

Influence of oxidation on the transport properties of IV–VI-thin films

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Abstract

The effect of oxidation at room temperature on the thickness dependences of transport properties of IV–VI (PbS, PbSe, PbTe) thin films was studied. The effect of charge carrier concentration on the character of these dependences in n-PbTe thin films was detected. The regularities in the behavior of IV–VI thin films exposed to air were established. The experimental results are interpreted within the framework of models taking into consideration the presence of compensating acceptor states created by oxygen on the film surface.

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1. Introduction

It is well known that oxidation significantly affects the transport properties of lead chalcogenides [1]. Oxygen acts as an acceptor, causing the appearance of p-type charge carriers in crystals and thin films. In Refs. [2,3], we showed that the presence of an oxidized layer on the surface of the IV–VI thin films with thicknesses $d = 5\text{--}200$ nm causes a strong d -dependence of the thermoelectric properties, including inversion of the dominant carrier sign from n to p at $d_1 \leq 80\text{--}125$ nm. The d -dependences were interpreted within

the framework of the models considering both n- and p-type carriers.

The goal of the present work is to compare the effect of oxidation on the thickness dependences of transport properties of PbS, PbSe, PbTe thin films and to investigate the influence of the charge carrier concentration n in the n-PbTe thin films on the character of these dependences.

2. Results

PbTe epitaxial thin films ($d = 2\text{--}400$ nm) were prepared by thermal evaporation in vacuum ($10^{-5}\text{--}10^{-6}$) Pa and deposition onto (001) KCl substrates. To increase n in PbTe films, a bulk sample of n-PbTe

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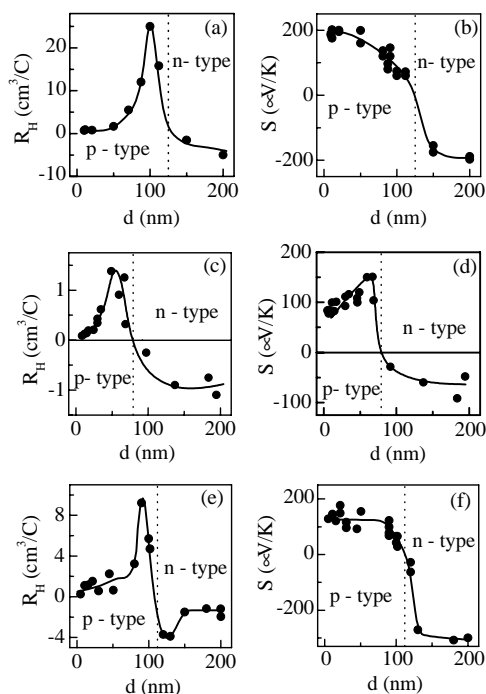


Fig. 1. Room temperature Hall coefficient R_H (a, c, e) and Seebeck coefficient S (b, d, f) vs. PbS (a, b), PbSe (c, d), PbTe (e, f) film thickness d . The dashed vertical line denotes the d_i value where the dominant carrier sign changes.

with 2 at% of excess Pb was used as a charge. The methods of measuring the Hall coefficient R_H and the Seebeck coefficient S were similar to the ones described in Refs. [2,3].

In Fig. 1, the results for $S(d)$ and $R_H(d)$ at room temperature for PbTe, PbSe, and PbS films reported in Refs. [2,3] are shown. For all these compounds, three regions with different characteristic behaviors may be distinguished: (1) a region of p-type conductivity where R_H and S increase with increasing d ; (2) the p–n-junction region $80 < d < 125$ nm where an inversion in the type of the dominant charge carriers occurs; (3) the region of n-type conductivity where all the parameters reach saturation, and bulk behavior is approached.

