MATERIALS
SCIENCE &
ENGINEERING

B

Directed synthesis and formation of the defects in thin films of PbTe

D.M. Freik *, V.V. Prokopiv, A.B. Nych, V.A. Shepetyuk, L.V. Tytova

Precarpathian University, Shevchenko str. 57, 284000 Ivano-Frankivsk, Ukraine

Abstract

We have determined the technological factors in the hot wall technique that determine the conditions of PbTe thin films with pre-assigned parameters. We have proposed the model that describes the processes of growth of PbTe thin films from the vapour phase. The general equations, that set the connection between the charge carriers concentration (n), inversion (n–p transition) temperature (T_s^*) of precipitation, evaporation temperature (T_e) of the sample, the pressure of the vapour of the components (P_{Te_2}) and condensation temperature (T_s) have been obtained. We have shown that the formation of defects like $PbTe_i^+ - V_{Pb}^{2-}$ is predominant in PbTe thin films grown from the vapour phase. © 1997 Elsevier Science S.A.

Keywords: Directed synthesis; PbTe; Hot wall technique

1. Introduction

PbTe is the base material for production of the detectors and sources of coherent infrared radiation [1]. In the range of carrier concentration of interest, its electrical properties are determined mostly by the intrinsic defects [2,3]. In the literature there are contradictory facts about the type of the own defects, as well as about their charge state condition [4–11]. The purpose of this work is to determine the technological conditions of the growth of PbTe thin films with the pre-assigned parameters from the vapour phase and to study the process of the formation of the own atomic defects in these thin films.

2. Experimental procedure

The PbTe thin films were deposited at the fresh chippings (111) of BaF_2 crystals [12]. The synthesized PbTe crystals with n-type conductivity and with the original concentration of charge carriers ~10^{18} cm^{-3} were used as the samples for the evaporation.

The rate of the layer growth at the evaporation temperature $T_e = 820$ K, the temperature of chamber walls $T_w = 850$ K and the temperature of the substrate $T_s = 420$–620 K was 3–8 nm s^{-1}. The thickness of the layers was 7–10 μm. It has been determined that the epitaxial layers of PbTe have electron conductivity at all the precipitation temperatures within the studied range $T_s = 420$–620 K.

3. Results

The increase in T_s within this range results in the decrease in the concentration of electrons (Fig. 1). It is known that besides the precipitation temperature T_s the pressure of the component vapour in the condensation zone is an important parameter influencing the character of the deviation from the stoichiometry and also the mechanism of the formation of the own defects of an atomic structure [12–15]. Thus, the n-type layers of PbTe are precipitated at the low pressures (Fig. 2, left branches), while the p-type layers are precipitated at high pressures (Fig. 2, right branches) of Te. The pressure, at which the inversion of the conductivity type occurs depends on the substrate temperature.

* Corresponding author.

4. Theoretical framework

For the description of the processes of the thin films growth the quasi-chemical method was used [16]. It was assumed that the concentration of the charge carriers is determined by the ionized Frenkel defects. Within the chosen model the process of the growth is described by the system of crystal–chemical reactions (Table 1). The reaction (I) describes the evaporation of the compound at the temperature T_e and takes into consideration the decomposition during the transformation from the solid phase (s) into vapour (v); reactions (II) and (III) represent the equilibrium of the own atomic defects (intersite Pb atoms Pb_i^+ and Pb vacancies V_{Pb}^{2-}) in the layers at the temperature of the substrate T_s. The equations (IV) and (V) are responsible for the expression of the own conductivity and of the full electroneutrality.

The concentration of the electrons can be expressed through the constants of the quasi-chemical reactions and through the partial pressure of Te vapour:

$$2 \cdot K_{Te_2, V}(T_s) \cdot K_i^{-2}(T_s) \cdot P_{Te_2}^{1/2} \cdot n^2 + n^2$$

$$- K_{Pb, V}(T_s) \cdot K_{PbTe}(T_e) \cdot P_{Te_2}^{-1/2} + K_i(T_s) = 0 \qquad (1)$$

