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Influence of Different Solvents on the Quality of Epitaxial Layers in Pb-Sn-Te-Se Systems

S.I. Ryabetbs, O.V. Volchanskyi,*

Volodymyr Vynnychenko Central Ukrainian State University, 1, Shevchenko st., 25006 Kropyvnytskyi, Ukraine

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The article is devoted to the study of various solvents influence on the quality of epitaxial layers A^4B^6 type semiconductor compounds growing during liquid-phase epitaxy. The choice of such compounds was primarily due to the instrumental characteristics of the obtained structures based on lead-tin chalcogenides, which are competitive in comparison with A^2B^6, among which there are significant sensitivity, response speed, thermal and radiation resistance, spectral homogeneity, and low noise level. The use of multicomponent heterolayers of the $Pb_{1-x}Sn_xTe_{1-y}Se_y$ type makes it possible, by changing the composition, to control the band gap and, within certain limits, to match the parameters of the substrate and the epitaxial layer crystal lattices. In addition, such advantages of liquid-phase epitaxy as low growth temperatures, relatively simple equipment, short duration and cost of the processes, make it possible to continue research in the above direction.

The analysis of the possibility of using In, Ga, Cd, Te, Bi and other solvent metals as alternatives to lead for growing by liquid epitaxy of solid solutions in the Pb-Sn-Te-Se system has been carried out. The use of only solvents based on Te, Tl, Bi in experimental studies is substantiated. In particular, the epitaxial growing with a tellurium solvent demonstrated that use of Bi (for concentrations of 50 atomic %) significantly affected not only the removal of the growth melt, but also the morphology of the grown layers: the surface was free from the wavy relief inherent in epitaxial layers grown from pure tellurium solutions-melts. The results show the promise of Bi-Te melt solutions using, which make it possible to obtain structurally perfect epitaxial layers of *n*-type conductivity with a dislocation density of $\sim 10^5 cm^{-2}$, a carrier concentration of $\sim 10^{18} cm^{-3}$ and a mobility of $(10^3\text{-}10^4)$ $cm^2/V{\cdot}s$ at 77 K.

Keywords: Pb-Sn-Te-Se Systems, Liquid phase epitaxy, Solvents, Epitaxial Layers Quality.

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1. INTRODUCTION

Narrow-gap semiconductors based on solid solutions of A^4B^6 compounds continue to be of interest to researchers as one of the instrumental materials in spectrometers for environmental monitoring of the atmosphere, in scientific work on the creation of highly efficient thermal and photoconverters, etc. [1-3]. Photodetectors based on them have high sensitivity, significant speed compared to detectors with impurity conduction, significant radiation and thermal resistance, spectral homogeneity and low noise level, which makes them competitive with similar ones based on A^2B^6 compounds. Among lead-tin chalcogenides, a special place is occupied by multicomponent solid solutions in the Pb-Sn-Te-Se system, in which changing the composition allows you to control the band gap and the crystal lattice parameter, and therefore control the properties of the resulting materials. Important here is also the possibility, within certain limits, to maximally match parameters of the substrate and the layer being grown crystal lattices.

The liquid-phase epitaxy (LPE) method still remains one of the inexpensive methods for obtaining device structures in the IR range, including those based on semiconductor compounds of the A^4B^6 type [1, 2]. The LPE method is primarily characterized by lower growth temperatures of epitaxial layers in comparison with the production of bulk single crystals, which helps to reduce the number of point defects, the concentration of which depends on the entire complex of growth aspects (thermodynamic, kinetic, hardware-methodical), as well as on the mechanism inclusions of impurities into the melt [3].

Number of point defects decreases due to a decrease in their solubility at low growth temperatures. In turn, the choice of the solvent material influences the achievement of the lowest possible crystallization temperatures. Liquid-phase epitaxy of A^4B^6 compounds is traditionally carried out using a lead-tin solvent. This choice is determined primarily by the low melting point of Pb and Sn, which minimizes the amount of foreign impurities. The use of other solvents in LPE in the Pb-Sn-Te-Se system has received insufficient attention in the literature. Thus, the study of the possibility of epitaxial growth of solid solutions of A^4B^6 compounds from alternative solvents is the subject of this work.

