Effect of oxidation on the thermoelectric properties of PbTe and PbS epitaxial films

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We report on the thickness d dependences of the Seebeck coefficient, electrical conductivity, and Hall coefficient of PbTe and PbS epitaxial thin films ($d = 5-200$ nm), prepared by thermal evaporation in vacuum and deposition on (001) KCl substrates. The oxidation of the films in air at 300 K leads to a sign inversion of the carrier type from n to p in films with $d \leq 125$ and 110 nm for PbTe and PbS, respectively. The observed d dependences are interpreted in terms of compensating acceptor states created by oxygen on the film surface. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1355995]

It is known that the surface adsorption of oxygen, acting as an acceptor, sensitively affects the properties of the lead chalcogenides and devices based on them.[1] Oxygen is a dopant in n-PbTe, which leads to an increase in the hole concentration with increasing oxygen concentration and eventually results in a sign inversion in carrier type.[2–13] This change in carrier type was observed for n-PbTe samples pressed in air as the grain size decreased,[3] for n-PbTe thin films under increasing oxygen pressure,[4–9] or upon annealing the films in air,[9,12] and for n-PbTe implanted with oxygen.[9,10] Oxygen near grain boundaries increases or reduces the height of the potential barriers near boundaries in n- and p-PbTe thin films, respectively.[11,12]

The annealing of PbS polycrystalline films in oxygen can lead to a change in the conductivity type ($n \rightarrow p$) and this approach is widely used for the preparation of photosensitive PbS layers.[4,13,14] As a result of oxidation, polycrystalline PbS thin films consist of n-type crystallites with p-type inversion layers on their surfaces.

Presently available results on PbTe and PbS film oxidation were obtained on relatively thick (0.1–10 μm) and usually polycrystalline films, where the O_2 pressure, the temperature, and time of annealing were variable parameters. Clearly, film thickness d is one of the most important parameters affecting the degree of oxidation of a film. With decreasing d, the role of the inversion layer in determining the film properties increases. Using monocrystalline films allows us to exclude the contribution to the electrical conductivity from the inversion layers in the crystallite or grain boundaries.

PbTe is considered to have a high potential for thermoelectric applications.[15,16] Recently, interest in the lead chalcogenides has been stimulated by theoretical predictions[17] and subsequent experimental observations[18–20] of the possibility of a significant enhancement in the thermoelectric figure of merit ZT in superlattices (SLs) based on IV–VI com-

pounds. Earlier we reported[21] an increase in the power factor for PbS/EuS SLs.

The goal of the present work is to study the d dependences of the thermoelectric properties of PbTe and PbS epitaxial thin films exposed to air at 300 K to reveal the influence of oxidation processes on the film properties. The study showed that already at 300 K, oxidation leads to a radical change in the properties of n-PbTe and n-PbS films with $d \leq 100-150$ nm and to a sharp dependence of the thermoelectric properties on d, including sign inversion of the dominant carrier type.

PbTe and PbS monocrystalline thin films ($d = 5-200$ nm) were prepared by the thermal evaporation of n-PbTe and n-PbS in vacuum ($10^{-5}-10^{-6}$ Pa) and the subsequent deposition onto (001) KCl surfaces at 520–570 K. The film thickness was monitored with a calibrated quartz resonator. Layers of EuS, used for protecting PbTe and PbS films from oxidation, were prepared by electron-beam evaporation of EuS. The thin film structure was studied by x-ray diffractometry. The Hall coefficient R_H and the electrical conductivity σ were measured using a conventional dc method in a magnetic field of 0.8 T. The measurement error of R_H and σ did not exceed 5%. The Seebeck coefficient S was determined with respect to Cu with an accuracy of better than 3%. All measurements were carried out on samples freshly extracted from the vacuum chamber at 300 K.

In Figs. 1 and 2, the d dependences of S, σ, R_H, and the thermoelectric power factor $P = S^2\sigma$ on PbTe and PbS film d are presented. S measurements [Figs. 1(a) and 1(b)] showed that thin PbTe films with $d \leq 125$ nm and PbS films with $d \leq 110$ nm are p type. In the vicinity of these d values, a sign inversion in the dominant carrier type occurs. Under further increase in d, S becomes saturated reaching values close to those observed in undoped n-PbTe single crystals. The results of R_H measurements [Figs. 1(c) and 1(d)] confirm the sign inversion of the dominant carrier with increasing d. In the range of $d \approx 150-250$ nm, R_H remains practically constant. In the $\sigma(T)$ curves [Figs. 1(e) and 1(f)] and in the $P(d)$ dependences (Fig. 2) in the vicinity of the sign inversion point, a minimum in $P(d)$ is observed.

