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SURFACE TRANSPORT OF CARRIERS IN EPITAXIAL $Pb_{0.82}Sn_{0.18}Te$ FILMS AT TEMPERATURE 77 K

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The dependences of the Hall coefficient on the thickness and on the Hall mobility for epitaxial $Pb_{0.82}Sn_{0.18}Te$ films deposited on a KCl substrate were measured for 77 K. The Petritz model was used in discussing these dependences. Also, size effects due to diffusive scattering of the carriers at the semiconductor-substrate interface were analysed. Diffusive scattering is the dominating scattering mechanism for both *p*- and *n*-type films.

1. Introduction

The electrical properties of bulk materials are greatly influenced by the transport phenomena occurring at the semiconductor surface. This is particularly distinct for semiconductor films having thicknesses below 1 μm and free carrier concentrations less than 10^{18} cm^{-3}. When the current flows through the thin semiconductor film, the charge carriers are scattered not only in the bulk of the semiconductor, but also at the semiconductor surface. Owing to this, the effective mobility of the charge carriers appears to be lower than the volume mobility.

It is known that as a result of oxygen adsorption on the surface of chalcogenide crystals a *p*-type surface layer is created [1, 2]. The effects of long aging in air on the electrical properties of PbTe films evaporated on a mica substrate were investigated by Egerton and Juhasz [2]. They noticed that the Hall coefficient increases for *n*-type and decreases for *p*-type films during the first few months after deposition. In the case of thin films, the Hall coefficient was found to even change its sign which indicates a change in the type of conductivity. The above mentioned changes in the Hall coefficient are interpreted as due to diffusion of the acceptor dopant which was found to be oxygen from the surrounding atmosphere. In view of the small radius of the oxygen atom, its interstitial diffusion is very probable.

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Similar changes in the Hall coefficient during long aging in atmospheric air were observed for $Pb_{0.82}Sn_{0.18}Te$ films on a mica substrate [3] as well as for single crystals of the same composition [4].

There is nothing in the literature on the surface transport of carriers in $Pb_{1-x}Sn_xTe$, where $x > 0$. The present paper initiates investigations in this area. These investigations seem to have considerable practical significance for optimization of devices fabricated from this material (infrared detectors with a Schottky barrier or *p–n* junction).

The Hall coefficient R_H and the Hall mobility μ_H of $Pb_{0.82}Sn_{0.18}Te$ films on KCl substrate were measured at 77 K as a function of the film thickness. For interpreting the R_H and μ_H dependence on film thickness the two-layer Petritz model was used. Size effects due to the scattering of charge carriers on the substrate-semiconductor interface are also considered, since they are not accounted for by the Petritz model due to its simplicity. Information has been obtained about the surface charge concentration, the surface mobility as well as the charge concentration and mobility inside the films.

2. *Experimental data*

$Pb_{0.82}Sn_{0.18}Te$ films were deposited on a fresh cleaved KCl substrate using a modified hot-wall evaporation technique (HWE) which has been described in detail in Ref. [5]. The evaporation arrangement includes two independent sources: the main source containing $Pb_{0.82}Sn_{0.18}Te_{0.99}$ with metal excess and an additional tellurium source. The temperature of the tellurium source renders control of the stoichiometric composition possible. The heated quartz channel with a baffle inside it constitutes the principal part of the arrangement. The baffle was found to improve the thermal equilibrium between the evaporated molecules and the channel.

Evaporation of the film was performed in a vacuum $\leqslant 3\times10^{-6}$ Tr with the $Pb_{0.82}Sn_{0.18}Te_{0.99}$ source temperature 853K, the channel temperature near the baffle 813K and the substrate temperature 573K. The tellurium source temperature was varied in the range 420—610K.

For temperatures of the tellurium source below ca. 500K the films revealed electron conductivity; at higher temperatures, hole conductivity was observed. The rate of film growth was about 5 μm/h.

The *n*-type and *p*-type films were deposited for the present investigation at tellurium source temperatures of 493K and 513K, respectively.

