Sputtering rates of lead chalcogenide-based ternary solid solutions during inductively coupled argon plasma treatment

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Abstract

In this work investigations of sputtering of monocrystalline (1 1 1)-oriented epitaxial films of semiconductor ternary solid solutions of $Pb_{1-x}Sn_xTe$ ($x = 0.00$–0.56), $Pb_{1-x}Eu_xTe$ ($x = 0.00$–0.05), $Pb_{1-x}Sn_xSe$ ($x = 0.00$–0.07), $Pb_{1-x}Eu_xSe$ ($x = 0.00$–0.16, $x = 1.00$), $Pb_{1-x}Sn_xS$ ($x = 0.00$–0.05) on Si(1 1 1) and BaF_2(1 1 1) substrates in RF high-density low-pressure inductively coupled argon plasma were carried out. It is determined that sputtering rates for the studied materials retain high values typical for binary solutions PbTe, PbSe, PbS. The results indicate the interrelation of the sputtering rates of ternary compounds and of the sublimation energy of binary compounds that constitute a solid solution. The physical model of this characteristic property of lead chalcogenide-based ternary alloys based on the expansion of a classic Sigmund solid sputtering theory explaining the observed sputtering rate behavior with the alloy composition variation is proposed.

1. Introduction

In recent decades, IV–VI semiconductors, and primarily lead chalcogenides have become one of the most important narrow gap materials in electronics. These semiconductors are widely applied in two basic directions of solid-state electronic device fabrication; firstly, in optoelectronic infrared devices (emitters and photodetectors covering the entire 3–30 μm range employing, e.g., binary and ternary lead chalcogenide alloys [1–6]), and secondly, in thermoelectric devices (generally, PbTe-based alloys and nanocomposites [7]). The facility to fabricate these numerous devices basically results from the unique possibility of growing binary and ternary alloy multilayered structures on monocrystalline Si [3] or BaF_2 [4]

substrates due to the outstanding lattice stability of these alloys with composition variation. The most interesting property of lead chalcogenide ternary compound semiconductors, such as $Pb_{1-x}Sn_xTe$, $Pb_{1-x}Eu_xTe$, $Pb_{1-x}Eu_xSe$ and others, is that their band gap and refractive index [3] can be tailored by choosing chemical composition, i.e. varying x, without a significant lattice constant or overall structural properties deviation. Considering specifically ternary solid solutions' applications, they have proven to be extremely useful when creating infrared photodetectors, as well as midinfrared semiconductor laser diodes tuned for a specific narrow spectral window. Practically, they are usually correspondingly based on resonant cavity-enhanced detectors (RCED) and vertical cavity surface emitting laser (VCSEL) type structures, both

requiring Bragg reflectors and quantum well structures, which are formed as alternating epitaxial layers of binary and ternary lead chalcogenide alloys [4–6]. For the fabrication of active elements of these devices monolithically on silicon or barium fluoride, e.g. air–hole arrays, microcavities, mesa structures, microdisk laser structures [2], it is necessary to apply highly efficient etching techniques. Current trends show the increasing relevance of plasma sputtering etching, which proves to be extremely fruitful in the fabrication of various devices based on III–V and other materials [8], while the number of works dedicated to IV–VI semiconductors plasma treatment is limited [9–12]. In our recent work [12] we have discussed the results of the study of the sputtering of binary compounds PbTe, PbSe, PbS. Along with enormously high and similar sputtering rates, there exists a special physical property of lead chalcogenide binary compounds during Ar plasma treatment, which is the physical ion sputtering of the entire molecules. The aim of the present work is to study the sputtering processes of lead chalcogenide-based ternary solid solutions and to describe the physical phenomena behind observed experimental results for these semiconductor materials.

