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Formation of the Sputtered Phase of PbTe Crystals by Ar$^+$ Plasma and Re-deposition of the Sputtered Species at Secondary Neutral Mass Spectrometry Conditions

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Formation of the Pb and Te sputtered phase under exposure of the lateral surface of PbTe crystals grown from melt by the Bridgman method by Ar$^+$ plasma at Secondary Neutral Mass Spectrometry (SNMS) conditions and re-deposition of the sputtered species on the sputtering crystal surface are investigated. Experimental evidence of mutual influence of the sputtering and re-deposition processes on each other during prolonged depth profiling of PbTe crystals is presented. Sputtering of the PbTe crystal surface forms the strongly supersaturated sputtered phase of Pb and Te. Re-deposition of the Pb and Te sputtered atoms on the crystal surface results in oscillations of sputtering rate of PbTe crystal and changes of average intensity of Pb and Te sputtering over sputtering time. A possible role of both the sub-critical nuclei of newly re-deposited phase and the re-deposited surface structures of post-critical sizes in generation of the features of PbTe crystal sputtering is discussed. It is concluded that formation and re-sputtering of the sub-critical nuclei of re-deposited phase leads to the oscillations of sputter yields of Pb and Te. Growth and re-sputtering of the re-deposited surface structures of post-critical sizes lead to changes of average values of Pb and Te sputter yields.

Keywords: Sputtering; Re-deposition; Nucleation; Semiconducting lead compounds.

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Introduction

Ion sputtering of different materials is widely used for growing of thin layers and self-organized nanopatterns on various substrates [1-3]. It is also efficiently used in Secondary Neutral Mass Spectrometry (SNMS) for composition analysis and depth profiling of multicomponent solids [4-6]. High sensitivity of SNMS method (down to ppm range) makes it suitable for successful analysis of solid surfaces and thin films and elemental characterization of samples in different fields [7-11].

One of the preconditions for the successful application of SNMS for the correct quantitative composition analysis is having the flat sputtered surface. However, for many practical objectives this requirement cannot be accomplished a priori. In particular, such a situation occurs in the case of lateral profiling of crystal ingots having a conical-cylindrical shape. The need for such investigations arises, primarily, in studying the distribution of doping impurities in the surface layers of crystals grown from doped melts [12].

Recently, studying the processes of depth profiling of PbTe crystals, we revealed the extremely non-uniform features of their sputtering. Most striking were the observations of aperiodical oscillations of Pb and Te sputtering outputs; a huge preference of Te sputtering reaching more than two orders of magnitude at the beginning of sputtering process; a significant excess of Te integrated sputter yield over that of Pb for prolonged sputtering by low energy plasma at 50 – 160 eV. Shortly these results were reported in [13]. In this work we give the expanded picture of these non-uniform sputtering phenomena with a focus on their relationship with the processes of re-deposition of the sputtered Pb and Te species on the PbTe crystal surface sputtering by Ar$^+$ plasma at SNMS conditions. Scanning electron microscopy (SEM) is used for study of the sputtered

PbTe crystal surfaces. Analysis the SNMS and SEM results are complemented by Energy Dispersive X-ray (EDX) data.

I. Experiment

The PbTe crystal ingot used for investigation was grown by the Bridgman method from melt of the high-purity initial components. The lateral surfaces were sputtered. Sputtering experiments were carried out on INA-X type SNMS system produced by SPECS GmbH, Berlin. The surface morphology of samples after ion sputtering has been analyzed by SEM (Hitachi S-4300 CFE). The composition of the different surfaces was verified by EDX analysis. The experimental conditions were the same as it is described in detail in [14].

II. Results

To get a general picture of the preferential and oscillated sputtering of PbTe crystal lateral surface let us start from consideration of the initial stage of sputtering process under different sputtering conditions. As example it is shown in Fig 1 for two samples sputtered by Ar^+ plasma with the beam energy of 50 and 350 eV.