The concentration of charge carriers, experimentally determined by the Hall's effect, is

$$n_H = n - p \qquad (2)$$

and

$$n \cdot p = K_i(T_s)$$

Finally,

$$n_H = n - K_i(T_s) \cdot n^{-1}. \qquad (3)$$

The expression for the substrate temperature T_s^* that corresponds to the conditions of layer growth in the region of the thermodynamic n–p junction can be found using the equations of the electroneutrality. The temperature of the thermodynamic n–p junction while the formation of the $Pb_i^+ - V_{Pb}^{2-}$ type defects:
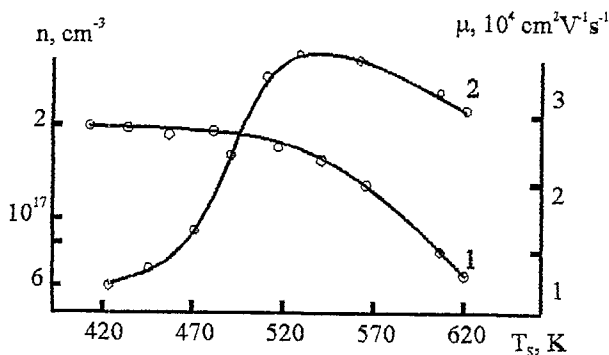

Fig. 1. Dependency of concentration (1) and mobility (2) of charge carriers at 77 K in PbTe thin films on the precipitation temperature T_s (method—hot wall, substrates—(111) BaF$_2$, T_e = 820 K, T_w = 850 K, PTe2 = 3.3·10^{-3} Pa).
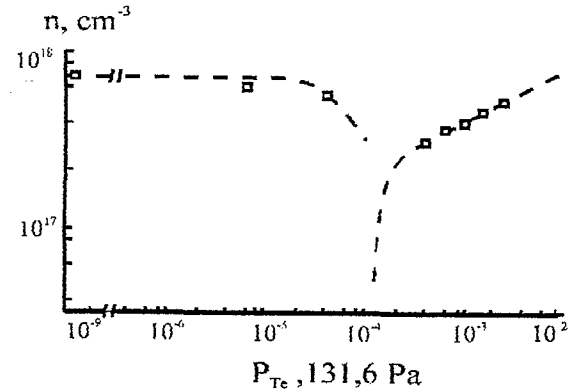

Fig. 2. Dependency of concentration of carriers in PbTe thin films on the partial pressure of Te$_2$ vapour P_{Te_2} (method—hot wall, substrates—(111) BaF$_2$).

$$T_s^* = \frac{0.5 \cdot \Delta H_i + \Delta H_{Pb, V} - \Delta H_{Te_2, V}}{k}$$

$$\times \left(\ln \frac{K_{Pb, V}^0}{2 \cdot K_{Te_2, V} \cdot P_{Te_2}} - \frac{\Delta H_{PbTe}}{k \cdot T_e} \right)^{-1}. \qquad (4)$$

5. Discussion

Some results of the theoretical calculations that determine the dependence of the charge carriers concentration in the PbTe thin layers on the technological factors are presented in Fig. 3. According to the received data (Fig. 3(a)), the increase in precipitation temperature T_s, while the evaporation temperature T_e and the partial pressure of the Te vapour P_{Te_2} remain constant, results in the original decrease in electron concentration, in the inversion of the conductivity type and in the further growth of hole concentration (T_s^* is the temperature, at which the thermodynamic n–p junction occurs). The reason for this is the predominance of acceptor Pb vacancies formation with the increase in T_s. On the other hand, the increase in Te vapour pressure P_{Te_2} results in decrease of the temperature T_s^* (Fig. 3(a)), while the increase in evaporation temperature T_e causes its growth. In the first case the Pb vacancies formation predominates, and in the second case mostly the donor intersite Pb atoms are formed. With the increase in partial pressure of Te vapour P_{Te_2}, as well as with the increase in precipitation temperature, the equilibrium concentration of Pb vacancies grows. This leads to the drop in electron concentration in PbTe films. The growth of the evaporation temperature T_e causes the increase in the concentration of the intersite Pb atoms and moves the thermodynamic n–p junction to the region of the higher values of P_{Te_2}, while the growth of T_s moves it in the direction of the reduction of P_{Te_2} (Fig. 3(b)).

Table 1

Reactions and equilibrium constants $K = K^0 \cdot \exp(-\Delta H/kT)$ of formation of the predominant atomic defects in PbTe layers

