Influence of ion-plasma treatment on the surface morphology of epitaxial lead-tin telluride films

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Abstract. The paper discusses the physical aspects of surface modification of Pb₁₋ₓSnₓTe (x = 0.00-0.80) epitaxial films during ion-plasma treatment in argon plasma. Lead–tin telluride films 1–2 µm thick were grown on (111) BaF₂ substrates by molecular beam epitaxy. The ion-plasma treatment of the samples was carried out in a high-density low-pressure radio frequency (RF) inductively coupled plasma at an ion energy of 75 eV. The duration of the process is 240 s. The evolution of the surface morphology of the films and the formation of micro- and nanostructures at different ratios of lead and tin are studied.

1. Introduction

A solid solution of lead-tin telluride Pb₁₋ₓSnₓTe is actively used in the manufacture of infrared photodiodes, lasers, optoelectronic pairs, thermoelectric devices, multilayer systems with quantum wells and superlattices [1,2, etc.]. Recently, much attention has been paid to studying the properties of a material during the transition from a trivial state to a topological one [3], which makes the development of surface nanostructuring processes relevant [4, 5]. In our previous works [6, etc.] it was shown that effective nanostructuring of the surface of lead-tin telluride is possible by ion-plasma treatment of the surface with argon ions with an energy of 25 and 200 eV. The purpose of this work was to continue research on the processes of micro- and nanostructuring of the surfaces of Pb₁₋ₓSnₓTe epitaxial films under the conditions of using argon ions with an energy of 75 eV.

2. Experimental details

(111) Pb₁₋ₓSnₓTe films with x=0.00; 0.40; 0.80 were grown by molecular beam epitaxy on a Riber 32 P setup (INPE, Brazil) on (111) BaF₂ substrates by the authors of [7]. The film thickness was 1–2 µm; the properties of the layers in the initial state are described in detail in [6]. The surface of the films was treated in argon plasma in a high-density low-pressure radio frequency (RF) inductively coupled plasma, which is described in [6]. Argon plasma was ignited by applying an RF power of 800 W (frequency 13.56 MHz) to the inductor. An average Ar⁺ ion energy (Ei) was of 75 eV. The ion current density was 5.2 mA cm⁻². Argon flow was 20 sccm, and the operating gas pressure was 0.15 Pa. The plasma treatment duration (t) was of 240 s. The surface morphology was studied with scanning electron microscopy (SEM) using a Supra 40 Carl Zeiss microscope. The local chemical composition of the crystal surface was determined using energy-dispersive X-ray (EDX) microanalysis using an INCAx-act spectrometer (Oxford Instruments).
3. Results and discussion
The original samples had a flat surface and were characterized by the presence of triangular pits of dislocation exit. The surface density of dislocation exit pits was in the range \((7–80) \times 10^8\) cm\(^{-2}\), increasing in this range as the Sn content in the sample increased [6]. Carrying out plasma treatment with ions with an energy of 75 eV for 240 s led to a significant modification of the surface. Estimation of the sputtering rates showed that they decrease from 5.5 nm/s to 0.4 nm/s as \(x\) increases from 0.00 to 0.80. Comparison with data from previous studies indicates that the sputtering rate under these conditions is higher than at an ion energy of 25 eV, but less than at \(E_i=200\) eV.

When treated with ions with an energy of 75 eV for 240 s for \(x=0\) (PbTe), against the background of small-scale roughness, the formation of identically oriented truncated triangular pyramids with triangle sides at the base of 450 nm on average was observed (Fig. 1). The height of the pyramids was 200–300 nm. The surface density of such truncated pyramids was \(6 \times 10^8\) cm\(^{-2}\), which is very close to the surface density of the dislocation exit regions, which was \(7 \times 10^8\) cm\(^{-2}\). This suggests that the formation of pyramids is associated with the well-known fact of micromasking in the places where dislocations emerge on the surface [8]. The shape of the triangular pyramids in this case is explained by the (111) orientation of lead telluride films, while the (100) orientation is characterized by the appearance of tetrahedral pyramids [9]. The pyramids in this experiment are truncated due to partial sputtering of the vertices and at the same time formation of the nanorelief.