The proper film geometry for peforming Hall measurements was obtained by using stainless steel masks. The electric properties of the films were measured one to two days after deposition immediately after the sample was removed from vacuum. The Hall voltage and the film conductivity were measured by the direct current method at a magnetic field of 0.1 Ts and current of 2 mA. The Hall mobility and carrier concentration were found from the relations $\mu_H = \sigma R_H$ and $R_H = -1/nq$, respectively.

The rentgenografic investigations revealed that the films are monocrystalline with a [100] orientation, i.e. they coincide with the cleaved KCl substrate orientation.

3. *Two-layer Petritz model*

The two-layer Petritz model has been applied to analyse the R_H and μ_H dependences on film thickness [6]. The model is shown in Fig. 1a. The sample is considered as consisting of two parallel layers: a surface layer of thickness d_s, conductivity σ_s, Hall coefficient R_s

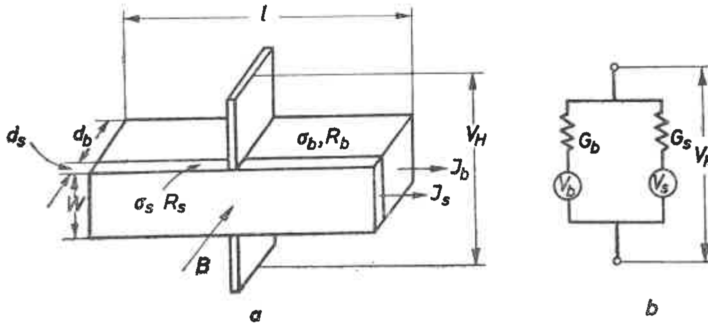

Fig. 1. Sample configuration (a) and the equivalent circuit according to the two-layer Petritz model (b).

and conductance G_s and the bulk layer with the parameters d_b, σ_b, R_b and G_b, respectively. The surface layer is not protected and, therefore, exposed to the action of the surrounding air.

The equivalent circuit of the two-layer model shown in Fig. 1b can be treated as two voltage sources in parallel. Considering the circuit we get:

$$V_H = \frac{V_s G_s + V_b G_b}{G_s + G_b}, \tag{1}$$

where

$$G_s = \frac{\sigma_s d_s l}{w}, \quad G_b = \frac{\sigma_b d_b l}{w}. \tag{2}$$

On the other hand

$$R_H = \frac{V_H d}{IB}, \tag{3}$$

where I is the current flowing through the sample, B is the magnetic field induction. Considering (1) and (2) we get:

$$R_H = \frac{(\sigma_s^2 d_s R_s + \sigma_b^2 d_b R_b) d}{(\sigma_s d_s + \sigma_b d_b)^2}. \tag{4}$$

The mean value of the film conductivity is

$$\sigma = \frac{\sigma_s d_s + \sigma_b d_b}{d} \tag{5}$$

and of the carrier mobility is

$$\mu_{\mathrm{H}} = \sigma R_{\mathrm{H}} = \frac{\sigma_{\mathrm{s}}^2 d_{\mathrm{s}} R_{\mathrm{s}} + \sigma_{\mathrm{b}}^2 d_{\mathrm{b}} R_{\mathrm{b}}}{\sigma_{\mathrm{s}} d_{\mathrm{s}} + \sigma_{\mathrm{b}} d_{\mathrm{b}}}. \tag{6}$$

Later in this work relations (4) and (6) will be used for choosing such parameters as $R_{\mathrm{H}}(d)$, $\mu_{\mathrm{H}}(d)$ which fit best the experimental data.

Knowing the values of d_{s} and R_{s} it is possible to estimate the concentration of excess charge in the surface phase:

$$\Delta P = \frac{d_{\mathrm{s}}}{q R_{\mathrm{s}}}. \tag{7}$$

4. Surface scattering of charge carriers

Charge carriers, when colliding with the semiconductor surface, may interact in different ways. Carrier mobility is that parameter sensitive to the type of interaction. Two extreme cases are distinguished here: weak and strong influence of the surface on the charge carrier mobility when drifting parallel to the surface.