2. JUSTIFICATION OF THE SOLVENTS CHOICE

Bi, Ga, In, Tl, Cd were chosen as objects of study. The main properties of these potential solvents are shown in Table 1, compiled from known reference data. An analysis of these data shows that not all of the above elements can be used in melt solutions as alternatives to lead. It is not advisable to use cadmium [4] and gallium [5] as solvents because of the high temperatures of formation of compounds with tellurium, as well as high volatility and a negative effect on the morphology of epitaxial layers. Indium could be used as an alternative, but the data [6] indicate that it was doped with PbTe to a considerable depth. The use of tin as a solvent metal in the LPE of lead-tin tellurides is undesirable: a continuous series of solid solutions is formed

* o.v.volchanskyi@cuspu.edu.ua

in the Pb-Sn-Te system.

Growing from the tellurium angle of the phase diagram is quite feasible, but here problems are possible due to the high adhesive properties of tellurium, which complicates the removal of the melt solution at the end of the LPE process. Tl can also be used as a solvent, although it has high diffusion properties [6]. The use of Bi [7] in the composition of melt solutions can be quite interesting, since its surface tension coefficient is 0.39 J/m^2, and the formation of compounds with tellurium begins at temperatures below 858 K. In general, the above analysis allows us to focus on Te, Tl and Bi at choosing alternative to Pb solvents.

Table 1 – Main properties of solvent metals used in the crystallization of semiconductor materials.

Metallic chemical element	Melting temperature, K	Surface tension coefficient, J/m^2	Compounds with tellurium	Melting temperature, K	Grating type of compound with tellurium
Ga	302,93	0,707	GaTe Ga_2Te_3 $GaTe_3$	1108 1065	zinc blende (sphalerite)
Gd	594,18	0,588	GdTe	1365	cubic (B3 type)
In	429,76	0,559	InTe In_2Te_3 In_2Te In_2Te_5 In_3Te_4	923 923 923 700 898	sphalerite (B 37 type)
Sn	505,05	0,554	SnTe	1063	cubic (NaCl type)
Te	722,65	0,170	–	–	–
Tl	576,65	0,490	Tl_2Te_3	511	Monoclinic
			TlTe	565	base-centered tetragonal
			Tl_5Te_4 Tl_3Te_2 Tl_5Te_3	– – 719	Volume-centered tetragonal
Pb	600,45	0,48-0,42	Pb Te	1197	cubic (NaCl type)
Bi	544,45	0,390	Bi_2Te_3	858	hexagonal
			BiTe	–	cubic (NaCl type)

3. EXPERIMENTAL TECHNIQUE

The LPE processes were carried out on an Epos vertical type installation in an atmosphere of hydrogen, purified to a dew point of at least 200 K. The preference for using vertical reactors is associated with the elimination of the surface tension influence of the growth solution by centrifugation, which is essential for A^4B^6 compounds, in contrast to A^3B^5. Single crystals of PbTe and $PbTe_{1-y}Se_y$ orientation <100> were used as substrates, which were preliminarily degreased in toluene and subjected to chemical-dynamic polishing in an etchant for 5 % Br_2 + 95 % HBr. After that, the substrates were repeatedly washed in deionized water and dried in ethanol vapor.

PbTe epilayers were grown on PbTe substrates, and $Pb_{1-x}Sn_xTe_{1-y}Se_y$ heterolayers were grown on $PbTe_{1-y}Se_y$ substrates. Elemental Pb, Sn, Te, Se, as well as Bi and Tl of the highest degree of purification were used to prepare growth solutions. The growth temperature varied within 673-873 K, the program cooling rate was 0.05-0.10 K/min, the cooling interval was 5-10 K. After the completion of the LPE processes, the remaining melt solutions were removed by centrifugation.

