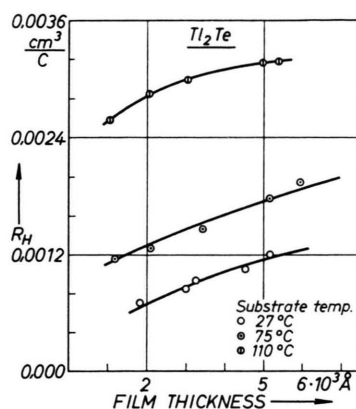


Fig. 2. R_H vs film thickness for Tl_2Te .
 \circ , \odot , $(|)$ see Fig. 1.

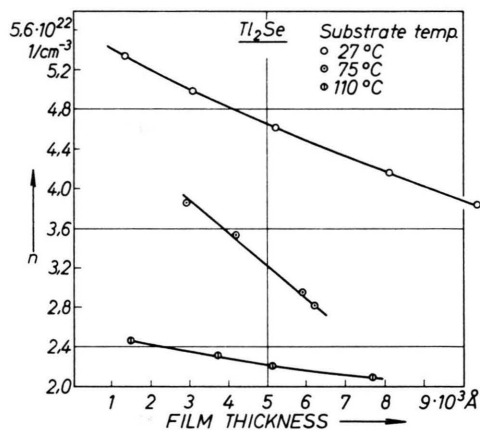


Fig. 3. n vs film thickness for Tl_2Se .
 \circ , \odot , $(|)$ see Fig. 1.

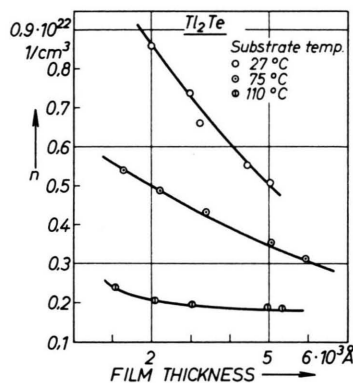


Fig. 4. n vs film thickness for Tl_2Te .
 \circ , \odot , $(|)$ see Fig. 1.

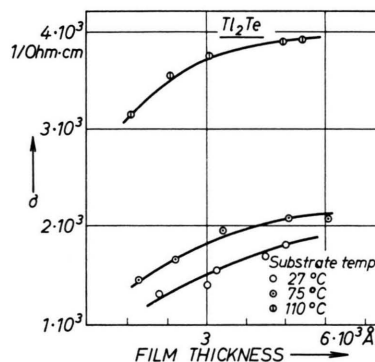
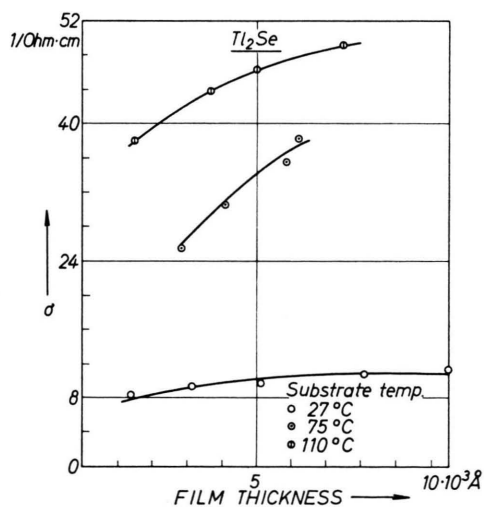


Fig. 6. σ vs film thickness for Tl_2Te .
 \circ , \odot , $(|)$ see Fig. 1.

Fig. 5. σ vs film thickness for Tl_2Se .
 \circ , \odot , $(|)$ see Fig. 1.

materials. The carrier concentration (n) was also calculated using the relation:

$$R_H = \pm \nu / n e,$$

where ν is the scattering factor ($\nu = 1$ to 1.2) and other symbols having their usual meaning.

Figs. 3 and 4 show the variation of the carrier concentration for different film thicknesses and substrate temperatures. It is evident from these curves that n decreased with increase of film thickness and substrate temperature.

The conductivity of these films was measured at room temperature. Figs. 5 and 6 show the variation of conductivity (σ) with film thickness and substrate temperature. It is seen that conductivity increases considerably with the film thickness as well as with substrate temperature.

The conductivity is given by the relation

$$\sigma = n l_0 \frac{1}{225 \sqrt{2} \pi m^* k T}$$

where l_0 is the mean free path and the other symbols have their usual meaning. It may be mentioned that the factor in parenthesis is constant at a particular temperature. Thus, it seems that the increase of σ is due to a great increase in l_0 , overcompensating for the decrease of n . Values of l_0 were calculated by using the expression based on the Lorentz-Sommerfeld theory

$$\mu_H = \frac{e l_0}{225 \sqrt{2} \pi m^* k T}$$

and also by using the relation

$$Q d = Q_\infty (d + 3/8 l_0)$$

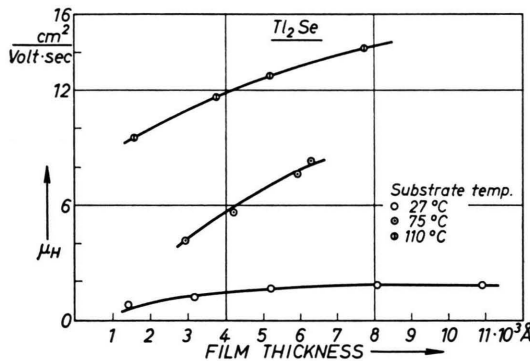


Fig. 7. μ_H vs film thickness for Tl_2Se .
○, ◐, (◑) see Fig. 1.

