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Onarqulov K. E.,
Rahmanqulov M. K.,
Zaynolobidinova S. M.,
Omonov B.U.,
Kamolova M. M.,
Ferghana State University, Fergana, Uzbekistan

ON THE KINETICS OF THE ELECTRICAL CONDUCTIVITY OF POLYCRYSTALLINE FILM STRUCTURES

Abstract. The manuscript presents the results of the research on the kinetics of the electrical conductivity of polycrystalline film structures during diffusion filling of crystallite boundaries with oxygen. The effects observed in the degeneracy state in PbTe films are considered. The influence of a potential barrier on transport phenomena is investigated.

Keywords: polycrystal, monocrystal, crystal, electron, energy, thermoelement, electrical conductivity, concentration, transparency, potential barrier, effective mass, concentration.

Introduction

One of the most studied and promising materials for the creation of polycrystalline film energy converters are lead chalcogenides. For example, lead telluride films are an effective component of thermal converters and thermoelements due to an anomalous increase in the thermos EMF coefficient. The effect of increasing the thermopower coefficient in films compared to bulk crystals was found in block-single-crystal n-PbTe films [1; 2]. However, with an increase in the thermos EMF coefficient (a), the electrical conductivity (σ) in them greatly decreased. The results obtained in [3] showed that the magnitude of the effect in films depends on the type of substrate, the electron concentration, and the composition of the initial material. Based on the experimental results obtained, the authors of [2] explained the effect of increasing the thermopower coefficient by the presence of an additional scattering mechanism associated with the block structure of the film, under the assumption that the boundaries of the blocks are dislocation walls [4; 5].

It was assumed in [6] that only those carriers that tunnel through a potential barrier of the type $\varphi = E_F - E_s$ (E_s - is the energy of unoccupied states) participate in the transport phenomena in films. In this case, the higher the carrier energy, the higher the probability of their passage, those again, as in the case of the model [2; 4], the barri-

er selects carriers by energy, causing an increase in the average energy in the heat flux, with the only difference that the selection is due not to scattering by barriers, but to an increase in the tunneling probability with increasing carrier energy.

It should be noted that the proposed interpretation of the transfer phenomena in films with anomalous thermos EMF states that the decisive contribution to the properties of films, in contrast to the properties of bulk materials, is made by the presence of barriers at the interfaces of crystallites or blocks.

We have considered the effects that are observed in the degeneracy state in PbTe films. If the potential barrier at structural disturbances has the nature proposed in [6; 7], then its height can be determined by solving the Poisson equation

$$\frac{d^2\varphi(x)}{dx^2} = \frac{e^2}{\varepsilon\varepsilon_0}\rho(x), \qquad (1)$$

where $\varepsilon\varepsilon_0$ – is the dielectric constant of the film material; $\rho(x)$ – is the cristanite border charge density distribution; $x = 0$ corresponds to the interface between two crystallites. If surface states with a concentration N_s are localized on the cristanite border, on which $n_s \le N_s$ electrons are captured on the surface states, the barrier height has the value $\varphi > E_F$, the edge of the conduction band E_c crosses the Fermi level near the cristanite border. In this case, taking into account the degeneracy and up to exponentially small terms, $\rho(x)$ takes the form

$$\rho(x) = N_d - n_s\delta(x) - \\ -\frac{\left\{2m_d\left[E_F-\varphi(x)\right]\right\}^{3/2}}{3\pi^2\hbar^3}U\left[E_F-\varphi(x)\right] \qquad (2),$$

here N_d – is the doping level, m_d is the effective mass of the density of states in the conduction band; $U(\xi)$ – impulse function

$$U(\xi) = \begin{cases} 1, \xi \ge 0, \\ 0, \xi < 0. \end{cases} \qquad (3)$$

The boundary conditions for (2) follow from the vanishing $\varphi(x)$ and $d\varphi(x)/dx$ at $x \to \infty$. The analytical solution of (1) and (2) in general form can be found up to a numerical factor of the order of unity.