The structural perfection and elemental composition of the grown epitaxial layers were studied using a JSM-35CF electron microscope-microanalyzer with a Link-860 detector (the error did not exceed 2 %). During the probe electron microanalysis, the sample was placed in such a way that the electron beam was incident at a normal angle on the polished surface of the heterostructure. The dislocations density on the surface of the grown structures was determined by single etching followed by counting the formed etch pits in accordance with the procedure [8]. The Hall effect was studied by the Van der Pauw method in a constant magnetic field of 0.5 Tl at currents through the sample of no more than 80 mA (the maximum error did not exceed 15 %).

4. RESULTS AND DISCUSSION

The results of the experiments are presented in Table 2. In the process of growing from tellurium melt solutions, epitaxial layers of satisfactory quality were obtained with a dislocation density of $\sim 10^5$ cm^{-2} on the surface, and the structural perfection was comparable (in some cases exceeded) with similar epitaxial layers using a lead solvent.

The surface of the structures during growing from the tellurium angle of the phase diagram was wavy in some cases and with the remains of a solution-melt – in others (Fig. 1). This is due to the good wettability of the substrate surface by tellurium, which complicates the removal of the growth solution at the end of the process. This fact allowed us to assume that the addition of thallium (bismuth) to the tellurium solution-melt should greatly facilitate the removal of the growth solution and affect the morphological perfection of the layers.

Table 2 – Characteristics of PbTe epitaxial layers grown from alternative melt solutions

Solvent	Concentration, atomic %	Dislocation density and features of structural perfection			Inclusion composition, atomic parts
		Nd, cm^{-2}	Pb-melt	Te- melt	
Tellurium	100	~10^5	–	wavy melt residues	
Bismuth	10	~10^5	without features	mirror-smooth surface	
	30	(4-8) ·10^5	without features	mirror-smooth surface	
	50	(2-4) ·10^5	honeycomb surface	the second phase appearance	
	70	–	separate areas of etching	inclusions identified	$Pb_{0,2}Bi_{0,8}BiTe$ $Pb_{0,3}Bi_{0,7}Bi_2Te_3$ $Bi_{0,6}Te_{0,4}$
Thallium	10	~10^5	–	–	
	20	~10^5	–	–	
	30	~$2{\cdot}10^5$	inclusions of a different nature		Tl_5Te_3

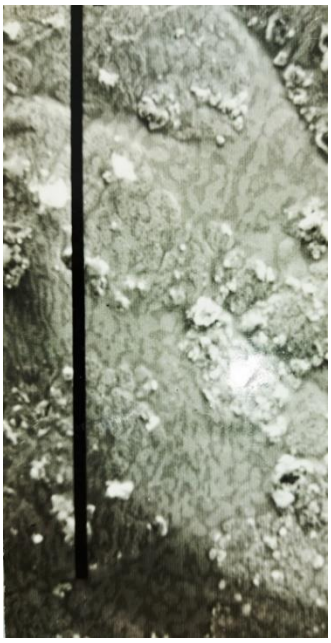

Fig. 1 – View of the epitaxial layer PbTe surface, grown by the LPE method from a tellurium solution-melt (×800)

The composition of Tl (Bi) varied from 10 to 70 wt %. For comparison, epitaxial layers were also grown from lead-tin solutions-melts with similar additives.

Introduction of thallium into the melt showed that in a lead solvent with a content of Tl up to 10 wt %, no significant improvement in morphology was observed, and with an increase in the concentration of thallium, the epitaxial layer was covered with inclusions of the composition Tl_2Te_3 and $T1_5Te_4$. In tellurium solutions-melts, layers with a smooth surface were obtained, the dislocation density was ~ 10^5 cm^{-2}. X-ray diffraction microanalysis showed the presence of $T1_5Te_3$ compounds in individual epitaxial layers. The absence of the latter was typical for program cooling rates of 0.1 K/min.

In general, a significant improvement in the structural perfection of the epitaxial layers with the addition of thallium failed to be obtained. In addition, thallium significantly diffused into the substrate – up to 10 μm.

