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Properties of the $Pb_{1-x}Sn_xTe_{1-y}Se_y$ epitaxial layers grown from the supersaturated melt-solution on dielectric and semiconductor substrates

O.N.Tsarenko, S.I.Ryabets, A.I.Tkachuk

V.Vynnychenko Kirovograd State Pedagogical University,
1 Shevchenko St., 25006 Kirovograd, Ukraine

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The epitaxial layers of $Pb_{1-x}Sn_xTe_{1-y}Se_y$ quaternary solid solution (thickness of 2 to 11 μm, $N_d \le 10^5$ cm^{-2}, $n(p)$ = (0.9 to 8.7)·10^{17} cm^{-3} and μ_H = (0.1 to 24)·10^3 cm^2·V^{-1}·s^{-1} at T ~ 80 K), lattice-matched with KCl, BaF_2, $Pb_{0.80}Sn_{0.20}Te$, and $PbTe_{0.92}Se_{0.08}$ substrates, were grown in a wide composition range by the liquid phase epitaxy technique at a programmed overcooling of supersaturated melt-solution.

Методом жидкофазной эпитаксии при программном переохлаждении пересыщенного раствора-расплава на подложках KCl, BaF_2, $Pb_{0,80}Sn_{0,20}Te$ и $PbTe_{0,92}Se_{0,08}$ в широком диапазоне составов выращены изопериодные эпитаксиальные слои четырёхкомпонентных твёрдых растворов $Pb_{1-x}Sn_xTe_{1-y}Se_y$ толщиной 2÷11 мкм с $N_d \le 10^5$ см$^{-2}$, $n(p)$ = (0,9÷8,7)·10^{17} см$^{-3}$ и μ_H = (0,1÷24)·10^{3}см^2· В$^{-1}$·с$^{-1}$ при T ~ 80 К.

Relatively low melting temperatures, rather small saturation vapor pressure of the constituent components, small distance between liquidus and solidus lines do the $Pb_{1-x}Sn_xTe_{1-y}Se_y$ quaternary solid solutions more technological in comparison with widespread materials for the device structures on the basis of $Hg_{1-x}Cd_xTe$ solid solutions [1, 2]. The liquid phase epitaxy is among prospective manufacturing methods of $Pb_{1-x}Sn_xTe_{1-y}Se_y$ epilayers with low carrier concentration and effective radiative recombination without additional heat treatment and doping [1, 3].

At the liquid phase epitaxy on the $Pb_{1-z}Sn_zTe$ and $PbTe_{1-z}Se_z$ semiconductor substrates, the crystallization of $Pb_{1-x}Sn_xTe_{1-y}Se_y$ solid solutions is defined by heterogeneous equilibrium character at the saturated $(Pb_{1-v}Sn_v)_{1-w}$ $(Te_{1-u}Se_u)_w$ melt-solution/substrate interface and diffusion-limited transfer of components [1, 4]. Differences in the crystal lattice parameters and thermal expansion coefficients play a most important part in the defect formation at the heteroepitaxy of the $Pb_{1-x}Sn_xTe_{1-y}Se_y$ solid solutions on KCl and BaF_2 dielectric substrates. These factors result in considerable mechanical stresses that arise in the epilayers immediately in the growth process or during their cooling to room temperature. Moreover, the existence of considerable concentration gradients over the layer thickness or area may be an additional source of such stresses at the growing of $Pb_{1-x}Sn_xTe_{1-y}Se_y$ epitaxial layers [5]. In this connection, the polycrystal epilayers are obtained rather often at the "classical" liquid phase epitaxy on BaF_2 substrates [5, 6]. That is why the preliminary growing of thin (300 to 600 Å) buffer layer from the supersaturated growth solutions in isothermal conditions was proposed [7, 8] for the formation of mesadiodes on the basis of p–$Pb_{1-x}Sn_xTe_{1-y}Se_y$/ n–$Pb_{1-x}Sn_xTe_{1-y}Se_y$/ BaF_2 heterostructures. The main goal of this

work was to investigate the properties of $Pb_{1-x}Sn_xTe_{1-y}Se_y$ solid solutions grown from supersaturated melt-solution by liquid phase epitaxy technique on KCl, BaF_2, $Pb_{0.80}Sn_{0.20}Te$, and $PbTe_{0.92}Se_{0.08}$ substrates.