2. Experimental details

The studied samples were epitaxial films of ternary solid solutions $Pb_{1-x}Sn_xTe$ ($x = 0.00$–0.56), $Pb_{1-x}Eu_xTe$ ($x = 0.00$–0.05), $Pb_{1-x}Sn_xSe$ ($x = 0.00$–0.07), $Pb_{1-x}Eu_xSe$ ($x = 0.00$–0.16, $x = 1.00$), and $Pb_{1-x}Sn_xS$ ($x = 0.00$–0.05) grown using molecular beam epitaxy (MBE) on $BaF_2(1\,1\,1)$ and $Si(1\,1\,1)$ substrates. In the latter case for the accomodation of lattice constants of the films and the substrate, a CaF_2 intermediate buffer layer [13] with a typical thickness of 2–4 nm was employed. The temperature of the substrate during film growth was 320–400 °C. The value of x was strictly determined during the MBE process by the control of the molecular fluxes ratio from the effusion cell sources. The epitaxial layers of ternary alloys were characterized with a monocrystalline structure and had a [1 1 1] orientation along the growth axis as was confirmed with x-ray diffractometry investigations [14]. The thickness of the films was typically in the range from 1 to 5 μm. All the films had a mirror-flat surface with minor cleavage steps in case of BaF_2 substrates [14] and nanoterraces of a few nm height in the case of Si substrates [15]. Only solid solutions with small values of x corresponding to the formation of single (1 1 1) phase solid solutions were used.

Plasma sputtering of the surface of the films was performed using a radio-frequency high-density low-pressure inductively coupled plasma (RF ICP) reactor according to a well-elaborated technique that previously was successfully used for the study of binary lead chalcogenides sputtering and fabrication of micro- and nanostructure arrays [11, 12]. The schematic of the ICP reactor is given in figure 1. The plasma discharge was excited in cylindrical quartz glass discharge chamber (D) filled with argon gas when applying RF power P (800 W, 13.56 MHz) on the inductor. Pressure p of the argon was in the range of 0.07–0.98 Pa, gas flow Q was 5–50 sccm. From the discharge chamber, the plasma spread
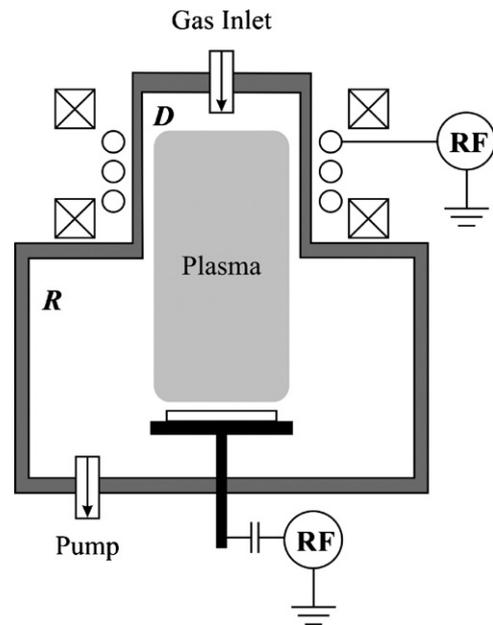
Figure 1. Schematic of the ICP reactor.

into the reaction chamber (R) with a substrate holder with an applied RF bias power P_{sb} (0–400 W, 13.56 MHz), which determined the average energy E_i of the Ar^+ ions (25–400 eV) bombarding the substrate surface. The height of the etch step on the border of the plasma sputtered area was measured using Talystep profilometer with 1 nm vertical resolution. The sputtering rate V measured in nm s^{-1} was deduced as the ratio of the etch step height to the sputtering duration. In order to provide identical plasma sputtering conditions, the processing was performed simultaneously for a number of samples. The processes of the sputtering of the films of the same composition did not depend on the substrate type (BaF_2 or Si) nor on the initial thickness of the film, which allowed us to differentiate the studied samples according only to their composition. ICP sputtering setup allowed us to effectively fabricate nano- and microstructured lead chalcogenide film-based structures. The electron microscopy image of an example of a mesa structure fabricated using ICP treatment of a $EuSe/PbSe/Pb_{0.93}Eu_{0.07}Se/CaF_2/Si(1\,1\,1)$ multilayered structure in a single plasma etching process is shown in figure 2. Previously, we have also studied in detail the processes of the modification of the surface morphology of lead chalcogenide epitaxial layers, in particular, the micromasking suppression technique allowed us to obtain self-assembling nanostructures with density of $(1–4) \times 10^9$ cm^{-2} and mean height of 10–25 nm with a standard deviation of 45–50% [11]. Morphological features of the surface and the electrical and optical properties of the films of ternary solid solutions after plasma sputtering will be described in our forthcoming papers.