The presented data clearly illustrate preferential and oscillated sputtering of PbTe crystal surface. Furthermore, they show that the preference strongly depends on the sputtering ion energy. For the least energy of 50 eV Te significantly dominates in the sputtered phase (Fig. 1, *a*). Besides, during the first seven seconds of sputtering another component of PbTe crystal Pb was not detected at all in the sputtered phase. Of course, there is the condition of unsteady plasma in the first several seconds of the sputtering, but the conditions for sputtering of both Te and Pb are the same. Farther, the same things take place also in the later stages of sputtering under minimal Ar^+ energy of 50 eV, when Pb from time to time is not observed in the sputtered phase

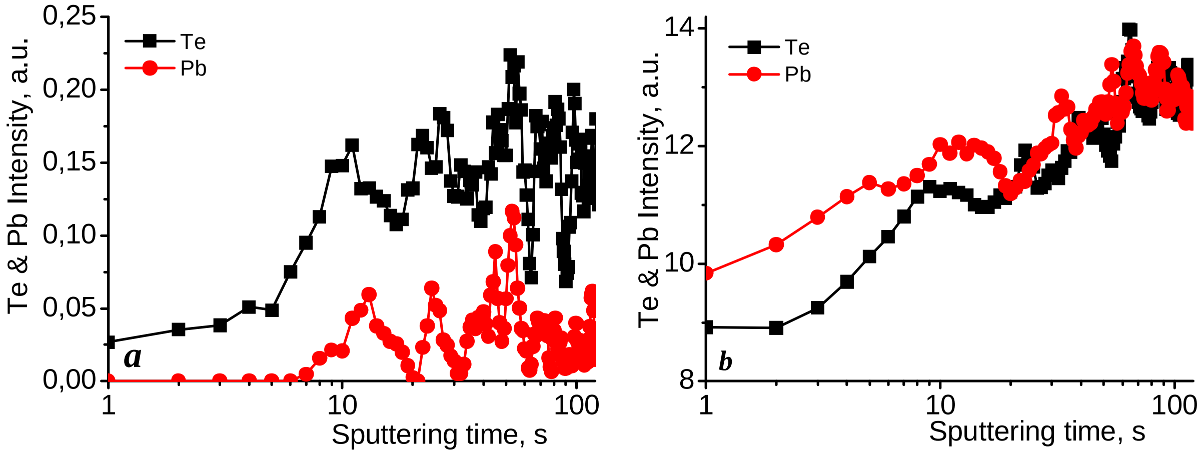

Fig. 1. Intensity of Te and Pb sputtering vs. the initial 100 s of sputtering time for a lateral surface of PbTe crystal grown from melt by the Bridgman method for sputtering Ar^+ beam energy of 50 (*a*) and 350 eV (*b*).

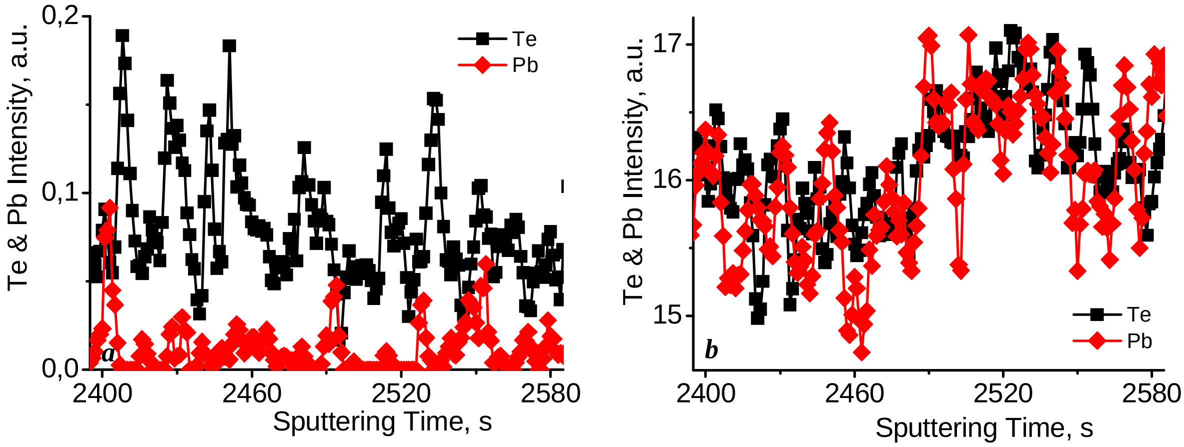

Fig. 2. Intensity of Te and Pb sputtering vs. sputtering time for the same PbTe crystal surfaces as in Fig 1 for sputtering Ar^+ beam energy of 50 (*a*) and 350 eV (*b*).