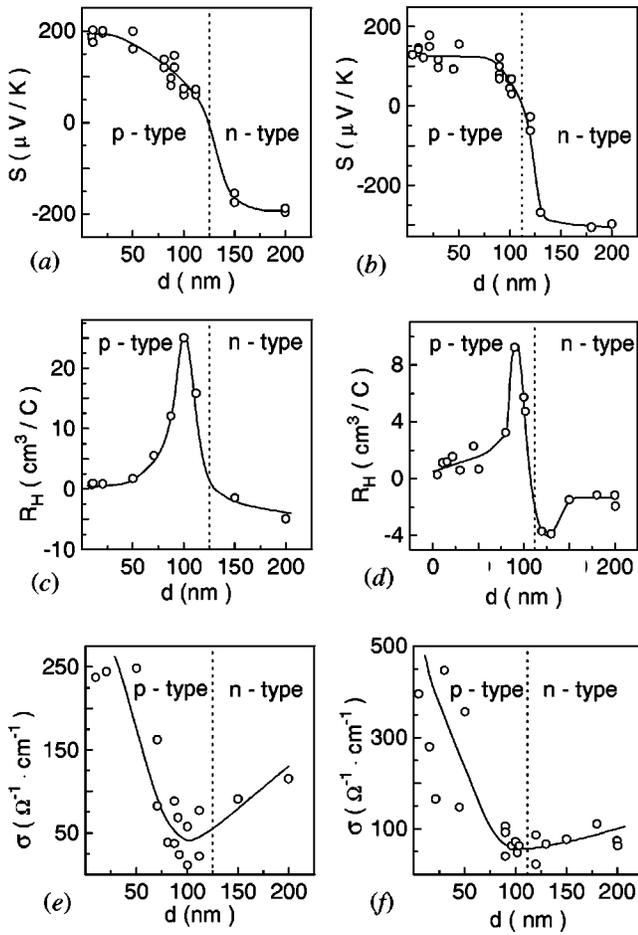[a] Author to whom correspondence should be addressed; electronic mail: millie@mgm.mit.edu

FIG. 1. Seebeck coefficient S (a), (b), Hall coefficient R_H (c), (d) and electrical conductivity σ (e), (f) vs thickness d of PbTe (a), (c), (e) and PbS (b), (d), (f) layers at 300 K. The points are experimental and the curves are a guide to the eyes.

Since Te and S are the most volatile components, one could then expect PbTe and PbS films to be enriched in Pb, and consequently to have higher concentrations of n-type charge carriers. This suggests that p-type charge carriers in PbTe and PbS thin films arise from the oxidation of the thin films in air at room temperature.

The d dependences of the electrical properties of the PbTe and PbS films observed in this work are interpreted in terms of two types of charge carriers, with n-type carriers dominating the transport of ideal PbTe and PbS films. However, oxygen is concentrated on the film surface and forms acceptor states, capturing electrons from the inner layers of the thin film. The electron contribution to the electrical con-

FIG. 2. Room temperature power factor $P = S^2\sigma$ vs d, the thickness of PbTe (a) and PbS (b) thin films.

ductivity is determined by the thickness of the oxidized layer d_p relative to d. The higher d is, the smaller this contribution will be. If d is small and $d \approx d_p$ and if d has the same order of magnitude as the Debye shielding distance,[22] the film can be considered as a semiconductor with two types of charge carriers, so that we can write relations for σ, S, and R_H as

$$\sigma = \sigma_p + \sigma_n = p\mu_p e + n\mu_n e, \tag{1}$$

$$S = \frac{S_p\sigma_p + S_n\sigma_n}{\sigma_p + \sigma_n}, \tag{2}$$

$$R_H = \frac{1}{e} \cdot \frac{\mu_p^2 p - \mu_n^2 n}{(\mu_p p + \mu_n n)^2}, \tag{3}$$

