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Formation of Pb-Sn Janus particles on the surface of lead-tin telluride films during ion-plasma sputtering

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Abstract. The formation of Janus-like particles of Pb-Sn during ion-plasma treatment of the surface of lead-tin telluride films was found. $Pb_{0.6}Sn_{0.4}Te$ films 2 μm thick were grown on (111) BaF_2 substrates by molecular beam epitaxy. The ion-plasma treatment of the samples was carried out in a high-density low-pressure radio frequency inductively coupled plasma at an ion energy of 75 eV and 25 eV. The duration of the sputtering process was 240 s. The evolution of the film surface morphology and the formation of Pb-Sn Janus particles with nano- and submicron sizes have been studied.

Keywords: lead-tin telluride, Janus particles, ion-plasma treatment, ion energy

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Образование Pb-Sn Янус-частиц на поверхности пленок теллурида свинца-олова при ионно-плазменном распылении

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Аннотация. Описано образование янус-подобных частиц Pb-Sn при ионно-плазменной обработке поверхности пленок $Pb_{0.6}Sn_{0.4}Te$, выращенных на подложках (111) BaF_2 методом молекулярно-лучевой эпитаксии. Ионно-плазменная обработка образцов осуществлялась в реакторе плотной аргоновой плазмы высокочастотного индукционного разряда низкого давления при энергии ионов 75 эВ и 25 эВ. Продолжительность процесса распыления составляла 240 с. Изучена эволюция морфологии поверхности пленки и формирование Pb-Sn Янус-частиц нано- и субмикронных размеров.

Ключевые слова: теллурид свинца-олова, янус-частицы, ионно-плазменная обработка, энергия иона

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Introduction

Semiconductor solid solutions of lead-tin telluride ($Pb_{1-x}Sn_xTe$) are important materials for use in IR photovoltaic devices, thermoelectric devices and laser systems [1]. The band gap of the material is capable of smoothly changing in the range of 0.32–0–0.18 eV (300 K) with varying the tin content $0 \leq x \leq 1$ [2]. The x value at which band inversion is observed in $Pb_{1-x}Sn_xTe$ increases from 0.35 to 0.65 with an increase in temperature in the range 4.2–300 K. It is known that the phenomenon of band inversion in lead–tin telluride is accompanied by a transition from the trivial state to the state of a topological crystalline insulator [3], which makes it important to form and study the processes of nanostructuring of $Pb_{1-x}Sn_xTe$ materials. One of the widely used approaches to the formation of nanorods and nanowires of lead-tin telluride is a method based on the vapor-liquid-solid (VLS) mechanism, in which gold [4–6] or a gold–tin alloy is usually used as a seed catalyst [7]. In our works, we have shown that an effective method for nanostructuring the surface of lead chalcogenides crystals and films is the ion-plasma treatment method. In particular, it was shown in [8] that, during ion-plasma treatment, lead-tin telluride nanocones can grow by a modified VLS mechanism with plasma-assisted self-formation of metal nanodroplets of the seed catalyst. At the same time, the question of the chemical composition of the droplets of the seed catalyst remains unclear. The purpose of this work is to study the role of lead and tin atoms in the formation of nanostructures by the VLS mechanism during ion-plasma surface modification.

Materials and Methods

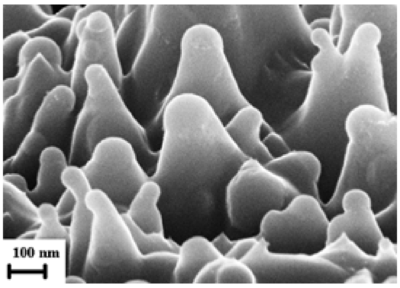
Single-crystal $Pb_{0.6}Sn_{0.4}Te$ films 2 μm thick were grown by molecular beam epitaxy on a Riber 32 P setup (INPE, Brazil) on (111) BaF_2 substrates. The energies of Ar+ ions (E_i) were 75 eV and 25 eV, the treatment time was 240 s. The ion current density was 5.2 mA·cm^{-2}. The surface morphology was studied by scanning electron microscopy (SEM) on a Supra 40 Carl Zeiss microscope; chemical analysis was carried out by energy dispersive X-ray (EDX) method on an INCA attachment. The technique of carrying out experiments is involved in [8]