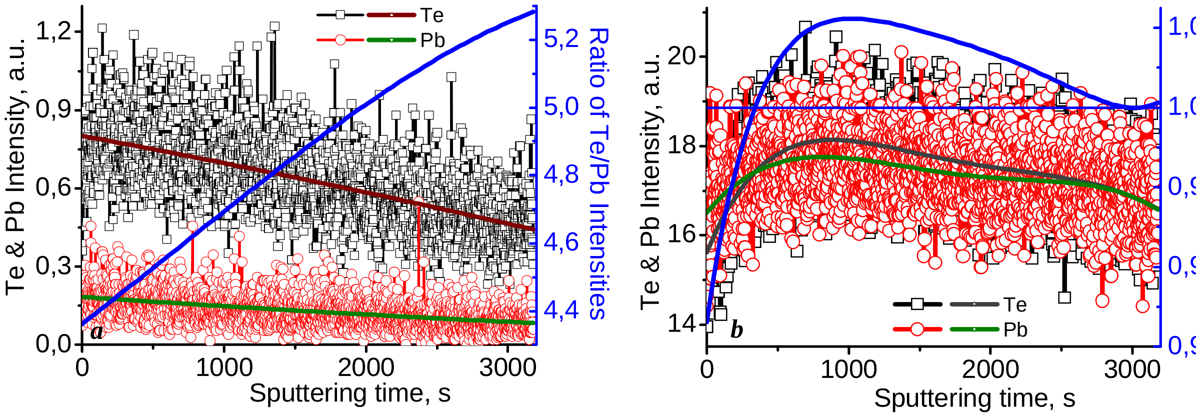

Fig. 3. Intensity of Te and Pb sputtering and the ratio of their averaged values vs. sputtering time of PbTe crystal by Ar$^+$ beam energy of 80 (*a*) and 550 eV (*b*). Symbol – the experimental data; solid lines – the averaged curves. The blue lines show the ratio between Pb and Te intensities.

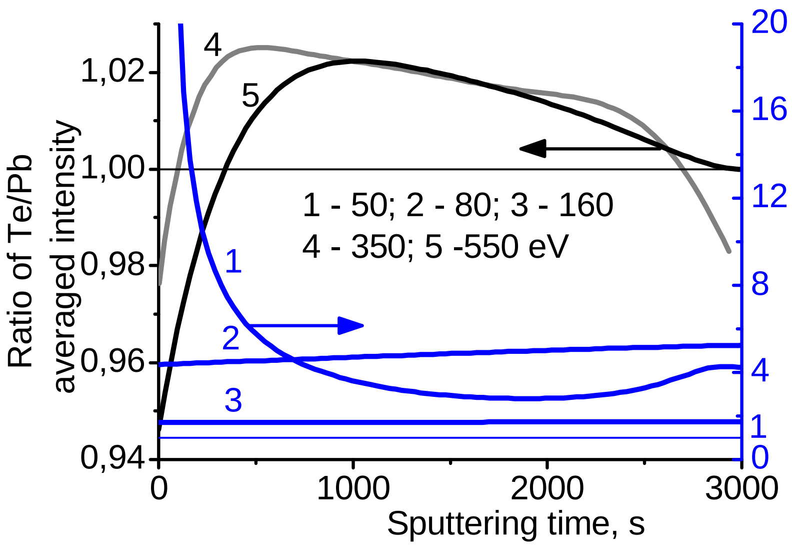

Fig. 4. Ratio of the averaged Te and Pb intensity of sputtering vs. sputtering time for different sputtering energies.