The room temperature dependences $S(d)$ and $R_H(d)$ for films prepared from PbTe with 2 at% excess Pb are shown in Fig. 2. The comparison of the results obtained in this work with those for PbTe films prepared from a stoichiometric PbTe charge [2] shows

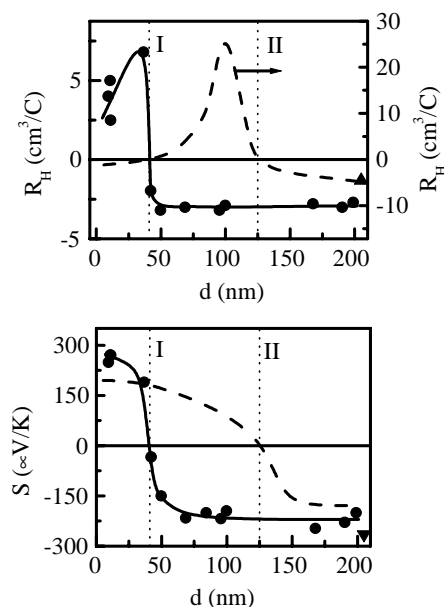


Fig. 2. Room temperature Hall coefficient R_H (a) and Seebeck coefficient S (b) vs. PbTe film thickness d , for PbTe films prepared from PbTe charge containing 2 at% excess Pb. The dependences for films prepared from a charge with a stoichiometric composition [2] are shown by the dashed curve. I and II denote the boundaries of p- and n-type conductivity regions in the present work and in Ref. [2] respectively. Triangles correspond to measurements on the bulk crystal of n-PbTe with 2 at% excess Pb.

that the increase in n results in a shift of the inversion point d_i from 125 to 40 nm.

The d -dependences of the transport properties of the PbTe films obtained in this work and the observed shift in the inversion point position are in good agreement with the two-carrier model as well as with the two-layer sandwich model we used [2,3] for considering oxidation processes in IV–VI thin films. These models are based on the following assumptions: (i) n-type carriers are present in the original film; (ii) oxygen is concentrated near the surface and forms acceptor states; (iii) the contribution to the electrical conductivity by holes is determined by the relative thicknesses of the oxidized layer (d_p) and of the film (d). The two-carrier model was used for very thin films when $d \approx d_p \approx L_D$, where d_p is the thickness of oxidized layer and L_D is the Debye shielding distance. In this case we can write expressions for S and R_H

as follows:

$$S = \frac{S_p \sigma_p - S_n \sigma_n}{\sigma_p + \sigma_n}, \quad (2.1)$$

$$R_H = \frac{r}{e} \frac{\mu_p^2 p - \mu_n^2 n}{(\mu_p p + \mu_n n)^2}, \quad (2.2)$$

where r is the Hall-factor, σ and μ are the electrical conductivity and charge carrier mobility respectively, p and n are volume concentrations of holes and electrons, and the p and n subscripts are related to holes and electrons, respectively. Since oxidation is mainly a surface effect for monocrystalline films, we can assume that the average surface concentration of acceptor levels (N_S) is constant. For the sake of simplicity, we consider μ_n , μ_p and n to be independent of d . In this case we obtain that the volume hole concentration $p = N_S/d$ and S and R_H depend on d . When d is small, the absolute value of the first term in the numerator in Eqs. (2.1) and (2.2) might be higher than that of the second term, and the carrier sign will change from n to p . As d increases, the first term decreases and so do S and R_H until $S \rightarrow 0$ and $R_H \rightarrow 0$. At large d , then S and R_H will be determined by the second term, and S and R_H will approach a constant value.

As is seen from the formulas, with increasing n -type charge carrier concentration in the thin film, the contribution of the negative term to S and R_H will increase, which will lead to a shifting of the inversion point to smaller d 's. This shift can be expected if we

consider the oxidation as a surface phenomenon and assume that the depth of oxygen atom penetration is constant and is approximately equal to the Debye shielding distance L_D . If the film is exposed to air for a long time, this condition may not be fulfilled due to diffusion processes. In the present work, all measurements were carried out on freshly prepared films.

It is seen from the results presented here that the character of the thickness dependences of the transport properties, at least for $d < 100$ nm, does not reflect the true relationship between the film thickness and these properties because of the oxidation taking place in thin films exposed to air.

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