Results and Discussion

The initial samples had a flat surface and were characterized by the presence of triangular dislocation pits. The surface density of the dislocation exit pits was ~10^9 cm^{-2}. When the surface was treated with ions with an energy of 75 eV for 240 seconds, the surface was strongly modified. Fig. 1, a shows the appearance of an ensemble of nanocones with a quasi-spherical cap on top. The diameter of the quasi-spherical caps was 40-100 nm. The formation of such cones is explained by the growth of nanostructures by the VLS mechanism under conditions of parallel action of the ion flow [8]. Confirmation of the possibility of realizing the VLS mechanism is the formation of nanostructures in the microgap under the mask, where there was no ion bombardment (Fig. 1, *b*). Under the mask, classical nanopillars with a quasi-spherical catalyst cap were formed [9]. The tilt of the nanopillars at an angle of 55° corresponded to the <100> orientations, which have minimal growth energy. This experiment allows us to conclude that the formation of cone-shaped structures with a quasi-spherical cap at the top (Fig. 1, *a*) can be explained by growth processes by the VLS mechanism in the presence of an accompanying flow of argon ions. After two-stage (75 eV, 240 s + 25 eV, 240 s) treatment, large hemispherical formations appeared on the surface, reaching 1 μm in diameter (Fig. 2, *c*).

The chemical composition of lead-tin telluride films in the initial state and after various conditions of plasma treatment is given in Table 1. The measurements were carried out on an area of 50×10 μm² when the sample is tilted at an angle of 70° relative to the normal to the surface. This geometry of the experiment provided an increase in the contribution of the surface compared to the volume. Microanalysis of the surface composition of $Pb_{1-x}Sn_xTe$ showed that plasma treatment with ions led to an increase in the metal content on the surface and a decrease in the tellurium content (Table 1).

a)



b)

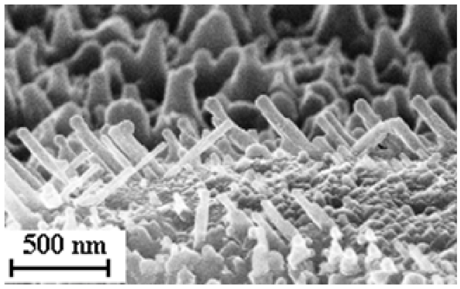


Fig. 1. Structures on the surface of the $Pb_{0.6}Sn_{0.4}Te$ film (*a*) and under the mask (*b*) after 240 s treatment at an ion energy of 75 eV

Table 1

Chemical composition of lead-tin telluride films in the initial state and after plasma treatment

Chemical element	Quantity, at.%		
	Initial state	Processing 75 eV, 240 s	Processing 75 eV, 240 s + 25 eV, 240 s
Pb	25.43	27.22	35.24
Sn	23.46	27.53	34.87
Te	51.11	45.25	29.90

Analysis of the nanostructured surface of $Pb_{0.6}Sn_{0.4}Te$ film in SEM in the backscattered electron mode showed that, in contrast to the analysis in secondary electrons (Fig. 2 *a*, *c*), it showed the presence of strongly contrasting regions (Fig. 2 *b*, *d*). It is known that the mode of backscattered electrons allows separating regions consisting of heavy and light elements [10], since the latter have a darker shade. In the backscattered electrons in (Fig. 2, *b)*, dark "caps" are observed at the top of the nanocones, which indicates that their composition differs from that of the film. In this mode of analysis, light and dark regions are clearly distinguished on structured $Pb_{0.6}Sn_{0.4}Te$ in the form of hemispheres (Fig. 2 *d*). This indicates that the hemispheres are Janus particles, consisting of areas with predominant localization of heavy (lead) and lighter (tin) chemical elements. It can be assumed that the quasi-spherical catalyst particles at the tops of the cones (Fig. 2, *b*) are also Janus particles. The occurrence of quasi-spherical Janus particles of the Au-Sn catalyst over SnTe nanowires was also described by Sadowski [7], where two regions consisted of Au and an Au-Sn alloy.