(*i*) In the case of weak interaction specular scattering takes place, where the interaction reduces to a change in the component of charge velocity normal to the surface while the parallel component is assumed to be constant, i.e. the charge mobility should be constant.

(*ii*) For the second case fully diffusive scattering takes place, where the component of the velocity parallel to the surface changes and the velocity assumes any arbitrarily selected direction in the area of the half sphere lying on the semiconductor surface; of course, the full diffusive scattering defines the maximum possible influence of the surface on the mobility of the carriers which interact with it, if the trapping processes are neglected.

Several reasons have been proposed for diffusive scattering of the carriers at the free surface of the film. According to Greene [7] diffusive scattering is related to:

(a) the presence of surface roughness as well as charged centers, dopants and defects in the lattice of the film surface region,
(b) a change in the number of scattering events with variation of the angle of electronic waves incident on the surface,
(c) thermal oscillation of the crystal lattice and the corresponding phonon waves,
(d) deviations of the surface from ideal,
(e) charge carrier wave function limitations at the boundary,
(f) appearance of surface states and of a charge gradient in the surface layer.

The Petritz model assumes that the surface layer is the front layer exposed to the action of the environment, whereas the influence of the substrate-semiconductor interface is neglected.

It is possible that reasons for scattering similar to those mentioned above are in effect for the surface layer at the film-substrate interface.

If the substrate-semiconductor interface is assumed to scatter the carriers in a diffusive

manner, the effective mobility for flat band conditions will depend on the sample thickness [8]:

$$\mu = \frac{\mu_b}{1+l/d_b}, \quad \text{for } d_b \gg d_s, \tag{8}$$

where l is the mean free path, μ_b is the mobility in the bulk layer and d_b is the bulk layer thickness. Assuming degenerate statistics, the mean free path is defined as:

$$l = (\mu_0 h/2q)(3n/\pi)^{1/3}, \tag{9}$$

where n is the carrier concentration in the bulk layer, and h is the Planck constant.

5. *Properties of n-type films*

The results of measurements of the Hall coefficient and Hall mobilities for many n-type samples versus film thickness are presented in Fig. 2. The solid curves have been calculated in terms of the Petritz model for the parameters given in Fig. 2. The values of R_b and μ_b have been obtained by extrapolating the $R_H(d)$ and $\mu_H(d)$ dependences to thick films. Since additional scattering of the carriers at the semiconductor-substrate

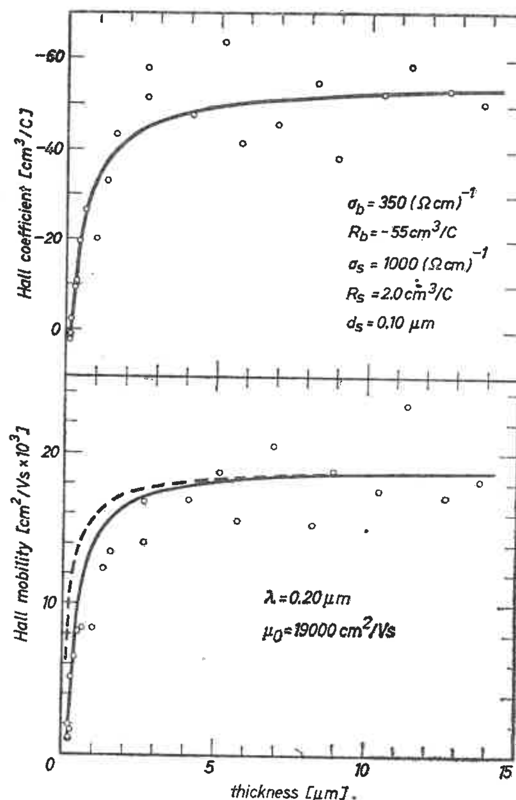

Fig. 2. Hall coefficient and Hall mobility at 77 K for n-type $Pb_{0.82}Sn_{0.18}Te$ films as a function of sample thickness

interface may occur, which was neglected in the Petritz model, special care was taken to fit the $R_H(d)$ dependence to the relevant measured dependence. The agreement between the calculated and measured Hall coefficient dependence on film thickness obtained in this way was found to be very good. Disagreement was observed, however, between the theoretical and experimental dependence $\mu_H(d)$. It was found impossible to obtain a fit for the parameters σ_b, R_b, σ_s, R_s and d_s for the dependence $\mu_H(d)$ as good as that for the dependence $R_H(d)$.