The $Pb_{1-x}Sn_xTe_{1-y}Se_y$ quaternary solid solutions were grown from a bounded volume of $(Pb_{1-v}Sn_v)_{1-w}$ $(Te_{1-u}Se_u)_w$ supersaturated melt-solution by the liquid phase epitaxy technique in a vertical reactor in the flow of purified hydrogen. As substrates, we used (111)BaF_2, (100)KCl, (100)$Pb_{0.80}Sn_{0.20}Te$ and (100)$PbTe_{0.92}Se_{0.08}$ single crystals with surface dislocation densities $N_d = (0.4 \div 9) \cdot 10^5$ cm^{-2}. These substrates were shaped as washers of 20 to 28 mm in diameter and 0.8 to 2 mm in thickness. The liquidus temperature was 773 to 873 K at the programmed cooling rate of 0.1 to 0.2 K/min. The range of the temperature decrease was 5 to 15 K at the initial overcooling of 1 to 6 K.

The compositions of $Pb_{1-x}Sn_xTe_{1-y}Se_y$ quaternary solid solutions, lattice-matched with BaF_2, KCl, $Pb_{0.80}Sn_{0.20}Te$, and $PbTe_{0.92}Se_{0.08}$, were selected along the isoperiodic lines $a_{epilayer} = a_{substrate}$ of the PbTe–SnTe–SnSe–PbSe concentration square, the lines being described by the following interpolation correlations:

a) $y = (0.031 - 0.134 \cdot x) / (0.3345 - 0.0175 \cdot x)$ [at. fract.], $0.09 \le x \le 0.18$ (at. fract.), $0.02 \le y \le 0.06$ (at. fract.) for $Pb_{0.80}Sn_{0.20}Te$ and $PbTe_{0.92}Se_{0.08}$ with $a(300\ K) = 6.43$ Å;

b) $y = (0.091 - 0.134 \cdot x) / (0.3345 - 0.0175 \cdot x)$ [at. fract.], $0.17 \le x \le 0.26$ (at. fract.), $0.17 \le y \le 0.21$ (at. fract.) for KCl with $a(573\ K) = 6.37$ Å;

c) $y = (0.261 - 0.134 \cdot x) / (0.3345 - 0.0175 \cdot x)$ [at. fract.], $0.00 \le x \le 0.70$ (at. fract.), $0.52 \le y \le 0.78$ (at. fract.) for BaF_2 with $a(300\ K) = 6.20$ Å.

The composition of $(Pb_{1-v}Sn_v)_{1-w}$ $(Te_{1-u}Se_u)_w$ equilibrium liquid phase was selected in accordance with phase and coherent state diagrams [1]:

a) $0.163 \le v \le 0.371$ (at. fract.),
$0.011 \le u \le 0.086$ (at. fract.),
$0.01 \le w \le 0.05$ (at. fract.) for $Pb_{0.80}Sn_{0.20}Te$ and $PbTe_{0.92}Se_{0.08}$ substrates;

b) $0.326 \le v \le 0.534$ (at. fract.),
$0.116 \le u \le 0.148$ (at. fract.),
$0.01 \le w \le 0.04$ (at. fract.) for KCl substrates;

c) $0.000 \le v \le 0.854$ (at. fract.),
$0.338 \le u \le 0.408$ (at. fract.),

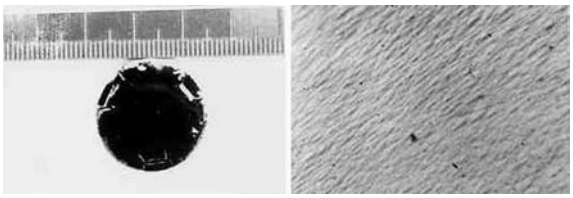

Fig. 1. Surface morphology of $Pb_{1-x}Sn_xTe_{1-y}Se_y$ epitaxial layers.