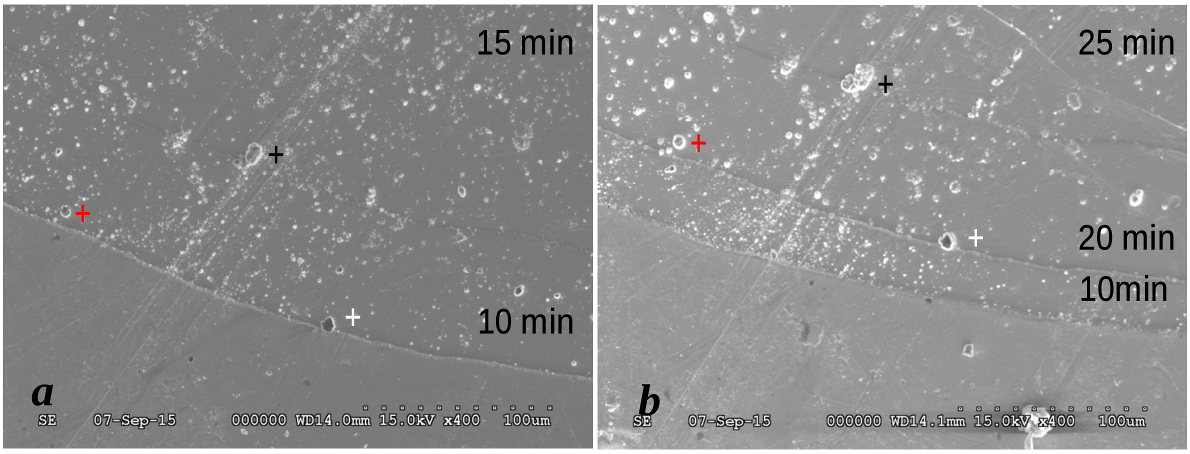

Fig. 5. SEM images of approximately the same fragment of PbTe crystal surface after sputtering by Ar plasma with 350 eV ions energy in two (*a*) and three (*b*) consecutive stages. Sputtering time of the different surface sections is indicated in the figure.

over fairly long periods up to 5-6 seconds. At the same time the Te atoms are always present in the sputtered phase. This feature of sputtering of the PbTe crystal under the least sputtering energy is clearly seen from data in Fig. 2, *a*.

For the sputtering energy of 350 eV we can observe absolutely the opposite situation. At the beginning of the sputtering process already Pb clearly dominates in the sputtered phase (Fig. 1, *b*). In the final stages of PbTe crystal sputtering the intensity of Pb and Te signals in the sputtered phase is close to each other (Fig. 2, *b*).

More clearly the specific features of preferential sputtering of PbTe crystals can be obtained by the way of averaging of the experimental results. The patterns of averaging are shown in Fig 3 for two samples sputtered by Ar^+ ion beams with energy of 80 and 550 eV.

Fig 4 shows changing of the averaged values of degree of preferential sputtering of the individual Te and Pb species during the prolonged sputtering of PbTe crystal surface by the Ar^+ ion beams of different energy.

Formation of Pb and Te sputtered phase under sputtering of PbTe crystal by Ar^+ plasma is accompanied by significant changes of the state of sputtering crystal surface. As we have shown recently [13, 14], the