Let us represent relation (2) in the form

$$\rho(x) = N_d\left\{1-\frac{\left\{2m_d\left[E_F-\varphi(x)\right]\right\}^{3/2}}{3\pi^2\hbar^3N_d}-U\left[E_F-\varphi(x)\right]\right\} - \\ -n_S\delta(x) \qquad (4).$$

Then, taking into account that the Fermi level is expressed N_d in terms of the relation

$$E_F = \frac{(3\pi^2)^{2/3}\hbar^2N_d^{2/3}}{2m_n} \qquad (5),$$

(4) can be greatly simplified:

$$\rho(x) = \frac{3}{2}N_d\frac{\varphi(x)}{E_F}\Omega(x) - n_S\delta(x) \qquad (6),$$

where

$$\Omega(x) = \frac{2}{3}\frac{E_F}{\varphi(x)}\left\{1-\left[1-\frac{\varphi(x)}{E_F}\right]^{3/2}U\left[E_F-\varphi(x)\right]\right\} \qquad (7).$$

Let's analyze the behavior of the function $\Omega(x)$ in half space $[0,\infty)$. According to the boundary conditions to (7) $\varphi(x) = 0$ at $x \to \infty$, So, according to L'Hopital's rule

$$\lim_{x\to\infty}\Omega(x) = \lim_{\varphi(x)\to 0}\Omega(x) = 1 \qquad (8).$$

Here $\varphi(x) = E_F$, $\Omega(x) = 2/3$, $x = 0$ equals $\Omega(x) = (2/3)\cdot E_F/\varphi(x)$

Considering that in the half-space $[0,\infty)$ function $\Omega(x)$ continuous and monotonous, we can claim $\left[\varphi(0)-E_F\right]/E_F \ll 1$ (takes place within the considered problem) the function $\Omega(x)$ in this half-space is a slowly varying function of order one. This means that, up to this function, the potential barrier is $\varphi(x)$ determined by the relation

$$\varphi(x) \approx \frac{e^2n_s}{2\varepsilon\varepsilon_0}l_э\exp\left(-\frac{|x|}{l_э}\right) \qquad (9),$$

here the left side at $x = 0$ is determined by the expression $\varphi = E_F - E_s$. The value of $l_э$, which plays

the role of the effective barrier half-thickness for cristanite border, is determined by the relation

$$l_э \approx \sqrt{\frac{\varepsilon\varepsilon_0(E_F + |E_S|)}{e^2 N_d}} \qquad (10).$$

According to the foregoing, we will discuss the influence of the barrier φ on the transfer phenomena.

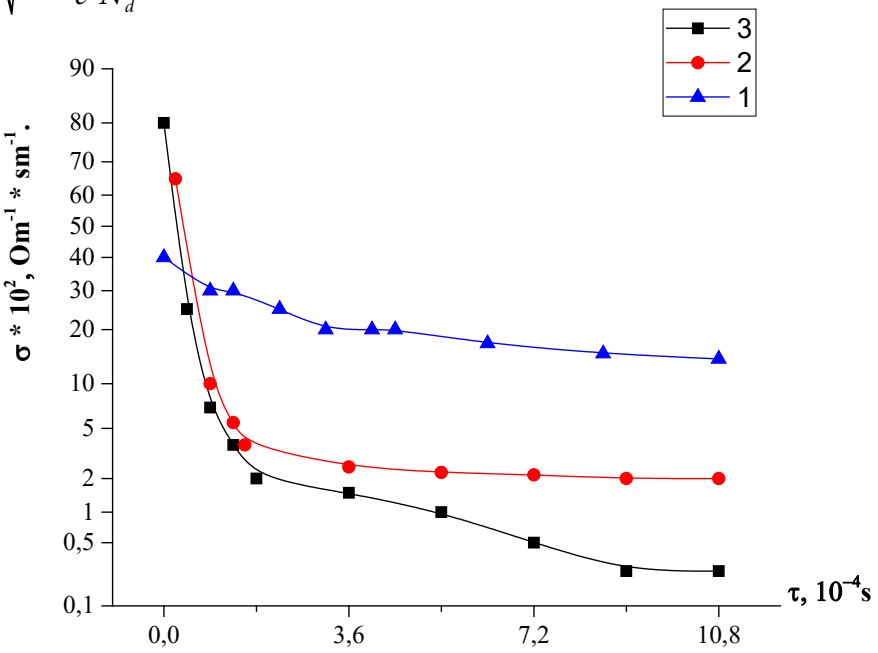

Figure 1. Influence of heat treatment in air on the electrical conductivity of n-PbTe films. 1 – at a temperature of 370 K; 2,3 – at a temperature of 470 K (2 – after implantation of oxygen ions with an integral dose of 10^{16} cm^{-2})

Turning to (Fig. 1), one can see that during heat treatment in air due to the filling of cristanite border with oxygen, the electrical conductivity of the films decreases significantly with respect to the initial value, i.e. becomes much smaller than in bulk crystals. According to the ratio

$$\sigma = \sigma_0 \left\{ 1 + \frac{2l_э\left[1 - P(E_F)\right]}{LP(E_F)} \right\}^{-1} \qquad (11)$$

it is possible with

$$1 + \frac{2l_э\left[1 - P(E_F)\right]}{L \cdot P(E_F)} \gg 1 \qquad (12).$$

The fulfillment of this condition implies that

$$P(E_F) \ll 1, \qquad (13)$$

As $L > 2l_э$.