3. Results and discussion

The results of the experimental measurements of the argon plasma sputtering rate V for the films of lead
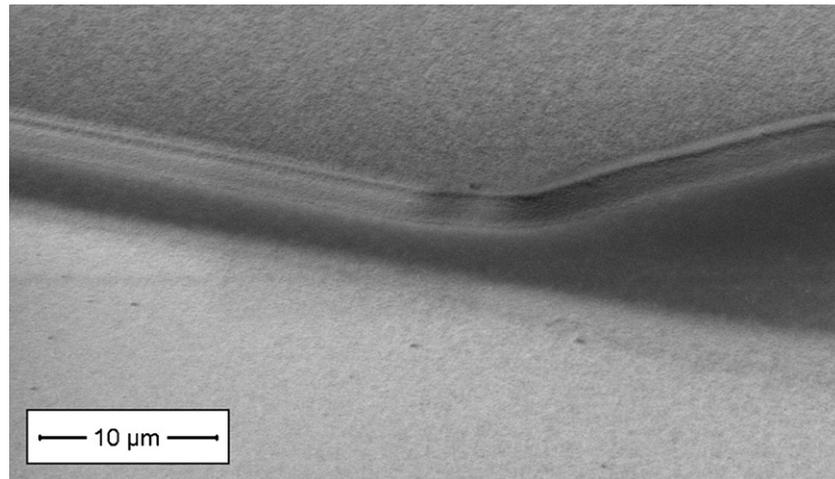
Figure 2. Electron microscopy image of a EuSe/PbSe/Pb$_{0.93}$Eu$_{0.07}$Se mesa structure on silicon substrate fabricated using argon plasma treatment.

chalcogenide-based ternary solid solutions are listed in table 1. The sputtering rates for the studied materials are close to the values for the corresponding binary compounds and are with that noticeably high in comparison with the other well-known semiconductor materials used in electronics, as was analyzed in detail in [12]. A fractional substitution of lead atoms with europium atoms results in a decrease of the sputtering rate for Pb$_{1-x}$Eu$_x$Se and Pb$_{1-x}$Eu$_x$Te solid solutions. On the other hand, in Pb$_{1-x}$Sn$_x$S solid solutions the value of V demonstrated an increase of 11% at the substitution of 5% of lead atoms with tin atoms, and in Pb$_{1-x}$Sn$_x$Se and Pb$_{1-x}$Sn$_x$Te solid solutions the sputtering rate within the experimental error did not depend on the value of x for the accounted compositions. Therefore, it is not possible to explain the obtained complex results by a simple application of the existing models of multicomponent materials sputtering based on accounting for sputtering yields and concentrations of individual components [16–18]. The sputtering yield for Pb for the applied argon ion energy values considerably exceeds sputtering yield for both Eu and Sn [19], but nevertheless the tendency for the sputtering rate variation for the studied solid solutions is not uniform (see table 1). Using such an approach it is only possible to explain the decrease in the sputtering rates for Pb$_{1-x}$Eu$_x$Se and Pb$_{1-x}$Eu$_x$Te solid solutions with the increase of mole fraction of europium chalcogenides, but it is not possible to justify the rest of the experimental results.

In order to explain the results on the sputtering of Pb$_{1-x}$Sn$_x$Se, Pb$_{1-x}$Sn$_x$Te, Pb$_{1-x}$Sn$_x$S solid solutions the following model should be introduced. In [12] we have demonstrated that for lead chalcogenide binary compounds it is necessary to consider the sputtering not of individual atoms but of the entire molecules PbX (X = Te, Se, S) and their clusters. The physical foundation of this phenomenon is the excess of the dissociation energy of PbX molecules over the sublimation energy. Hence, it can be assumed that this characteristic of sputtering is maintained for PbX-based solid solutions as well, especially when SnX binary molecules' sublimation energy is also smaller than the dissociation energy. In the theory of ternary solid solutions there is a primary clause stating that

Table 1. Sputtering rates of lead chalcogenide-based solid solutions.