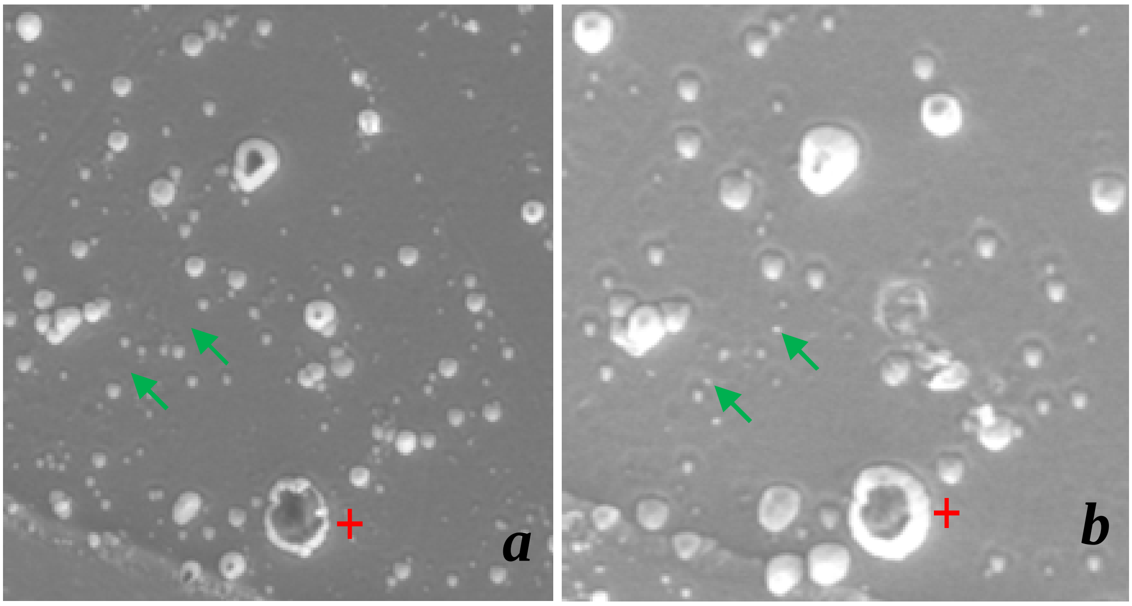

Fig. 6. Enlarged fragments of the same part of the surface shown in Fig 5 (red cross region) after sputtering for 10 (*a*) and 10+10 (*b*) minutes. Magnification is the same in both figures.

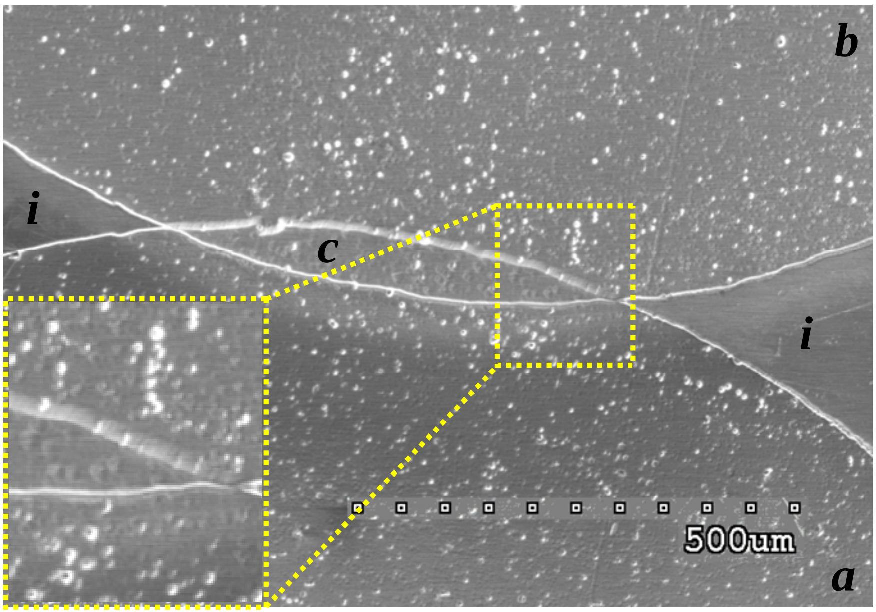

Fig. 7. SEM image of PbTe crystal lateral surface after sputtering of both its segments *a* (sputtered first) and *b* (sputtered second) by Ar plasma with 350 eV ions energy for 50 minutes each: (*i*) – un-sputtered initial surface, (*a*) and (*b*) – the segments of single sputtered surface, (*c*) – the twice sputtered area due to overlapping of the segments (*a*) and (*b*). Insert: Enlarged image of the sputtered segments at the overlap region.

sputtering surface is covered by the array of surface structures, density and average sizes of which strongly depends on the sputtering energy. The lower is sputtering energy, the higher is density of re-deposited surface structures and smaller their average sizes.