![Figure 1. Surface modification of PbTe films at an ion energy of 75 eV in 240 s. View at an angle of 70° (a) and from above (b).](image)

The surface morphology of Pb\(_{0.60}\)Sn\(_{0.40}\)Te films after plasma treatment (\(E_i=75\) eV, \(t=240\) s) is shown in Fig.2. Under these conditions, cone-shaped structures with a quasi-spherical cap at the top were formed on the surface. The surface density of these structures was \((2–3) \times 10^{10}\) cm\(^{-2}\), and the dimensions of the quasi-spherical cap were on average 65 nm. The inclination of the structures at an angle same structures of up to 55° from the normal is traced.
To elucidate the mechanism of formation of such structures, an additional experiment was carried out, which consisted in the fact that a mask was placed on the surface, between which and the surface there was a microgap of ~1 μm (Fig. 3). During plasma treatment, cone-shaped structures with a quasi-spherical cap at the top appeared on the free surface. In the microgap under the mask, inclined columnar structures with a spherical cap were formed. The inclination of the columnar structures by 55° from the vertical is associated with growth in the <100> directions, which corresponds to the crystal growth in the directions, which have minimal free energy [6]. These structures grow by the vapor-liquid-solid (VLS) mechanism [10]. It is possible that in an open area, structures also grow according to the VLS mechanism. As a result ion bombardment, the formed nanocones have specific shape. Same structures described earlier in [6]. The use of methods of local EDX analysis and electron microscopy in backscattered electrons has shown that quasi-spherical caps are two-phase and consist of separate phases of lead and tin. These experiments will be described in detail in our next paper.
The surface morphology of the Pb$_{0.20}$Sn$_{0.80}$Te films after plasma treatment is shown in Fig. 4. At a high content of tin (x=0.80), quasi-spherical nanodroplet structures with sizes of 30–60 nm were formed on the surface. The surface density of all quasi-spherical structures was $\sim 3.5 \times 10^{10}$ cm$^{-2}$. EDX analysis showed that the surface under these plasma treatment conditions is enriched in tin and depleted in tellurium.

![Image of Pb$_{0.20}$Sn$_{0.80}$Te films after plasma treatment](image1)

**Figure 4.** Surface modification of Pb$_{0.2}$Sn$_{0.8}$Te films after plasma treatment at an ion energy of 75 eV for 240 s. (a) and (b) - view at an angle of 70˚ and 0˚.

![Image of PbTe films after plasma treatment](image2)

**Figure 5.** Surface modification of PbTe films after plasma treatment at an ion energy of 25 eV for 240 s.

The mechanism of formation of the observed structures on the surface of Pb$_{0.2}$Sn$_{0.8}$Te films requires further study. Similar structures have been described by us when the surface of PbTe was treated with ions with an energy of 25 eV (Fig.5). Now, by analogy with the results of [11], it can be assumed that under these conditions, the processes of nucleation of metallic quasi-spherical particles can take place, which can become hollow with an increase in the process time.

4. Conclusions
The results of this work showed that during ion-plasma treatment of Pb$_{1-x}$Sn$_x$Te epitaxial films at an ion energy of 75 eV, nano- and microstructures of various types appear on their surface, the formation
of which depends on the ratio of lead and tin in the solid solution films. If at an ion energy of 25 eV self-formation of faceted and quasi-spherical structures occurred on the surface, as well as the formation of nanodrops and nanorods with a drop-like “cap”, then during plasma treatment of the surface with ions with an energy of 75 eV at a similar duration of the process, the surface morphology of Pb$_{1-x}$Sn$_x$Te was different. Under these technological conditions, depending on the tin content on the surface, identically oriented truncated triangular pyramids, conical and quasi-conical structures with spherical formations at the top, or ensembles of quasi-spherical structures were formed. The obtained results of the surface nanostructuring during ion-plasma treatment at an ion energy of 75 eV, together with the data for Ei 25 and 200 eV [6, etc.], indicate a variety of shapes and geometric dimensions of the resulting nanostructures, which allows them to be used in instrument devices for various purposes.

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