Peculiar properties of preferential sputtering of PbTe, SnTe, and GeTe by Ar$^+$ ion plasma

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ABSTRACT

Sputtering of PbTe, SnTe and GeTe compounds having both small and large differences in the individual components' masses by Ar$^+$ plasma under Secondary Neutral Mass Spectrometry (SNMS) conditions are investigated. The effect of preferential sputtering and its peculiar features caused by the different ratios between masses of the IVB atoms and tellurium were observed. The method and the empirical relationships for determination of the relative detection factor (RDF) of the intrinsic components of the compounds are suggested. It is shown that RDF of Te and metal species of the investigated samples isn't a constant, but depends on sputtering energy. These dependences are explained by the changes of the sputtering surface morphology and the impact of mass of the sputtered species on the fraction of the species flux ejected into the solid angle collected by the spectrometer mass analyzer. The limits of applicability of SNMS for quantitative analysis of composite samples with big differences in masses of their constituents are established. A possible solution for such cases is proposed. It is shown that in the sequence of PbTe-SnTe-GeTe compounds the surface binding energy of the metal components decreases in the direction from lighter to heavier atom.

1. Introduction

Sputtering by ion plasma is widely used process for composition analysis and depth profiling of multicomponent and doped solids. It underlies such modern methods of analysis as Secondary Ion Mass Spectrometry (SIMS) and Secondary Neutral Mass Spectrometry (SNMS) [1–3]. Sputtering of multicomponent solids is always preferential [3,4]. Therefore the composition of the flux of sputtered species from multicomponent target differs from the composition of the outermost layers of the initial pattern. These differences raise the problem of correct determination of the composition of the investigated object based on the composition of the sputtered phase [4,5].

Our recent researches of sputtering of PbTe crystal surfaces under SNMS conditions have shown that this phenomenon is in particular a serious problem for the IV-VI semiconductors [6,7]. The IV-VI crystals, primarily PbTe, SnTe, GeTe and their solid solutions, are widely used for practical applications, such as for manufacturing of infrared photodetectors, lasers [8,9], thermoelectric devices [10–12], and spintronics structures [13–15]. The success of the use of any given material for the manufacturing of devices depends, in particular, on the exact knowledge of its chemical composition. Therefore, there is a need for a

deeper study of the possibilities of composition analysis of the various IV-VI semiconductors by SNMS method.

2. The motivation of the work

Preferential sputtering of polyatomic solids is primarily due to differences in the atomic masses of their constituents [3]. In the sequence of tellurides PbTe-SnTe-GeTe the ratio of masses of the metal component to tellurium varies considerably. Therefore, one should expect a different degree of preferential sputtering for the various members of this group of materials. Since these semiconductor compounds and their solid solutions, as noted above, have a wide range of practical application, this work is devoted to the comparative study of peculiar properties of preferential sputtering of PbTe, SnTe, and GeTe by Ar$^+$ ion plasma in the conditions of SNMS. The main emphasis is the study of the influence of IV-VI crystalline matrix composition on the ratio of the sputter fluxes of metal and tellurium atoms. This knowledge is necessary primarily as the basis for quantitative estimates of distribution of the native components of solid solutions and the doping elements into semiconductor structures of different architectures.

We have studied sputtering of the patterns manufactured from the

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crystals grown from melt by Bridgman method (PbTe, GeTe), and from the synthesized ingot (SnTe). High-purity initial materials were used for synthesis and growth of the ingots. The conditions of synthesis and growth of crystals corresponded to those described in detail in [16]. The composition of the studied samples was verified by EDX analysis. The natural lateral surfaces of crystal ingots, and the surfaces processed mechanically during cutting of the crystals were used for the sputtering experiments.

3. Experimental details

Sputtering experiments were carried out on INA-X type SNMS system produced by SPECS GmbH, Berlin. The surface bombardment and post-ionization of sputtered neutral particles were done by the Electron Cyclotron Wave Resonance argon plasma [17]. In the direct bombardment mode, Ar^+ ions are extracted from low pressure plasma and bombard a negatively biased (-50…-550 V) sample surface with a current density of $\sim 1\,mA/cm^2$, performing a controlled surface erosion. Since very low ion bombardment energies are used while the sample current densities are uniform over the entire analyzed area, the resolution of the depth profile analysis is in the range of the atomic scale. The sputtered area was confined to a circle of 2 mm in diameter by a Ta mask. Post-ionized neutral particles are directed into a quadruple mass spectrometer Balzers QMA 410 by electrostatic lenses.

4. Results

The sputtering PbTe, SnTe, and GeTe sample surfaces had different quality. It is well known that the target structure is important in experiments on sputtering, particularly impacting the variation of sputter yield with angle of incident and the angular distribution of the sputtered material [5]. Therefore, it was necessary to first of all estimate the validity of the comparative studies of different materials with different perfection of the sample surface. For this we carried out the statistical studies of sputtering of the PbTe sample surfaces with various origins. Two different sputtering energies (50 and 350 eV) and two different types of the sample surfaces (natural – with low surface roughness, and mechanically treated – with high surface roughness) were used. The obtained results are presented in Fig. 1 on an example of the experimental integral intensities Pb $I_{tot}(Pb)$ and Te $I_{tot}(Te)$ normalized by abundance.