To test the impact of the sputtering duration on the state of PbTe sputtering surface the same crystal surfaces were sputtered three times. Duration of the first sputtering stage was 5 minutes; duration of two subsequent sputtering stages was 10 minutes each. For reference with each consecutive sputtering the Ta mask, through hole in which exposure was carried out, was shifted a short distance. The experimental results are shown in Fig 5. The crosses mark the "anchor points" on the surface.

Sputtering time like sputtering energy impacts the parameters of the re-deposited structures. The longer is sputtering time, the larger is the average sizes of structures formed on the sputtering surface and lower their surface density.

Let us consider the enlarged fragments of the surface, sputtered for 10 minutes once and twice (Fig. 6).

Comparing in detail the SEM pictures in Fig. 6, *a* and Fig. 6, *b* we can see that a large number of small surface structures, formed on the sputtered surface during the first 10 minutes of sputtering, were sputtered away on the next stage. Together with disappearance of the previously formed structures some new structures were formed on the test fragment of surface during the second stage of sputtering (two structures that could clearly be identified marked by arrows in Fig. 6). This indicates that the processes of condensation of sputtered species and nucleation of a new phase on the PbTe sputtering surface are continuous, but prolonged PbTe crystal sputtering worsens the conditions for nucleation.

To clarify that, we have sputtered for prolonged time two partially overlapping adjacent areas of the crystal surface. The experimental results are presented in Fig. 7. The segment (*a*) of the surface was sputtered first and the segment (*b*) was sputtered second. The fragment (*c*) is the twice sputtered area due to overlapping of the segments (*a*) and (*b*). Two entirely different results were obtained. The very rich and virtually the same arrays of the surface structures were formed on the sputtered initial crystal surface of the both segments (*a*) and (*b*). In the same time, only the dimple relief essentially free from such structures was formed on the crystal surface pre-modified by Ar plasma (fragment (*c*)). Thus, even though the sputtering conditions of the whole segment (*b*) are the same, the result of re-deposition of sputtered species is completely different depending on the original PbTe sputtering surface. The initial lateral PbTe crystal surface provides effective conditions for nucleation of re-deposited surface structures. The crystal surface pre-modified by Ar$^+$ plasma largely loses these properties.

To compare the composition of the crystal sputtered surface and the surface of structures re-deposited on it, we carried out EDX analysis of the sample subjected to sputtering for 50 minutes by Ar plasma with energy of 50 eV. Ten statistically random points of un-sputtered and sputtered surfaces and ten re-deposited pyramidal surface structures were investigated. Within accuracy of the method the un-sputtered surface was stoichiometric. The composition of sputtered surface averaging over ten measurements was found to be slightly enriched with lead, namely $Pb_{0.517}Te_{0.483}$. Such result was expected, given strong Te enrichment of the PbTe sputtered phase [13]. The composition of the predominant pyramidal structures was intermediate between the compositions of un-sputtered and sputtered surfaces – its average value was found to be $Pb_{0.508}Te_{0.492}$.

III. Discussion

As follows from the experimental data presented above during depth profiling of the lateral surface of PbTe crystal grown from melt by the Bridgman method the crystal surface is simultaneously a target for material sputtering and an efficient substrate for re-deposition of the sputtered species. So, one can definitely assume that the sputtered phase of PbTe crystals and the Pb and Te output analysed at SNMS measurements are formed as the result of superposition of two simultaneous processes – sputtering of PbTe crystal by the Ar$^+$ plasma and deposition of the sputtered species on the sputtering surface.

According Sigmund’s linear collision cascade theory [15, 16] the sputter yield Y of any sputtering element is proportional to its surface concentration C^S and depends also on the element mass M and surface binding energy U:

$$Y \sim C^S / M^{2m} U^{1-2m} , \qquad (1)$$

where m is the exponent in the low energy power cross section.

Sputtering of the PbTe crystals is preferential. Preferential sputtering changes the surface concentrations of all components of the crystal. It depletes the sputtering surface of the species with higher sputter yield and enriches it by the species with lower one. As a result, the sputter yields of Pb and Te under the PbTe crystal depth profiling change over time. If sputtering is the only process forming the crystal sputtered phase, these changes have to be monotonous [17].