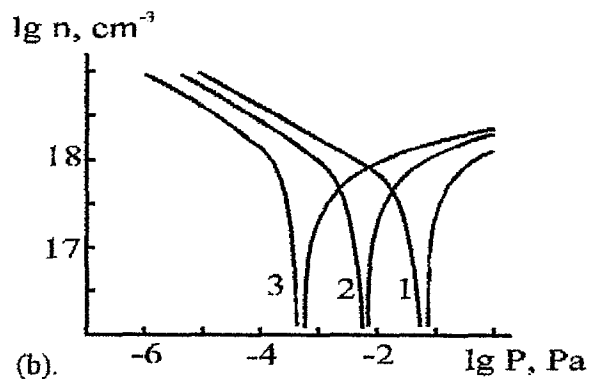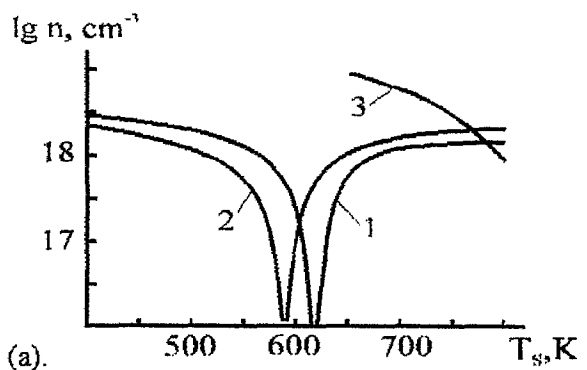| No.	Reactions	K $(P,$ Pa; n, cm$^{-3})$	K^0	ΔH, eV
I	$PbTe^S = Pb^V + \frac{1}{2}Te_2^V$	$K_{PbTe}(T_e) = P_{Pb} \cdot P_{Te}^{1/2}$	$1.40 \cdot 10^{16}$	3.51
II	$Pb^V = Pb_i^+ + e^-$	$K_{Pb,\ V}(T_s) = [Pb_i^+] \cdot n \cdot P_{Pb}^{-1}$	$5.45 \cdot 10^{30}$	-1.01
III	$\frac{1}{2}Te_2^V = V_{Pb}^{2-} + Te_{Te}^0 + 2h+$	$K_{Te_2,\ V}(T_s) = [V_{Pb}^{2-}] \cdot p^2 \cdot P_{Te_2}^{-1/2}$	$7.59 \cdot 10^{58}$	0.39
IV	'0' $= e - + h+$	$K_i(T_s) = n \cdot p$	$1.06 \cdot 10^{41}$	0.58
V	$2[V_{Pb}^{2-}] + n = [Pb_i^+] + p$			

(a).

(b).

Fig. 3. Calculated dependencies of charge carriers concentration n_H in PbTe thin films on: (a) precipitation temperature T_s $(P_{Te_2},$ Pa: $3.3 \cdot 10^{-3}$ (1); 10^{-6} (2); 10^{-2} (3); $T_e = 820$ K); (b) partial pressure of Te vapour P_{Te_2} $(T_s,$ K: 550 (1); 600 (2); 650 (3); $T_e = 820$ K).

The calculations (Fig. 3) prove that the mechanism of Frenkel defects formations in cation sublattice can qualitatively explain the experimental results.

References

[1] F.F. Sizov, Foreign Electronic Technic. 2 (1977) 31.
[2] N.H. Abrikosov, L.E. Shelimova, Semiconductor Materials Based on A^{IV}B^{VI} Compounds, Nauka, Moskow, 1975.
[3] V.P. Zlomanov, A.V. Novoselova, P-T-x-diagrams of Two-component Systems, Nauka, Moskow, 1980.
[4] D.M. Zayachuk, V.A. Shenderovsky, UFZh. 36 (1991) 1692.
[5] F.F. Sizov, Izv. AN SSSR. Inorganic materials. 24 (1988) 1972.
[6] M. Shenk, H. Berger, A. Klimakov, Cryst. Res. and Techol. 23 (1988) 77.
[7] K.R. Mendybaev, V.P. Zlomanov, V.N. Vugdorovych, A.M. Sokolov, Izv. AN SSSR. Inorganic materials. 25 (1989) 942.
[8] Yu.G. Sidorov, I.V. Sabina, Zh. fiz. chim. 59 (1985) 2723.
[9] H. Heinrich, Lect. Notes Phys. 133 (1980) 407.
[10] N.I. Parada, Phys. Rev. 3 (1971) 2042.
[11] G.S. Lent, M.A. Bowen, R.S. Allgaier, Solid state Communs. 61 (1987) 83.
[12] D.M. Freik, M.A. Galushchak, L.T. Mezhilovzka, Physics and Technology of Semiconductor Films, Vyshcha shkola, Lviv, 1988.
[13] A. Lopez-Ofero, Appl. Phys. Lett. 26 (1975) 470.
[14] A. Lopez-Ofero, L.D. Haas, Thin Solid films 23 (1974) 1.
[15] D. Borkovska, A. Kogalski, H. Zienuk, Biul. Wojskowej Akademii Tochnisznej im. j Dabrowkiegi. 18 (1978) 83.
[16] F. Kreger, Chemistry of Imperfect Crystals, Mir Moscow, 1969.