The above mentioned discrepancies can be due to size effects, which considerably reduce the mobility of carriers in thin films. The dashed curve in Fig. 2 was obtained under the assumption that the diffusive mechanism occurs at the semiconductor-substrate interface. It was assumed in the calculations that $\mu_b = 19000\ cm^2/Vs$ and the mean free path calculated from equation (9) $l = 0.20\ \mu m$. The calculated curve suggests that the size effects are responsible for some reduction in mobility in films having thicknesses below 1 μm.

The low value of surface mobility $\mu_s = \sigma_s/en_s = 2000\ cm^2/Vs$ as compared to $\mu_b = 19000\ cm^2/Vs$ points to the considerable contribution of diffusive scattering at the surface exposed to the action of surrounding air. The small value of the $\mu_s/\mu_b = 0.11$ ratio may also be explained by diffusive scattering at the semiconductor-substrate interface.

A surface layer of thickness d_s reveals p-type conductivity, as distinguished from the bulk film which shows n-type conductivity. The surface layer may be treated as an inversion layer. The excess concentration of charge carriers in the surface layer has been found from Eq. (7) to be 3.1×10^{13} holes/cm².

As was mentioned at the beginning of the present work the acceptor dopant creating the hole conductivity of the surface layer is oxygen from the surrounding air.

6. *Properties of p-type films*

Figure 3 presents the measured $R_H(d)$ and $\mu_H(d)$ relations for p-type samples. These relations calculated in terms of the Petritz model are represented in Fig. 3 by solid curves for the parameters denoted in the figure. Like for n-type films, attempts were made to obtain the best fit of the Hall coefficient dependence on film thicknesses to experimental data. The contribution of diffusive scattering at the semiconductor-substrate interface is represented by a dashed curve; the following parameters were assumed: $\mu_b = 15000\ cm^2/Vs$ and $l = 0.22\ \mu m$.

From Fig. 3 we see that diffusive scattering decreases significantly the effective mobility in thin samples of less than 1 μm.

The lack of a change in sign of R_H for the data given in Fig. 3 makes it difficult to obtain an accurate value for d_s. From Eqs. (4) and (6) it is seen that the calculated curves are sensitive to the σ_s variations, the accuracy of d_s being poor.

The surface mobility of the p-type was found to be $\mu_s = 7500\ cm^2/Vs$, so $\mu_s/\mu_b = 0.5$. This value indicates that the contribution of diffusive scattering at one or both film surfaces is smaller for p-type than for n-type films. The surface charge concentration was found to be 6.2×10^{13} holes/cm² i.e. it is of the same order of magnitude as for n-type films.

Differences in the thermal expansion coefficients of film and substrate may cause scattering for both n-type and p-type films at the film-substrate interface. These coefficients are known to be $37 \times 10^{-6} K^{-1}$ and $20 \times 10^{-6} K^{-1}$ for KCl and $Pb_{0.82}Sn_{0.18}Te$, respectively [9].