The situation could change drastically if we consider re-deposition of the sputtered species on the sputtering crystal surface. There are three physical processes necessary for deposition of atoms on a substrate, but playing, as we believe, absolutely different roles in the process of non-uniform sputtering of PbTe crystal surface at SNMS conditions – atom adsorption, formation of sub-critical nuclei of re-deposited phase, and formation of re-deposited surface structures of post-critical sizes.

Deposition of atoms on any substrate starts with their adsorption, the first stage of which is the physical adsorption. On the stage of physical adsorption the adsorbed atoms do not form any chemical bonds. So, their surface binding energy U_{ads} should be much lower than the surface binding energy of the own crystal atoms U. It means that the newly adsorbed atoms will be re-sputtered with high rate and their lifetime under continuous impact of the bombarding Ar^+ ions will be much smaller than the time of signal accumulation at SNMS. Thus, if all adsorbed atoms are sputtered again, the presence of adsorption practically does not have effect on the result of the measurement.

It's a different matter if some fraction of the re-deposited and adsorbed atoms is retained on the sputtering surface for some time. This is possible if adsorbed atoms have enough time to form nuclei of a new phase due to surface diffusion.

At the first stage of nucleation the sub-critical nuclei are formed on the substrate surface [18]. As we saw composition of the predominant surface structures formed on the sputtering PbTe crystal surface is close to stoichiometric. It is reasonable to assume that the sub-critical nuclei should also be close to stoichiometric PbTe. Formation of the stoichiometric sub-critical nuclei on the surface, enriched by one of the native components, will change the surface composition toward its initial state. Preferential re-sputtering of newly formed structure again causes enrichment of the total crystal surface. Formation of the new stoichiometric sub-critical nuclei again reduces the degree of enrichment, and so on. Thus, due to the formation of the sub-critical nuclei and their re-sputtering the composition of the sputtering PbTe crystal surface will continuously and randomly oscillate. According to (1), the sputter yields of Pb and Te also have to oscillate non-periodically what was indeed observed experimentally.

Re-sputtering of sub-critical nuclei should be a rather rapid process. It is logical to expect that the higher energy of sputtering Ar^+ ions is, the greater the rate of re-sputtering of sub-critical nuclei. The high rate of sputtering results in the high degree of supersaturation of the sputtered phase. The higher supersaturation of the sputtered Pb and Te phase is, the higher is rate of re-deposition of the sputtered species. So, we may expect the increase of the average frequency of oscillations of Pb and Te sputtering when the sputtering energy of PbTe crystal increases what we observed before [13].

In addition to the changes of the Pb and Te surface concentrations there is another reason why formation of the sub-critical nuclei leads to oscillations of the sputtered phase of PbTe crystals. To form a near-stoichiometric nucleus on the sputtering surface, Pb and Te atoms must be removed from the PbTe sputtered phase and re-deposited on the sputtering surface in approximately equal amounts. This will change the non-stoichiometric composition of the residue of sputtered phase, which is analyzed in the SNMS. These additional changes will show themselves the stronger, the smaller the intensity of signals of sputtered Pb and Te is, i.e. the lower is the sputtering energy. Evidently, that is the reason why the relative changes of Pb and Te intensities increases when the sputtering energy of PbTe crystal surface decreases [13]. This can explain also why during sputtering of PbTe crystals under minimal ion energy of 50 eV, when the Pb and Te signal intensities are sufficiently small and the degree of preferential Te sputtering exceeds two orders of magnitude, Pb from time to time is not observed in the sputtered phase over fairly long periods of time (Fig. 2, *a*).

At the further stages of nucleation and nuclei growth, when a potential barrier of a critical nucleus formation is overcome, the sub-critical nuclei are transformed to the post-critical ones. These are the stable formations able to grow [18].

