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DEGRADATION OF THE THERMOELECTRIC PROPERTIES OF *n*-PbTe FILMS IN ATMOSPHERIC OXYGEN

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It has been shown that the behavior of the thermoelectric properties of n-PbTe films produced at different condensation temperatures T_c depends on the time of storage in air, which is related to the physical processes responsible for the diffusion of oxygen along the crystallite boundary and on its state prescribed by condensation conditions.

The thermoelectric properties of thin films of lead chalcogenides substantially depend on the processes occurring on their surface and, in particular, those related to the adsorption of oxygen molecules on it [1]. Therefore, the possibility of employing thin *n*-PbTe films condensed on PM-1 amorphous polyamide substrates as *n*-branches in thermal converters depends on the results of study of the action of atmospheric oxygen on the electrophysical and thermoelectric properties of these films.

Two reasons are mainly responsible for the interest in investigating the interaction between lead-telluride films and oxygen. The first reason is the necessity of activating heat treatment of the PbTe films in an oxygen-containing medium in manufacturing IR photodetectors [2]. This in turn results in a positive effect: a photosensitivity increase is ensured, as in the case of PbS layers. One of the first investigations devoted to a search for the optimum regimes of activating treatment of PbTe films was the work of Bode [3], in which an increase in the resistance and the photosensitivity in the case of oxygen treatment of the films was disclosed. The second reason is a search for methods of elimination of the spurious action of oxygen on thermoelements that in most cases are operated in air at temperatures higher than room temperature (up to 400 K) and are subjected to the active action of atmospheric oxygen.

The problem on studying the regularities of the interaction between *n*-PbTe films employed in thermoelectricity and atmospheric oxygen remains to be solved. An analogous investigation has been carried out in [4] for $Pb_{1-x}Sn_xTe\langle Te\rangle$ solid solutions.

One of the most important problems arising in the case of employment of PbTe films in thermoelectric converters is the establishment of the regularities of change in their electron properties in contact with an oxygen-containing medium [1, 5]. The contact of thermoelectric *n*-PbTe films with such a medium results in the degradation of their thermoelectric properties, the intensity of whose degradation increases with the temperature of the medium. This process begins at the instant of their withdrawal from the technological chamber after the completion of condensation. In this connection, we carried out a detailed investigation of the regularities of the degradation of the properties of *n*-PbTe films on their storage in air for one year and studied the influence of heat treatment in the atmosphere.

Our investigations show that the films possess a high value of $\alpha^2\sigma$ at T_c = (630 ± 10) K. Figure 1 gives the experimental data on the dependence of $\alpha^2\sigma$ of *n*-PbTe films condensed at temperatures of 590, 620, and 640 K on the time of storage in air for one year. The experiment carried out shows that the *n*-PbTe films condensed at temperatures $T_c \le 590$ K and $T_c \ge 640$ K have a smaller $\alpha^2\sigma$; therefore, they are unstable. For this reason we have investigated films produced at temperatures $590\ \text{K} \le T_c \le 640$ K with a step of 10 K. From these data it is clear that the *n*-PbTe films condensed at $T_c \approx 620$ K have the most stable thermoelectric properties. The behavior of the parameters of the films produced at different T_c as a function of the time of storage in air can be correlated with the interrelationship between the physical processes responsible for the diffusion of oxygen along the crystallite boundary (CB) and the state of the crystallite boundary prescribed by condensation conditions.

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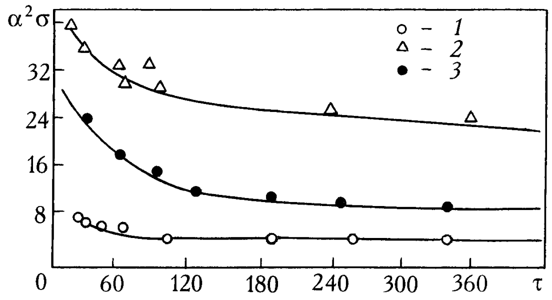

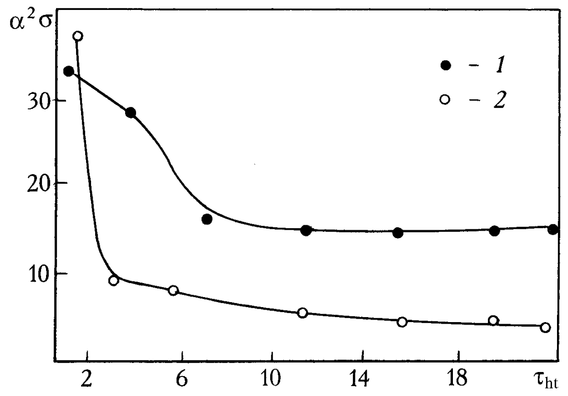

Fig. 1. Coefficient of thermoelectric power of *n*-PbTe films vs. time of storage in air at 300 K: 1) T_c = 590, 2) 620, and 3) 640 K. $\alpha^2\sigma$, μW/(K^2·cm); τ, days.

Fig. 2. Coefficient of thermoelectric power of *n*-PbTe films condensed at T_c = 620 K vs. treatment time: 1) T_{ht} = 370 and 2) 470 K. $\alpha^2\sigma$, μW/(K^2·cm); τ_{ht}, h.

It is well known [6] that the most perfect structure in *n*-PbTe films corresponds to a condensation temperature of 620 K. At lower and higher T_c, the size of single-crystal fragments decreases. They correspond to the most weakly disoriented crystallites; the weaker the disorientation, the closer the structure of the regions near the crystallite boundary to the structure of massive crystallites and consequently the smaller the difference in the coefficients of diffusion of the impurities along the crystallite boundary and in the volume. The coefficient of diffusion of the impurities along the crystallite boundary D_{CB} in polycrystals is much higher than the volume diffusion coefficient D_v [7]. The D_{CB}/D_v ratio must increase with improvement in the polycrystalline structure. In *n*-PbTe films, the polycrystallinity of the structure is more pronounced with increase in T_c; the quantity D_{CB} accordingly increases. The larger the quantity D_{CB}, the more intense the penetration of oxygen to the crystallite boundary. This in turn increases potential barriers due to the accelerated growth in the concentration of the oxygen states, which results in a limited number of the carriers involved in transport phenomena. As a result, the electrical conductivity σ decreases.

With allowance for the data of Fig. 1, we annealed thermally in air the films condensed only at T_c = 620 K. The annealing temperature varied within T_{ht} = 370–570 K.

Figure 2 gives the dependences of the coefficient of thermoelectric power of the *n*-PbTe films on the time of heat treatment in air. These experimental data show that the intensity of degradation of the properties of the films increases as the treatment temperature increases (in the region of temperatures $T_{ht} > 400$ K). For example, the $\alpha^2\sigma$ of the films decreases.

Thus, our investigations show that (a) the most optimum temperatures of operation of *n*-PbTe films employed, for example, as *n*-branches in thermal converters lie lower than 400 K; (b) the most stable thermoelectric properties are displayed by the *n*-PbTe films produced at T_c = 620 K, since their polycrystalline structures [6] are more perfect.

NOTATION

D, diffusion coefficient; *n*, concentration of electrons, cm^{-3}; *T*, temperature, K; $\alpha^2\sigma$, thermoelectric-power coefficient, μW/(K^2·cm); σ, electrical conductivity of the semiconductor film, $\Omega^{-1}\cdot$cm^{-1}; α, thermoelectric coefficient, μW/K; τ_{ht}, time of heat treatment, h; τ, time of storage of the films in air, days. Subscripts: c, condensation; ht, heat treatment; v, volume; CB, crystallite boundary.

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