$0.01 \le w \le 0.05$ (at. fract.) for BaF_2 substrates.

The morphologic perfection of the semiconductor structures and the layer thickness were examined using a JSM-35 CF electron microscope and the compositions, by PCMA (Camebax-microbeam). For galvanomagnetic measurements, the Van-der-Pau method was used at a constant magnetic field and constant current through the sample.

The $Pb_{1-x}Sn_xTe_{1-y}Se_y$ epitaxial layers grown at the initial overcooling of 1 to 3 K were mirror-smooth or had slightly terrace structure (Fig. 1), that may be explained by insignificant (0.1 to 0.3°) misorientation of the substrates in relation to the growth plane. At the thickness of 2 to 11 μm, their surface dislocation density did not exceed 10^5 cm^{-2}. The yield of such layers was about 70 to 90 %. Dislocation density distribution in thickness for the $Pb_{1-x}Sn_xTe_{1-y}Se_y$/$Pb_{0.80}Sn_{0.20}Te$ and $Pb_{1-x}Sn_xTe_{1-y}Se_y$/$PbTe_{0.92}Se_{0.08}$ isoperiodic heterostructures was approximated fairly well by exponential dependence (Fig. 2,a). The substrate/layer interface was highly planar; the roughness did not exceed 100 Å. However, increasing of melt supersaturation to 4–6 K resulted in a rather fast crystallization of an interlayer having imperfect crystal structure, thus causing formation of cracks, low-angle boundaries and other structure defects in the main epilayer. Moreover, at the initial overcooling exceeding 5 K, the inclusions of metal character were found out in the grown layers.

Investigation of the dislocation density distribution in thickness of the $Pb_{1-x}Sn_xTe_{1-y}Se_y$/KCl and $Pb_{1-x}Sn_xTe_{1-y}Se_y$/BaF_2 isoperiodic heterostructures (Fig. 2,b) evidences absence of sharp increasing of the dislocation number at the substrate/layer interface. At the same time, the considerable overcooling of liquid phase (>4 K) resulted in an essential increasing of dislocation density or in formation of unhomogenous layers at all. In our opinion, at the liquid phase epitaxy on the dielectric substrates without melt-solu-

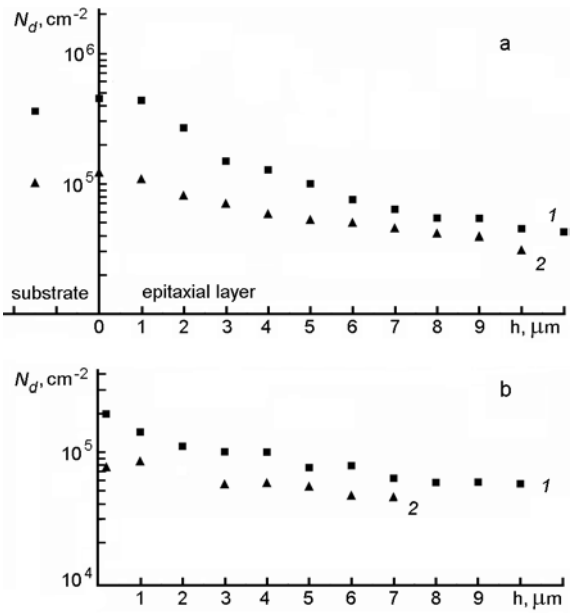

Fig. 2. Typical dislocation density distribution in thickness of the $Pb_{1-x}Sn_xTe_{1-y}Se_y$ epitaxial layers grown on the substrates:
a — $Pb_{0.80}Sn_{0.20}Te$ (*1*) and $PbTe_{0.92}Se_{0.08}$ (*2*);
b — KCl and BaF_2 (*2*).

tion overcooling, the crystallization on the heteroboundary takes place in the regions of accelerated growth (surface defects of substrate), thus resulting in the islet growth. The uniform sewing of surface by germs takes place at a low supersaturating (1 to 3 K), that permit to obtain the continuous single-crystal layers. However, further increasing of the melt- solution overcooling (>4 K) results in an intense growth of dendrites caused by release of the considerable quantity of the crystallization heat (actually, concentration overcooling takes place).