If condition (13) is satisfied, then the electrical conductivity value

$$\sigma = \sigma_0 \left\{ 1 + \frac{2l_э\left[1 - P(E_F)\right]}{LP(E_F)} \right\}^{-1} \qquad (14),$$

can be written in the form

$$\sigma \approx \sigma_0 \frac{L}{2l_э} P(E_F). \qquad (15)$$

Given the explicit expression for, which is given as

$$P(E) = P_a(E^*) \cdot P_T(E + E^*) \approx \exp\left[-\frac{8l_э\sqrt{2m_n^*}}{\hbar} \times \left(\sqrt{E_F + |E_S| - E - E^*} - \sqrt{E + E^*}\, arctg \sqrt{\frac{E_F + |E_S|}{E + E^*} - 1} \right) - \frac{E^*}{kT} \right] \qquad (16),$$

(15) is transformed into the relation

$$\sigma \approx \sigma^* \exp\left(-\frac{E^*}{kT}\right) \quad (17),$$

where σ^* according to

$$P(E) = P_a(E^*) \cdot P_T(E+E^*) \approx \exp\left[-\frac{8l_э\sqrt{2m_n^*}}{\hbar} \times \left(\sqrt{E_F+|E_S|-E-E^*} - \sqrt{E+E^*}\, arctg\sqrt{\frac{E_F+|E_S|}{E+E^*}-1}\right) - \frac{E^*}{kT}\right] \quad (18)$$

and (15) takes the form

$$\sigma^* = \sigma_0 \frac{L}{2l_э} P_T(E_F+E^*) \quad (19).$$

Let us find out the nature of the change in the electrical conductivity of the film when cristanite border is filled with oxygen. We believe that at the time moment $t=\tau$, after the beginning of the diffusion filling of cristanite border with oxygen, charge carriers are trapped on the localized electronic states near the surface of the crystallites. Then the height of the potential barrier near the cristanite border is given by n_s the relation

$$\varphi(x) \approx \frac{e^2 n_s}{2\varepsilon\varepsilon_0} l_э \exp\left(-\frac{|x|}{l_э}\right) \quad (20).$$

Since the physical essence of the quantity $l_э$ appearing in (20) is the length at which the charge of electrons localized on the cristanite border is almost completely screened, it can be approximated as

$$l_э \approx \frac{n_s}{2N_d}. \quad (21)$$

which is the quasi-neutrality condition in the barrier region. When (21) is taken into account, relation (20) takes the form

$$\varphi(x,\tau) = \varphi(0,\tau) \approx \frac{e^2 n_s^2}{4\varepsilon\varepsilon_0 N_d} \quad (22).$$

This reflects that the potential barrier height is a function of time.

Let us assume that over time $\Delta\tau$ the concentration of oxygen states on the cristanite border increased by a value ΔN_s and all these states were filled with electrons. Then, provided that $\Delta N_s \ll n_s$, we can estimate the change in the barrier height as

$$\varphi(0,\tau+\Delta\tau) \approx \frac{e^2(n_s+\triangle N_s)^2}{4\varepsilon\varepsilon_0 N_d} \approx \approx \varphi(0,\tau) + \frac{e^2 n_s}{2\varepsilon\varepsilon_0 N_d}\Delta N_s \quad (23).$$

The second term on the right side of the equation indicates the change in the height of the potential barrier over time $\Delta\tau$. This change is equal to

$$\Delta\varphi(\Delta\tau) \approx \frac{e^2 n_s}{2\varepsilon\varepsilon_0 N_d}\Delta N_s \approx \frac{e^2 l_э}{\varepsilon\varepsilon_0}\Delta N_s = B\Delta N_s \quad (24).$$

Let us analyze how such a change in the height of the potential barrier will affect its transparency and, accordingly, the electrical conductivity. If the cristanite border has a potential barrier of arbitrary height φ, relation (16) can be transformed as

$$P(E_F) \approx \exp\left[-\frac{8l_э\sqrt{2m_n^*}}{\hbar}\left(\sqrt{\varphi-E_F-E^*} - \sqrt{E_F+E^*}\, arctg\sqrt{\frac{\varphi}{E+E^*}-1}\right) - \frac{T^*}{kT}\right] \quad (25),$$

and the equation to calculate E^*

$$4l_э kT\sqrt{2m_n^*}\, arctg\sqrt{\frac{E_F+|E_S|}{E+E^*}-1} = \hbar\sqrt{E+E^*} \quad (26),$$

takes the form

$$4l_э kT\sqrt{2m_n^*}\, arctg\sqrt{\frac{\varphi}{E_F+E^*}-1} = \hbar\sqrt{E_F+E^*} \quad (27).$$

It can be seen from this that with an increase φ in the transparency of the barrier, it will change both due to a change in the height of the barrier, and due to a change in E^*.