At using of Bi in the process of epitaxy from lead-tin solutions-melts, the quality of the epitaxial layers did not improve. On the other hand, its use with a tellurium solvent at a concentration of 50 at. % significantly affected not only the process of removal of the growth melt, but also the morphology of the grown layers. The dislocation density in such layers at $T = 855$ K did not exceed $(2-6)\cdot 10^5$ cm^{-2}, and the surface was free from wavy relief inherent in epitaxial layers grown from pure tellurium melt solutions. As expected, when the content of bismuth in the tellurium growth solution varied from 10 to 50 wt. %, EPMA revealed inclusions of phases of Te with Bi compounds in various ratios. With the growth temperature increasing to 860 – 873 K, almost no precipitation of such phases was observed.

5. CONCLUSIONS

Thus, for all the tested metal solvents, only the use of a tellurium solution with the addition of bismuth (40 wt. %) leads to the production of mirror-smooth epitaxial layers at growing temperatures of 863 – 873 K, $\Delta T = 5$ K, $u_{cool} = 0.1$ K/min. The centrifugation speed to remove the melt solution was 900 – 1000 rot/min. The same results were obtained for epitaxial layers of $Pb_{1-x}Sn_xTe_{1-y}Se_y$ four-component solid solutions.

To eliminate the influence of the semiconductor substrate in the study of electrical properties, the latter were grown on fresh cleavages of the KCl {100} dielectric. All epitaxial layers grown by the LPE method in the Pb-Sn-Te-Se system from (Bi-Te) + (Pb-Sn-Se) melt solutions had *n*-type conductivity, the best of which were characterized by a dislocation density of $2{\cdot}10^4$ cm^{-2}, concentration main charge carriers $5{\cdot}10^{17}$ cm^{-3} and mobility $8{\cdot}10^3$ $cm^2/V{\cdot}sec$.

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Вплив різних розчинників у системі PЬ-Sn-Te-Se на якість епітаксіальних шарів

С.І. Рябець, О.В. Волчанський

Центральноукраїнський державний університет імені Володимира Винниченка, вул. Шевченка, 1, 25006 Кропивницький, Україна

Стаття присвячена дослідженню впливу різних розчинників на якість епітаксійних шарів напівпровідникових сполук типу A^4B^6 при рідиннофазній епітаксії. Вибір таких сполук був зумовлений насамперед конкурентними порівняно з A^2B^6 приладними характеристиками одержуваних структур на основі халькогенідів свинцю-олова, серед яких виділяють значну чутливість, швидкодію, термічну та радіаційну стійкість, спектральну однорідність, низький рівень шумів. Застосування багатокомпонентних гетерошарів типу $Pb_{1-x}Sn_xTe_{1-y}Se_y$ дозволяє змінюючи склад, регулювати ширину забороненої зони і в певних межах узгоджувати параметри кристалічних решіток підкладки та епітаксійного шару. Крім того, такі переваги рідкофазної епітаксії як невисокі температури росту, відносно нескладне обладнання, невелика тривалість та собівартість процесів дозволяють продовжити дослідження у вищевказаному напрямку. Проведено аналіз можливості застосування In, Ga, Cd, Te, Bi та інших металів-розчинників як альтернативних свинцю для вирощування методом рідинної епітаксії твердих розчинів у системі Pb-Sn-Te-Se. В експериментальних дослідженнях обґрунтовано використання розчинників на основі Te, Tl, Bi. При цьому, в процесі епітаксії з телуровим розчинником виявлено, що використання Bi (для концентрацій 50 атомних %) істотно впливало не тільки на видалення ростового розплаву, але і на морфологію шарів, що вирощуються: поверхня була вільна від хвилястого рельєфу, властивого епітаксійним шарам, вирощеним з чистих телурових розчинів-розплавів. Результати показують перспективність використання Bi-Te розчинів-розплавів, які дозволяють отримувати структурно-досконалі епітаксійні шари n-типу провідності із щільністю дислокацій ~10^5 $см^{-2}$, концентрацією носіїв ~10^{18} $см^{-3}$ та рухливістю (10^3-10^4) $см^2$/В·сек при 77 К.

Ключові слова: Системи Pb-Sn-Te-Se, Рідкофазна епітаксія, Розчинники, Якість епітаксійних шарів.