Investigations of the electric parameters of $Pb_{1-x}Sn_xTe_{1-y}Se_y$ solid solutions (Table) have shown that, independent of the growth temperature, epilayers with $0.00 \le x \le 0.25$ (at. fract.) and $0.69 \le y \le 0.78$ (at. fract.) were always of the *n*-type conductivity, and epilayers with $0.60 \le x \le 0.70$ (at. fract.) and $0.52 \le y \le 0.56$ (at. fract.) were of the *p*-type. However, the conduction type of the epitaxial structures with $0.25 \le x \le 0.40$ (at. fract.) and $0.63 \le y \le 0.69$ (at. fract.) changed from process to process, and carrier concentrations were rather small ($<10^{16}$ cm^{-3}), since in the investigated composition region, there is no prevailing mechanism formation of electrically active native point defects of donor (V_{Te}^+, V_{Se}^+, Pb_i^+, Sn_i^+) or acceptor (V_{Pb}^-, V_{Sn}^-, Se_i^-, Te_i^-) type, and their concentrations ($n-p = a \cdot N_D^{(a+)} - b \cdot N_A^{(b-)}$) differ only little one from another. At the same time, conductivity of the epilayers with $0.40 \le x \le 0.60$ and $0.56 \le y \le 0.63$ are depending on the growth temperature: epilayers were always of *n*-type if the initial growth temperature was below about 790 K and were always of *p*-type at temperatures above about 820 K. Moreover, in the studied layers, the carrier concentration increased and Hall mobility decreased at the elevation of initial growth temperature and increasing contents of tin and tellurium (Table).

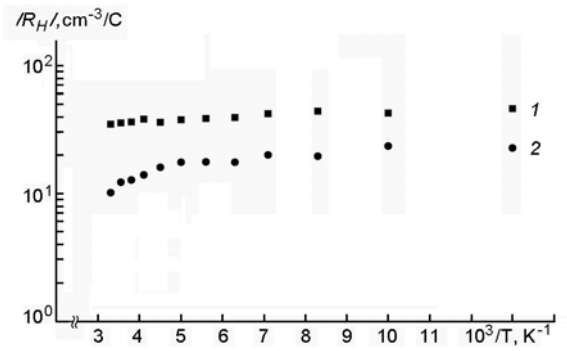

Fig. 3. Temperature dependences of the Hall coefficient absolute values:
1 — *n*–$Pb_{0.98}Sn_{0.02}Te_{0.23}Se_{0.77}$/ BaF_2,
2 — *p*–$Pb_{0.55}Sn_{0.45}Te_{0.39}Se_{0.61}$/ BaF_2.

In Fig. 3, shown are the typical temperature dependences of the Hall coefficient (R_H) for the $Pb_{1-x}Sn_xTe_{1-y}Se_y$ quaternary solid solutions lattice-matched with BaF_2 substrates. Weak temperature dependences of R_H are characteristic of the *n*-type epilayers with $0.00 \le x \le 0.25$ (at.fract.) and $0.69 \le y \le 0.78$ (at.fract.) in the temperature interval of 77 to 300 K. In our opinion, the insignificant R_H decrease with temperature is caused by temperature dependence of Hall-factor, which decreases with the temperature increasing due to changing of its components — anisotropy factor and statistical factor. *p*–$Pb_{1-x}Sn_xTe_{1-y}Se_y$/ BaF_2 epilayers show a heavier temperature dependence of R_H (Fig. 3), that may be explained by trend to self-compensation at the growth process of solid solutions with post-inverse disposition of L_6^- and L_6^+ terms. The homogeneity region of the grown $Pb_{1-x}Sn_xTe_{1-y}Se_y$/KCl epilayers was shifted towards the metal, that is why the electrically active native defects of donor type were predominant (Table). These layers also show a weak temperature dependence of carrier concentration, and their R_H decreased at increasing initial growth temperature and

Table. Elemental composition and electric parameters of $Pb_{1-x}Sn_xTe_{1-y}Se_y$ epitaxial layers at T ~ 80 K (N denotes the conduction type)