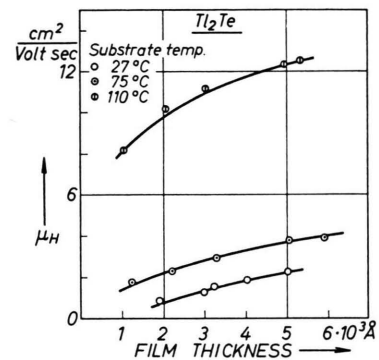


Fig. 8. μ_H vs film thickness for Tl_2Te .
○, ◐, (◑) see Fig. 1.

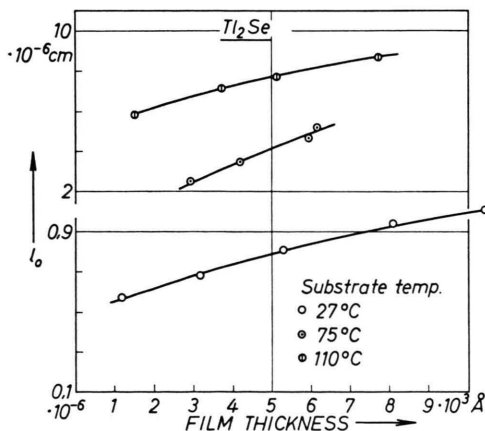


Fig. 9. l_0 vs film thickness for Tl_2Se .
○, ◐, (◑) see Fig. 1.

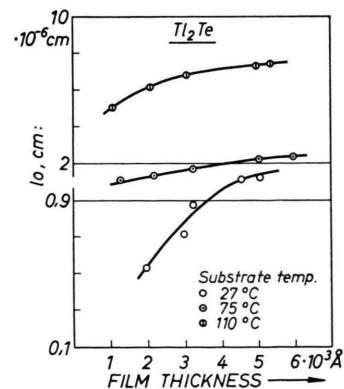


Fig. 10. l_0 vs film thickness for Tl_2Te .
○, ◐, (◑) see Fig. 1.

derived by Sondheimer and later used by MAYER⁶, where d = thickness of the film, ρ = resistivity of the film, ρ_{∞} = resistivity of the bulk material having the same structure and approximately the same number of defects as the films, l_0 = mean free path of the charge carriers. The values of l_0 calculated by the two methods were found to agree satisfactorily.

Figs. 7 and 8 show the variation of the Hall mobility (μ_H) with film thickness and substrate tem-

perature; the mobility being the product of Hall coefficient and conductivity: i. e. $\mu_H = R_H \sigma$.

Figs. 9 and 10 show the variation of the mean free path with film thickness and substrate temperature. The mean free path increases considerably with increasing film thickness and substrate temperature. Thus, as suggested before, the rise in conductivity was primarily due to a rise in the value of the mean free path.

The above studies clearly show that the substrate temperature at the time of deposition considerably modifies the film properties.

⁶ H. MAYER, Proc. of Int. Conf. "Structure and Properties of Thin Film", Bolton, Landing, New York, 225 (Sept. 1959).

Oxide and Hydroxide Activity Determination in Oxide Doped Lithium Fluoride

II. Total Oxygen Content Determination

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Results of independent measurements of thermodynamic activity (by a mass spectrometric method) and concentration (by neutron activation analysis) of lithium oxide in solid lithium fluoride are discussed. The analytical procedures involved as well as the potential uses of these experimental techniques for investigating fluoride-oxide systems are also described.

In a previous paper¹ dealing with the solubility of lithium hydroxide and lithium-oxide in solid lithium fluoride at temperatures ranging between about 600 °C and 760 °C, a method for determining the oxide and hydroxide activity (based on measurements of the partial pressures of water and hydrofluoric acid) was described. An indirect evaluation of the activity coefficient of lithium hydroxide was carried out, by utilizing the phase diagram of the system² LiOH—LiF, which indicates that its value is very near to one, in the range of the very diluted solid solutions we studied. Unfortunately, due to the lack of information on the solid state solubility of lithium oxide in lithium fluoride³, activity coefficients of lithium oxide could not be calculated in the same manner, and the direct evaluation of the total oxygen content was necessary.

The present paper deals with the results of independent measurements of lithium oxide activity and concentration in lithium fluoride.

Experimental

1. Oxide and hydroxide activity determination

The oxide and hydroxide activity was determined according to the procedures outlined in a previous paper¹ by measuring the water and hydrofluoric acid partial pressures in equilibrium over a solid lithium fluoride sample. The sample (contained in a double walled silica cell) was doped with lithium oxide and hydroxide by keeping it for a period of about 40 hours at about 600 °C and $1 \cdot 10^{-6}$ Torr water partial pressure.

Immediately before quenching the sample was analyzed for oxide and hydroxide activities by measuring the water and hydrofluoric acid partial pressures.

The samples were quenched by streaming cold gas in the cell jacket. After quenching the cell was filled with inert gas at reduced pressure, sealed off, disconnected from the vacuum plant and transferred into a dry box filled with argon. There the cell was opened, the sintered sample milled and thereafter transferred into a small fused silica spheric capsule of 10 mm diameter at the end of a thin silica tube provided with a stopcock on the top.

¹ G. TREVISAN and S. PIZZINI, Z. Naturforsch. **22 a**, 651 [1967].

² G. SCARPA, Atti Accad. Naz. Lincei Rend. **24**, II Sem. V Serie 476 [1915].

³ Y. HAVEN, Rec. Trav. Chim. **69**, 1505 [1950].