One can see that the type of sputtering surface does not affect the dominant features of the temporal changes of sputtering spectra. At the initial stage of sputtering the changes of the ratio $I_{tot}(Te)/I_{tot}(Pb)$ are fast and have opposite sign for low and high sputtering energies. For the sputtering energy of 350 eV the ratio increases rapidly with sputtering
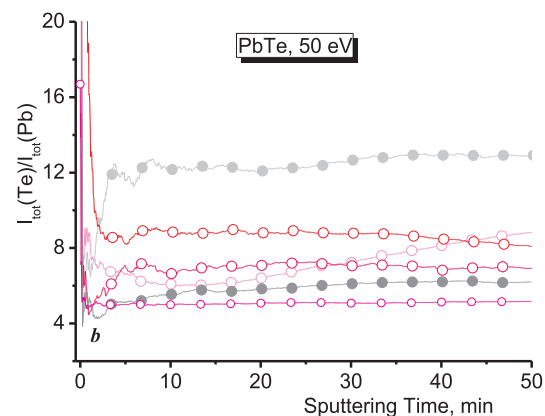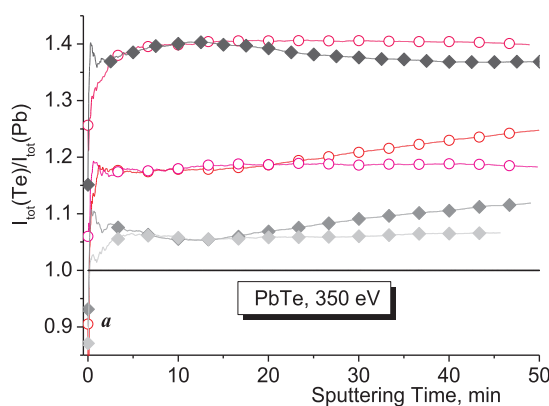

Fig. 2. Ratio $I_{tot}(Te)/I_{tot}(Pb)$ averaged over the whole set of the experimental data for the PbTe samples at the final stage of their sputtering from 20th till 50th minutes of sputtering time vs. sputtering energy.

time, while for 50 eV we observe exactly the opposite and much stronger changes. After several minutes of sputtering the ratio of measured integral intensities of the sputtered matrix constituents is stabilized. At this for some of the samples the ratio $I_{tot}(Te)/I_{tot}(Pb)$ virtually does not change with sputtering time, for the others a slight increase or decrease of the ratio is observed.

The experimental results also indicate that decrease of the sputtering energy leads to the increase of the ratio $I_{tot}(Te)/I_{tot}(Pb)$ and the scatter of its values. For the high sputtering energy of 350 eV the average value of the ratios $I_{tot}(Te)/I_{tot}(Pb)$ presented in Fig. 1 is equal to 1.22 with a standard deviation of 0.14, i.e. about 11% of the average value. For the low sputtering energy of 50 eV the average value of the ratios $I_{tot}(Te)/I_{tot}(Pb)$ is equal to 8.3 with a standard deviation of 3.3, i.e. about 40% of the average value.

The dependence of the measured integral intensities ratio of sputtered Te and Pb species for PbTe patterns is shown in Fig. 2. On the graph the averaged value over the whole set of the obtained experimental data for each of the sputtering energy at the final stage of sputtering is presented.

The obtained data clearly show that the ratio of Te and Pb sputtering signals of PbTe patterns measured experimentally significantly changes if the Ar^+ energy changes. The rate of these changes depends on the sputtering energy range. In the 160–550 eV range it is small. When the sputtering energy decreases from 550 to 160 eV the intensity ratio increases slightly from 1.18 to 1.77. With a further decrease of the sputtering energy the rate of the ratio changes rapidly goes up. In the

Fig. 1. Ratio $I_{tot}(Te)/I_{tot}(Pb)$ of the experimental integral intensities of Te and Pb sputtering for different PbTe samples vs. sputtering time for the sputtering energies of 350 and 50 eV: the solid symbols of different shades of gray show the results of sputtering of the mechanically treated surfaces, the hollow symbols of different shades of red and pink show the results of sp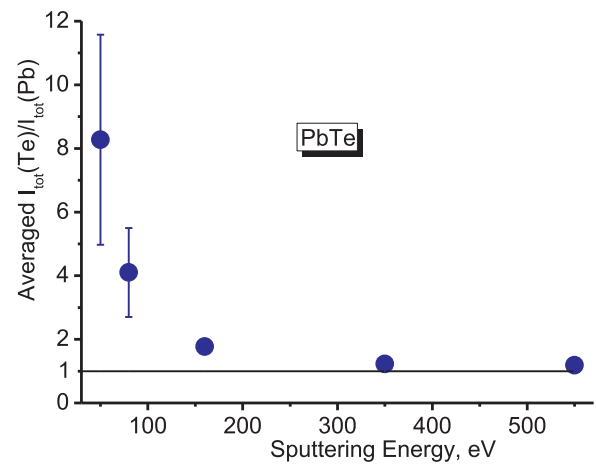uttering of the natural surfaces.