Heterostructure	N	$n(p)$, $\times 10^{17}$ cm^{-3}	μ_H, $\times 10^3$ cm^2·V^{-1}·s^{-1}
$BaF_2/Pb_{0.98}Sn_{0.02}Te_{0.22}Se_{0.78}$	n	1.5÷2.1	9.3÷9.8
$BaF_2/Pb_{0.93}Sn_{0.07}Te_{0.24}Se_{0.76}$	n	2.3÷2.6	8.6÷8.9
$BaF_2/Pb_{0.89}Sn_{0.11}Te_{0.26}Se_{0.74}$	n	2.6÷2.9	7.8÷8.2
$BaF_2/Pb_{0.81}Sn_{0.19}Te_{0.28}Se_{0.72}$	n	3.9÷4.4	6.5÷7.1
$BaF_2/Pb_{0.59}Sn_{0.41}Te_{0.37}Se_{0.63}$	p	3.1÷3.4	2.3÷2.6
$BaF_2/Pb_{0.48}Sn_{0.52}Te_{0.41}Se_{0.59}$	p	5.2÷5.4	1.0÷1.2
$BaF_2/Pb_{0.42}Sn_{0.58}Te_{0.44}Se_{0.56}$	p	6.6÷7.2	0.5÷0.9
$BaF_2/Pb_{0.31}Sn_{0.69}Te_{0.48}Se_{0.52}$	p	8.1÷8.7	0.1÷0.3
$KCl/Pb_{0.83}Sn_{0.17}Te_{0.79}Se_{0.21}$	n	0.9÷1.3	9.7÷10.1
$KCl/Pb_{0.80}Sn_{0.20}Te_{0.81}Se_{0.19}$	n	1.8÷2.2	9.1÷9.4
$KCl/Pb_{0.77}Sn_{0.23}Te_{0.82}Se_{0.18}$	n	2.5÷2.7	8.5÷8.8
$KCl/Pb_{0.74}Sn_{0.26}Te_{0.83}Se_{0.17}$	n	3.5÷3.8	6.1÷6.6
$Pb_{0.80}Sn_{0.20}Te/Pb_{0.91}Sn_{0.09}Te_{0.94}$ $Se_{0.06}$	p	2.1÷2.4	5.8÷6.3
$Pb_{0.80}Sn_{0.20}Te/Pb_{0.87}Sn_{0.13}Te_{0.96}$ $Se_{0.04}$	p	4.6÷4.9	3.7÷4.1
$Pb_{0.80}Sn_{0.20}Te/Pb_{0.82}Sn_{0.18}Te_{0.98}$ $Se_{0.02}$	p	7.1÷7.6	0.9÷1.5
$PbTe_{0.92}Se_{0.08}/$ $Pb_{0.89}Sn_{0.11}Te_{0.95}Se_{0.05}$	n	3.7÷4.5	18÷24
$PbTe_{0.92}Se_{0.08}/Pb_{0.85}Sn_{0.15}Te_{0.97}$ $Se_{0.03}$	n	6.4÷6.7	12÷16

contents of tin and tellurium. The free carrier concentration in the $Pb_{1-x}Sn_xTe_{1-y}Se_y$ solid solutions lattice-matched with semiconductor substrates is found to be dependent on the conductivity type and carrier concentration in the substrates. So, the p-type layer growth instead of the expected n-type was revealed for the epilayers grown on the p–$Pb_{0.80}Sn_{0.20}Te$ substrates (p ~ (5÷8)·10^{18} cm^{-3}). That can be explained by diffusive distribution of the electrically active native defects between the epilayer and substrate in the course of growth.

Experimental investigations of the temperature dependence of Hall carrier mobility (Fig. 4) have shown that μ_H in the obtained epilayers decreased as the temperature increased in accordance with the law $\mu_H \sim T^{-\nu}$, where ν increased from 0.9 to 2.0 at the temperature increasing from 77 to 300 K and decreasing contents of tin and tellurium. Such temperature dependence of ν at the $T < 100$ K can be explained by predominance of carrier dispersion on the Coulomb potential of ionized impurities. But at $T > 150$ K, the prevailing mechanisms are the following: dispersion on the straining potential of low-frequency phonons; isotropic dispersion on the polarization potential of long-wave longitudinal high-frequency phonons; elastic dispersion on the alloyed potential caused by the accidental disposition of Pb and Sn atoms in the crystal lattice sites of solid solution. The composition dependence of ν can be explained by essential changing of solid solution band structure at the increasing of tin and tellurium contents.