Argon plasma sputtering conditions	Solid solution	V (nm s^{-1})
$P_{sb} = 400$ W, $Q = 5$ sccm, $p = 0.07$ Pa	PbSe	18.6 ± 0.5
	Pb$_{0.94}$Eu$_{0.06}$Se	17.3 ± 0.5
	Pb$_{0.84}$Eu$_{0.16}$Se	14.7 ± 0.5
	EuSe	1.1 ± 0.1
$P_{sb} = 400$ W, $Q = 5$ sccm, $p = 0.07$ Pa	PbTe	18.3 ± 0.5
	Pb$_{0.95}$Eu$_{0.05}$Te	14.6 ± 0.5
$P_{sb} = 200$ W, $Q = 10$ sccm, $p = 0.08$ Pa	PbSe	8.9 ± 0.3
	Pb$_{0.97}$Sn$_{0.03}$Se	9.0 ± 0.3
	Pb$_{0.93}$Sn$_{0.07}$Se	9.3 ± 0.3
$P_{sb} = 200$ W, $Q = 10$ sccm, $p = 0.08$ Pa	PbS	8.8 ± 0.3
	Pb$_{0.95}$Sn$_{0.05}$S	9.8 ± 0.4
$P_{sb} = 300$ W, $Q = 5$ sccm, $p = 0.07$ Pa	PbTe	15.1 ± 0.5
	Pb$_{0.85}$Sn$_{0.15}$Te	14.9 ± 0.4
	Pb$_{0.74}$Sn$_{0.26}$Te	14.8 ± 0.4
	Pb$_{0.61}$Sn$_{0.39}$Te	14.3 ± 0.4
	Pb$_{0.44}$Sn$_{0.56}$Te	14.9 ± 0.4

their properties are determined by the properties of individual binary compounds that constitute the compound and by their ratio x. Therefore, it is safe to assume that during the plasma sputtering it is the molecules of binary compounds forming the solid solution that leave the surface. In general, the equation for sputtering rate on the basis of [12, 20] can be written as

$$V = \frac{Y J M_{SS}}{\rho_{SS} e N_A},\qquad(1)$$

where Y (molecule/ion) is the sputtering yield of the solid solution material, J—ion current density, M_{SS}—molar mass of the solid solution, ρ_{SS}—solid solution density, e—elementary charge, N_A—the Avogadro constant.

Going forward we will use the denotation of Y according to the classic Sigmund theory of sputtering of a random monoatomic target in the linear collision cascade regime,

based on transport theory. Applicability of this model in the case of PbX-based ternary solid solutions is implicated by the feasibility of a straightforward substitution of sputtered atoms of one kind to the molecules. For the sputtering yield of a single-component target in an interval of moderate ion energies, Sigmund has obtained a general equation [21]

$$Y = \frac{K \alpha S_n}{U_0}, \qquad (2)$$

where α is the factor depending on the ratio of masses of the target atom and of the primary ion, S_n is the nuclear cross section, U_0 is the surface binding energy, which is often substituted with the cohesion or sublimation energy, and K is the dimensionless coefficient. During the sputtering of the surface of the solid solution, molecules of two kinds (PbX, SnX) would leave the surface and the generalized sputtering yield, when taking into account Vegard's law, will be formulated as following:

$$Y = (1 - x) Y_{PbX} + x Y_{SnX}$$
$$= (1 - x) \frac{K \alpha_{PbX} S_{nPbX}}{U_{0PbX}} + x \frac{K \alpha_{SnX} S_{nSnX}}{U_{0SnX}}, \qquad (3)$$

where x is the mole ratio of tin chalcogenide, U_{0PbX} and U_{0SnX}—sublimation energy values for lead chalcogenide and tin chalcogenide. As a result, equation (1) can be revised as

$$V = C Y \frac{M_{SS}}{\rho_{SS}}, \qquad (4)$$

where C is a constant and Y is determined according to (3). It is important to note that due to the small mass of argon ions with respect to PbX and SnX molecules, the value of αS_n does not undergo significant change with the solid solution composition transition from binary compound PbTe (PbSe, PbS) to SnTe (SnSe, SnS). Molar mass and density for PbX-based ternary alloys are generally calculated according to Vegard's law. Hence, partial replacement of lead with a metal of a smaller molar mass (tin) results in the decrease of the molar mass and density of the ternary solid solution practically the same number of times, and therefore the last factor in (4) during the transition from binary to ternary compound in the interval of small x values varies from unity at no more than 1%. Consequently, the primary factor, which can result in the variation in the sputtering rate, is the difference in the values of sublimation energies E_{subl} of PbX and SnX binary compounds. Table 2 lists the values of this energy [22] for binary compounds forming the studied solid solutions. For $Pb_{1-x}Sn_xTe$ and $Pb_{1-x}Sn_xSe$ there are minimal differences in the values of the sublimation energy for binary compounds forming a solid solution, and as a result the sputtering rates of these materials do not depend on the value of x within the accuracy of the measurements. For $Pb_{1-x}Sn_xS$ solid solution the differences in the sublimation energies of binary compounds are maximal among all the cases considered, which determines the trend toward a slight increase in the sputtering rate in the transition from the binary compound PbS to the ternary solid solution of lead sulphide—tin sulphide. From the standpoint of mesa structure fabrication technology the sputtering rates of binary compounds and PbX-SnX solid solutions can be considered virtually identical and