To form the stable re-deposited structures on the sputtering crystal surface some amount of the sputtered species must leave the sputtered phase. This will reduce the output of surface sputtering in comparison with the output without re-deposition. Re-sputtering of some fraction of re-deposited structures will act as a compensating factor. Superposition of these two processes will determine the changes of average intensity of the sputtered species signals. In general case, the loss of sputtered phase because of the formation of the stable surface structures and its replenishing due to re-sputtering of the structures will not equal each other. The relation between them will determine the direction of change of the average intensity of sputtering over time.

Based on these provisions, let's consider the changes of the average sputter outputs of Pb and Te under PbTe crystal surface sputtering [13].

For the average sputtering intensity of Pb and Te to decrease over time, the losses of sputtered phase due to overgrowth of the large re-deposited structures of post-critical sizes at the actual stage of sputtering have to outweigh re-sputtering of the surface structures re-deposited at the previous stage. Such a situation occurs when the sputtering energy is quite small – above of 160 eV and less. In opposite case the average sputtering intensity of Pb and Te will increase over time what we observe if sputtering energy is above of 350 eV and higher [13].

We also believe that formation and growth of the post-critical structures on the sputtering PbTe crystal surface are responsible for significant deviation of the ratio of integrated outputs Te/Pb from unity for large sputtering times at low energies of about 160 eV and less (curves 1-3, Fig 4). These processes constantly move off the composition of the surface, enriched by preferential sputtering, from the value which provides the ratio between the component sputter yields that is equal to the ratio of their bulk concentration, i.e. unity in the case of PbTe crystal.

Conclusions

During depth profiling of the lateral surface of PbTe crystal grown from melt by the Bridgman method under SNMS conditions the crystal surface is simultaneously both a target for material sputtering and an efficient substrate for re-deposition of the sputtered species. Therefore the sputtered phase of PbTe crystals and the Pb and Te output analysed at SNMS measurements are a result of superposition of two simultaneous processes – sputtering of PbTe crystal by the Ar$^+$ plasma and re-deposition of the sputtered species on the sputtering surface. The initial PbTe crystal surface provides effective conditions for nucleation of the new phase of re-deposited surface structures. On the surface of the PbTe crystal, pre-modified by Ar$^+$ plasma, the probability of re-deposition of the sputtered species is much lower.

There are complementary dependences between the non-uniform sputtering of PbTe crystals and the processes of re-deposition of the sputtered Pb and Te atoms on the sputtering surface. The oscillations of sputter yields of Pb and Te we explaine by the formation and re-sputtering of the sub-critical nuclei of the new phase on the sputtering PbTe crystal surface. The changes of average values of Pb and Te sputter yields can be explained by the growth and re-sputtering of the re-deposited surface structures of post-critical sizes.

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Формування фази розпорошення кристалів PbTe плазмою іонів Ar$^+$ і переосадження розпорошених елементів в умовах вторинної нейтральної масспектрометрії

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Досліджено формування фази розпорошення та переосадження розпорошених Pb і Te при опроміненні іонами Ar$^+$ в умовах вторинної нейтральної масспектрометрії бічних поверхонь кристалів PbTe, вирощених з розплаву методом Бріджмена. Наведено експериментальні докази взаємного впливу один на одного цих процесів підчас профілювання вглиб кристалів PbTe. Розпорошення кристалічної поверхні PbTe формує сильно пересичену фазу розпорошених Pb і Te. Переосадження розпорошених атомів Pb і Te на поверхню кристалу PbTe, що розпорошується, веде до коливань у часі швидкості розпорошення кристалу, а також змін середніх інтенсивностей розпорошення Pb і Te. Обговорена можлива роль докритичних зародків переосаджуваної фази і її поверхневих структур посткритичних розмірів у формуванні особливостей розпорошення кристалів PbTe. Зроблено висновок, що формування і повторне розпорошення докритичних зародків переосаджуваної фази веде до коливань в часі виходів розпорошення Pb і Te. Ріст і повторне розпорошення переосаджених поверхневих структур посткритичних розмірів спричиняє зміни середніх значень виходів розпорошення Pb і Te з часом.

Ключові слова:розпорошення,переосадження,зародкоутворення,напівпровідникові сполуки свинцю.