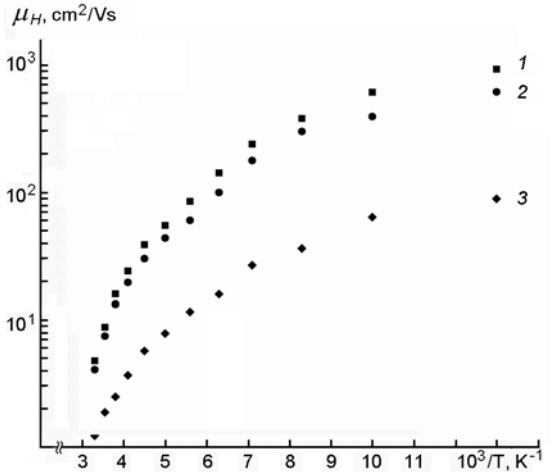

Fig. 4. Temperature dependences of μ_H:
1 — n–$Pb_{0.98}Sn_{0.02}Te_{0.23}Se_{0.77}/$ BaF_2,
2 — n–$Pb_{0.74}Sn_{0.26}Te_{0.83}Se_{0.17}$/KCl,
3 — p–$Pb_{0.82}Sn_{0.18}Te_{0.98}Se_{0.02}/$ $Pb_{0.8}Sn_{0.2}Te$.

So, the complex investigation of electric-physical parameters of the $Pb_{1-x}Sn_xTe_{1-y}Se_y$ quaternary solid solutions lattice-matched with (100)KCl, (111)BaF_2, (100)$Pb_{0.80}Sn_{0.20}Te$ and (100)$PbTe_{0.92}Se_{0.08}$ substrates, which were grown by the liquid phase epitaxy technique at a programmed cooling of $(Pb_{1-v}Sn_v)_{1-w}$ $(Te_{1-u}Se_u)_w$ supersaturated melt-solution without doping, has shown that epitaxial layers of of 2 to 11 μm thickness, surface dislocation density $N_d \le 10^5$ cm^{-2}, carrier concentration $n(p) = (0.9 \div 8.7) \cdot 10^{17}$ cm^{-3} and Hall carrier mobility $\mu_H = (0.1 \div 24) \cdot 10^3$ cm$^2 \cdot$V$^{-1} \cdot$s^{-1} at T ~ 80 K are obtained at the liquidus temperature of 773 to 873 K, cooling rate of 0.1 to 0.2 K/min, temperature decrease range of 5 to 15 K and initial overcooling of 1 to 3 K. Such electric-physical parameters make it possible to predict the good promise of these solid solutions as the material for IR-devices.

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Властивості епітаксійних шарів $Pb_{1-x}Sn_xTe_{1-y}Se_y$ вирощених з пересиченого розчину-розплаву на діелектричних та напівпровідникових підкладках

О.М.Царенко, С.І.Рябець, А.І.Ткачук

Методом рідинної епітаксії при програмному переохолодженні пересиченого розчину-розплаву на підкладках KCl, BaF_2, $Pb_{0,80}Sn_{0,20}Te$ і $PbTe_{0,92}Se_{0,08}$ у широкому діапазоні складів вирощені ізоперіодні епітаксійні шари чотирикомпонентних твердих розчинів $Pb_{1-x}Sn_xTe_{1-y}Se_y$ товщиною 2÷11 мкм з $N_d \le 10^5$ см$^{-2}$, $n(p) = (0{,}9 \div 8{,}7) \cdot 10^{17}$ см$^{-3}$ та $\mu_H = (0{,}1 \div 24) \cdot 10^3$ см$^2 \cdot$В$^{-1} \cdot$с$^{-1}$ при T ~ 80 К.