Table 2. Sublimation energy values for binary compounds PbX and SnX.

Material	E_{subl} (kcal mol^{-1}), 300 K [22]	Energy ratio
$Pb_{1-x}Sn_xTe$	PbTe – 53.5 SnTe – 52.7	$E_{sublPbTe}/E_{sublSnTe} = 1.02$
$Pb_{1-x}Sn_xSe$	PbSe – 54.0 SnSe – 51.2	$E_{sublPbSe}/E_{sublSnSe} = 1.05$
$Pb_{1-x}Sn_xS$	PbS – 56.7 SnS – 52.7	$E_{sublPbS}/E_{sublSnS} = 1.08$

any corrections in the sputtering of multilayer film systems, superlattices and quantum well structures are not necessary.

For solid solutions of $Pb_{1-x}Eu_xSe$ and $Pb_{1-x}Eu_xTe$ (PbX-EuX) for the interval of small mole fraction the situation would however change. During sputtering with argon ions still majorly PbX molecules would be sputtered, providing a high sputtering rate of this material. However, due to the thermodynamic properties of europium chalcogenides (high E_{subl} [23]), it should be considered poorly sputtered. Besides, the process will be accompanied with the decomposition of EuX molecules at individual atoms, which ultimately results in the decrease of the sputtering rate of $Pb_{1-x}Eu_xSe$ and $Pb_{1-x}Eu_xTe$ ternary solid solutions with the increase of x. An observed alteration of the V value should be considered during the detailed analysis of secondary ion mass spectrometry results for the multilayered structures with lead chalcogenides containing EuX.

To conclude, it should be noted that currently a unified fundamental theoretical approach which would describe the variation of sputtering rates of ternary solid solutions with the composition variation is yet to be proposed. A set of experimental data on the argon ion etching of solid solutions III–V, III–V nitrides, II–VI can be found in [24–29]. The analysis of our results with the consideration of these references allowed us to formulate three fundamental principles. Firstly, the sputtering rate for ternary solid solution with the variation of x is monotonically varied in the interval between the sputtering rates of the constituent binary compounds. Secondly, maximum variations of the sputtering rate take place in the interval of small mole fractions of one of the binary components. And thirdly, the sputtering rate of a ternary solid solution decreases with the increase of a fraction of a binary compound with a higher value of sublimation energy. In order to develop a universal theory of sputtering of ternary and quaternary solid solutions, additional experimental studies are required that would analyze a variety of physical processes of sputtering of polyatomic targets taking into account the various thermodynamic aspects of sputtered materials and other physical aspects as well.

4. Conclusions

In the framework of this work it was shown that for the inductively coupled argon plasma sputtering of the investigated lead chalcogenide-based ternary solid solutions specific regularities are manifested. In $Pb_{1-x}Sn_xTe$, $Pb_{1-x}Sn_xSe$,

$Pb_{1-x}Sn_xS$ (PbX-SnX) solid solutions, due to the proximity of thermodynamic constants of lead chalcogenides and tin chalcogenides and also due to the preferential sputtering of solid solutions by the entire PbX and SnX molecules, the sputtering rate remains practically constant with the variation of the composition under the condition of a single-phase solution. On the other hand, in $Pb_{1-x}Eu_xTe$, $Pb_{1-x}Eu_xSe$ (PbX-EuX) solid solutions, where europium chalcogenides have high values of sublimation energy, the sputtering rate decreases with the increase of a mole fraction of EuX. Obtained results indicate that the inert gas plasma sputtering technique is promising for the fabrication of mesa structures in the technology of optoelectronic and thermoelectric devices based on binary and ternary compounds of lead chalcogenides.