The size of the droplets made it possible to carry out their local EDX analysis. Analysis of the chemical composition of light and dark areas of Janus-like droplets (Fig. 3) showed that the content of tellurium in these areas is low and does not exceed 2-11 at.% for different samples. For the light region (region 1, on the Fig. 3), the content of lead and tin was 76 and 13 at.%, respectively.

For the dark region (region 2), these indicators were 3 and 95 at.%. This suggests that the submicron Janus structures observed on the surface consist of two regions with a predominant content of either lead or tin.

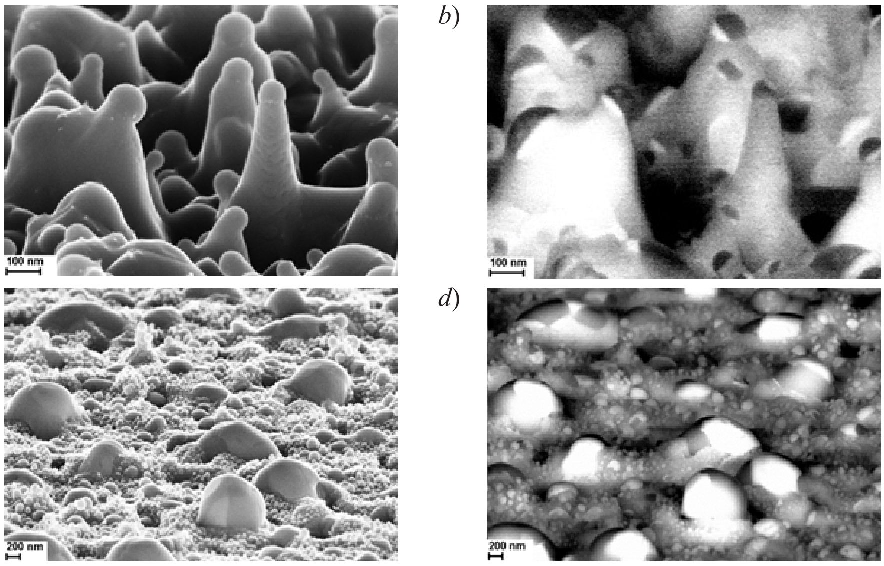


Fig. 2. SEM images of the $Pb_{0.6}Sn_{0.4}Te$ film surface after treatment with argon ions E_i=75 eV (*a*, *b*) for 240 s and after two-step processing 75 eV, 240 s+25 eV, 240 s (*c*, *d*) in the secondary electron mode (*a*, *c*) and in the backscattered electron mode (*b*, *d*)

The ratio of elements in two areas the Janus-like droplets (76 at.% Pb, 13 at.% Sn; 3 at.% Pb, 95 at.% Sn) is very close to the solidification of drops from the liquid phase according to the Pb–Sn phase diagram and close to the experimental values obtained in [11].

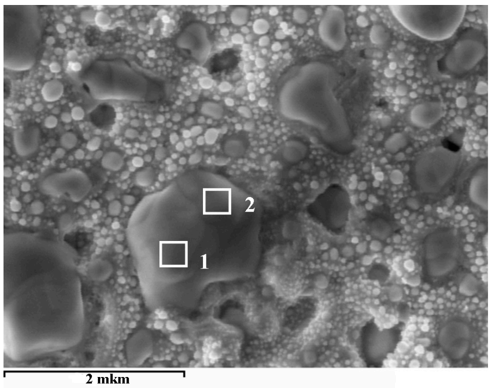


Fig. 3. Local energy-dispersive analysis of a large Janus drop at two different points

Conclusion

The results of this work showed that, as a result of plasma treatment of $Pb_{0.6}Sn_{0.4}Te$ films, nano- or submicron Pb-Sn Janus particles are formed on their surface. It is known that Janus-like Pb-Sn nanoparticles have features of transition to the liquid state [12], which should be taken into account when using them as a seed catalyst in the process of nanostructure formation by the VLS mechanism.

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