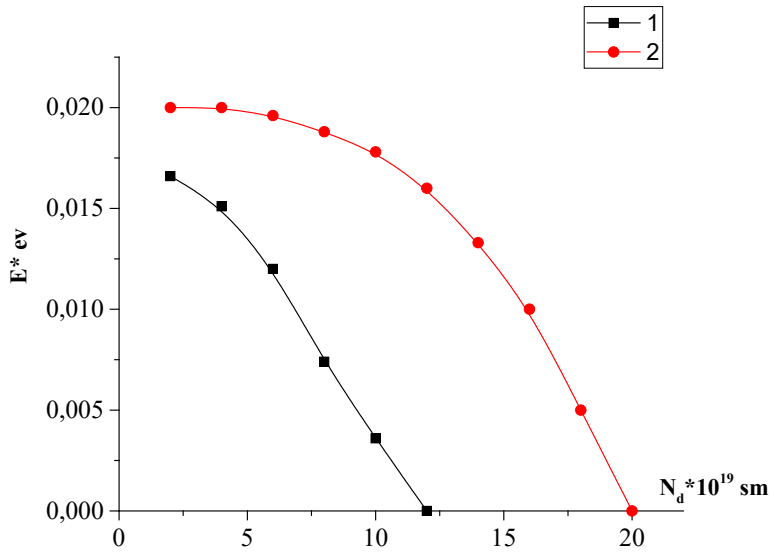

Figure 2. Concentration dependence of the activation energy of electrons passing through the potential barrier T, K: 100 (1), 300 (2)

Let's study the dependence E^* on φ. Taking into account (27) relatively E^* is solved only numerically, we will make numerical estimates. Figure 2 shows the concentration dependence E^* obtained by numerically solving equation (27) under the assumption that the potential barrier height for cristanite border is determined by the relation $\varphi = E_F - E_s$, in E_s which it has two values:

$$E_{s1} = E_c - 0{,}02eV, \quad (28)$$

$$E_{s2} = E_c - 0{,}03eV. \quad (29)$$

Where E_c is the bottom of the conduction band. According to the data in (Fig. 2), at the doping levels $N_d \le 10^{19} см^{-3}$ $E^* \approx |E_s|$, and in addition, at the specified N_d, the growth of the potential barrier is accompanied by an increase E^* by the same value, those can be imagined

$$E^*(\tau + \Delta\tau) \approx E^*(\tau) + \Delta\varphi(\Delta\tau) \quad (30).$$

The numerical calculation also shows that when (30) is satisfied, the transparency of the barrier $P(E)$ changes mainly due to the change in the last term in (25), those due to change $P_a(E^*)$

Taking into account (30) and the last remark, the evolution of the electrical conductivity of the film in the framework of the problem under consideration can be expressed by the relation

$$\sigma(\tau + \Delta\tau) \approx \sigma^* \exp\left[-\frac{E^*(\tau + \Delta\tau)}{kT}\right] \approx \approx \sigma(\tau)\exp\left[-\frac{\Delta\varphi(\Delta\tau)}{kT}\right] \quad (31),$$

where $\sigma(\tau)$ is given (17). Combining (24) and (31), we obtain

$$\sigma(\tau + \Delta\tau) \approx \sigma(\tau)\exp\left(-\frac{B\Delta N_s}{kT}\right) \quad (32).$$

At the initial moment of the diffusion process $N_d \approx n_H \approx 10^{19}$ cm^{-3} (Fig. 1), the value $l_э$, can be numerically found through N_d and the electrical conductivity value. Expression (32) describes the kinetics of changes in the electrical conductivity of the film during diffusion filling of cristanite border with oxygen. In (32), by the quantity ΔN_s we mean the change in the concentration of oxygen states in the cross section N_d. An approximate estimate according to the data in (Fig. 1) gives that B/kT $\approx 8 \cdot 10^{14}$ sm^2. It should be noted that the diffusion coefficient of oxygen and other impurities along the crystallite boundaries depends on the film structure [6].

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