where the p and n subscripts are related to electrons and holes, respectively, and we note that S_p and S_n have opposite signs. It is also proposed that the Hall factor $r = 1$. Since oxidation is mainly a surface effect for monocrystalline films, we assume that d_p and the concentration of acceptor levels n_a are constant [$d_p \approx 30-40$ nm based on Eqs. (6) and (7) below and Figs. 1(a) and 1(b)]. Then, the hole concentration in the film volume is

$$p = n_a d_p / d, \tag{4}$$

and assuming for simplicity that μ_n, μ_p, and n do not depend on d, we write

$$\sigma_p = p\mu_p e = \frac{n_a d_p}{d} \cdot \mu_p e = \frac{A}{d}, \tag{5}$$

where $A = n_a d_p \mu_p e$. As a result, σ, S, and R_H depend on d. When d is small, the absolute value of the first term in the numerator of Eq. (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 does S until $S \to 0$. At large d, then S will be determined by the second term, and $S(d)$ approaches a constant value. Assuming that in the thinnest films, the main contribution to the electrical conductivity is made by p-type carriers (holes), we can estimate this hole concentration based on the data in Figs. 1(e) and 1(f) as $p \sim (4-7) \times 10^{18}/cm^3$ for both PbS and PbTe films.

In thick films ($d_p \ll d$), charge is transferred by the holes moving along the film surface and a film can be considered as a two-layer sandwich, consisting of a surface p layer with thickness d_p and an underlying n layer with thickness ($d_n = d - d_p$), each layer type being characterized by certain electrophysical parameters. In this case, the observed d dependences of σ, S, and R_H can also be interpreted within the simple two-layer model.[8,23] Assuming that such a bilayer composition will behave like two power sources connected in parallel, we obtain the d dependence of the kinetic coefficients for the case when the current is flowing parallel to the layer through the relations

$$\sigma = \frac{\sigma_p d_p + \sigma_n d_n}{d_p + d_n}, \tag{6}$$

$$S = \frac{S_p\sigma_p d_p + S_n\sigma_n d_n}{\sigma_p d_p + \sigma_n d_n}, \tag{7}$$

where we write $d_n = d - d_p$, and the p and n subscripts refer
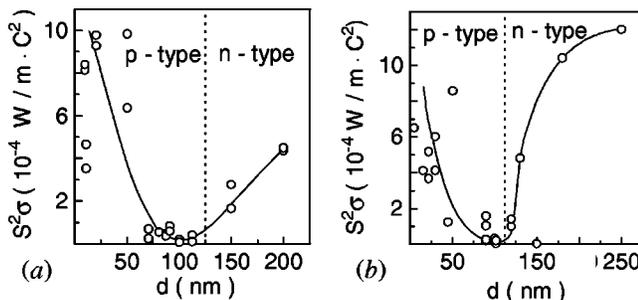
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to *p*- and *n*-type layers. If $d_p \approx d$, it is difficult to single out the layers, and it appears more sensible to interpret the results within the framework of the two-carrier model.

For protection from oxidation, PbTe and PbS films were covered with EuS layers of thickness d_{EuS} in the range of 6–60 nm. EuS was used as a spreading layer, because this wide band gap semiconducting layer makes practically no contribution to the electrical conductivity. It was established that only at $d_{EuS} > 30$ nm is a lead salt film totally protected from oxidation. For $d_{EuS} < 30$ nm, the sign of the inversion point is shifted to smaller thicknesses of PbTe and PbS. For example, for $d_{EuS} = 8$ nm, the sign inversion point corresponds to $d_{PbS} \sim 12$ nm. Therefore, the conductivity type of PbTe and PbS can be controlled by varying d and d_{EuS}. In this case, an inhomogeneous structure with anisotropic properties, in particular anisotropic thermoelectric properties, is formed.

In conclusion, it is shown that the presence of an oxidized layer on the PbTe and PbS film surface causes a strong d dependence of the thermoelectric properties, including inversion of the carrier sign from *n* to *p* at $d \lesssim 110$–125 nm. The observed d dependences of the kinetic coefficients are interpreted on the basis of simple models, which take into account the existence of compensating acceptor states. The contribution of holes to the kinetic coefficients is determined by the thickness of the oxidized layer relative to the total width of the thin film. It was established that PbTe and PbS films covered by a thin layer of EuS (~ 30 nm) are fully protected from oxidation and preserve their *n*-type conductivity. Similar behavior of the d dependences of the transport properties are obtained for PbS and PbTe thin films, which proves that there are similar mechanisms occurring in IV–VI thin films under oxidation.

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