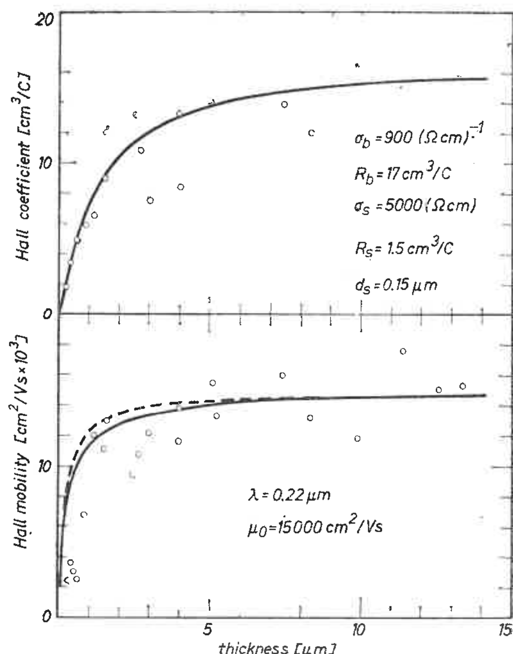

Fig. 3. Hall coefficient and Hall mobility at 77 K for p-type $Pb_{0.82}Sn_{0.18}Te$ films as a function of sample thickness

The differences of thermal expansion coefficients cause stresses in the region of layer near the substrate surface. The latter in turn may cause the generation of defects. These defects may be the reason of diffusive scattering described in Section 4 of the work (group (a) of the possible reasons).

7. *Conclusions*

Oxygen atoms adsorbed on the surface of $Pb_{0.82}Sn_{0.18}Te$ films create an excess surface charge of concentration of the order of 10^{13}—10^{14} cm^{-2}. This charge causes the bending of the energy bands in such a manner that an inversion layer is formed on n-type samples and an enriched layer on the p-type samples. However, it does not seem possible that the surface layer of thickness $d_s = 0.10$—0.15 μm is the result of oxygen adsorption only. In the case of pure adsorption d_s ought to be smaller. Attempts were made to fit the experimental dependences $R_H(d)$ and $\mu_H(d)$ by choosing smaller values of d_s and

higher values of σ_s than those given in Figs 2 and 3. A divergence was, however, found to exist between the calculated and measured values of $R_H(d)$, especially for $d < 1$ μm. This divergence appears to be more distinct for $\mu_H(d)$.

Probably the surface layer thickness d_s is defined by processes, which can be classified with respect to their duration into long and short ones. Among the short processes, we can mention the adsorption of oxygen on the surface or the formation of the surface oxide layer, whereas the gradual diffusive penetration of oxygen into the film is a long process.

Other mechanisms may also be decisive. Recently, Parker and Williams [10] proposed another mechanism of oxygen adsorbtion on the PbTe film surface. They claim that oxygen dopes the *n*-type PbTe films as a result of its reaction with excess lead which diffuses interstitially from the interior of the films to the surface (the diffusion coefficient of lead is of the order of 10^{-14} cm^2/s).

The effects seem to be quite complex and, therefore, difficult to interpret. The investigation of the kinetics of the influence of oxygen on the electric properties of the film can provide some information. Such investigations are in progress.

The Petritz model does not seem to describe the properties of the carrier transport in the films very precisely since, in this model, the film is treated as composed of two homogeneous layers. It is, however, convenient in use as it allows one to easily obtain information about the surface transport of the carriers.

For *n*-type as well as *p*-type films, diffusive scattering seems to be the dominant mechanism of surface scattering (at both surfaces of the film). However, the contribution of diffusive scattering in *n*-type films is greater. This may be a consequence of that on the surface of *n*-type films metallic precipitates are deposited [11]. The precipitates as surface inhomogeneities may be additional scattering centers. No such precipitate is observed on *p*-type films.

The results obtained seem to have some practical significance. The creation of an enriched layer on the *p*-type film surface is disadvantageous to ward the construction of Schottky barrier infrared detectors, and is probably the main reason why the present author failed to fabricate metal-semiconductor infrared detectors (Pb $-$ (*p*) $Pb_{0.82}Sn_{0.18}Te$) with high detection parameters. Such a technology should be developed which would allow one to evaporate the lead electrode and then protect the M–S contact site by applying an insulating film, for instance SiO_x, As_2Se_3, directly after deposition of the $Pb_{0.82}Sn_{0.18}Te$ *p*-type film with the required parameters (concentration of carriers below 5×10^{17} at 77K) is completed without interrupting the vacuum.

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