Acknowledgments

References

[1] Khiar A, Rahim M, Fill M, Felder F, Hobrecker F and Zogg H 2010 *Appl. Phys. Lett.* **97** 151104

[2] Eibelhuber M, Schwarzl T, Pichler S, Heiss W and Springholz G 2010 *Appl. Phys. Lett.* **97** 061103

[3] Zogg H, Arnold M, Felder F, Rahim M, Ebneter C, Zasavitskiy I, Quack N, Blunier S and Dual J 2008 *J. Electron. Mater.* **37** 1497

[4] Abramof E, de Andrada e Silva E A, Ferreira S O, Motisuke P, Rappl P H O and Ueta A Y 2001 *Phys. Rev.* B **63** 085304

[5] Arnold M, Zimin D and Zogg H 2005 *Appl. Phys. Lett.* **87** 141103

[6] Schwarzl T, Springholz G, Böberl M, Kaufmann E, Roither J, Heiss W, Fürst J and Pascher H 2005 *Appl. Phys. Lett.* **86** 031102

[7] Dmitriev A V and Zvyagin I P 2010 *Phys.-Usp.* **53** 789

[8] Pearton S J, Zolper J C, Shul R J and Ren F 1999 *J. Appl. Phys.* **86** 1

[9] Schwarzl Th, Heiß W, Kocher-Oberlehner G and Springholz G 1999 *Semicond. Sci. Technol.* **14** L11

[10] Boniche I, Morgan B C, Taylor P J, Meyer C D and Arnold D P 2008 *J. Vac. Sci. Technol.* A **26** 739

[11] Zimin S P, Gorlachev E S, Amirov I I and Zogg H 2009 *J. Phys. D: Appl. Phys.* **42** 165205

[12] Zimin S P, Amirov I I and Gorlachev E S 2011 *Semicond. Sci. Technol.* **26** 055018

[13] Li D, Ma J, Mukherjee S, Bi G, Zhao F, Elizondo S L and Shi Z 2009 *J. Cryst. Growth* **311** 3395

[14] Rappl P H O, Closs H, Ferreira S O, Abramof E, Boschetti C, Motisuke P, Ueta A Y and Bandeira I N 1998 *J. Cryst. Growth* **191** 466

[15] Zimin S P, Bogoyavlenskaya E A, Gorlachev E S, Naumov V V, Zimin D S, Zogg H and Arnold M 2007 *Semicond. Sci. Technol.* **22** 1317

[16] Roth J 1983 Chemical sputtering *Sputtering by Particle Bombardment II* ed R Behrisch (Berlin: Springer) p 91

[17] Haff P K and Switkowski Z E 1976 *Appl. Phys. Lett.* **29** 549

[18] Volpyas V A and Dymashevskii P M 2001 *Tech. Phys.* **46** 1347

[19] http://www.npl.co.uk/nanoscience/surface-nanoanalysis/products-and-services/sputter-yield-values

[20] Harper J M E 1989 *Plasma Etching: An Introduction* ed D M Manos and D L Flamm (San Diego: Academic) p 391

[21] Sigmund P 1969 *Phys. Rev.* **184** 383

[22] Hirayama C 1964 *J. Chem. Eng. Data* **9** 65

[23] Springholz G 2003 *Lead Chalcogenides—Physics and Applications* ed D Khoklov (New York: Taylor and Francis) p 123

[24] Kinoshita H, Ishida T and Kaminishi K 1986 *Appl. Phys. Lett.* **49** 204

[25] Bert N A and Soshnikov I P 1997 *Tech. Phys.* **42** 688

[26] Shul R J, Baca A G, Reiger D J, Han H, Pearton S J and Ren F 1996 *Mater. Res. Soc. Symp. Proc.* **421** 245

[27] Fang G-J, Li D and Zhao X 2003 *Phys. Stat. Sol.* **a 200** 361

[28] Ping A T, Asif Khan M and Adesida I 1997 *Semicond. Sci. Technol.* **12** 133

[29] Cho H, Vartuli C B, Donovan S M, Abernathy C R, Pearton S J, Shul R J and Constantine C 1998 *J. Vac. Sci. Technol.* A **16** 1631