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Abstract

Pulsed laser deposition was used to prepare amorphous thin films from $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ system (x = 0, 5, 10, 20, 30, 40, 50 and 60). From a wide variety of chalcogenide glass-forming systems, Ge-Sb-Se one, especially in thin films form, already proved to offer a great potential for photonic devices such as chemical sensors. This system has a large glass-forming region which gives the possibility to adjust the chemical composition of the glasses

according to required physical characteristics. The chemical composition of fabricated thin films was analyzed via X-ray photoelectron spectroscopy (XPS) and compared to energy dispersive spectroscopy (EDS) data. The results of both techniques agree well: a small deficiency in chalcogen element and an excess of antimony was found. The structure of as-deposited thin films has been investigated by XPS. The presence of the two main structural units, [GeSe$_4$] and [SbSe$_3$] proposed by Raman scattering spectroscopy data analysis, was confirmed by XPS. Moreover, XPS core level spectra analysis revealed the presence of M-M bonds (M = Ge, Sb) in (Ge,Sb)-Ge-(Se)$_3$ and (Ge,Sb)-Sb-(Se)$_2$ entities that could correspond to Ge-based tetrahedra and Sb-based pyramids where one of its Se atoms at corners is substituted by Ge or Sb ones. The content of depicted M-M bonds tends to increase with introduction of antimony in the amorphous network of as-deposited thin films from x=0 to x=40 and then it decreases. XPS analysis of as-deposited thin films shows also the presence of the (Ge,Sb)-Se-(Ge,Sb) and Se-Se-(Ge,Sb) entities.

I.   Introduction

Chalcogenide glasses are amorphous materials based on S, Se or Te element in combination with a suitable element from 13th (Ga, In), 14th (Si, Ge) or 15th (As, Sb) group of the periodical table. They form an important class of inorganic materials studied many years for their specific properties leading to many interesting applications. Amorphous chalcogenides present unusual characteristics such as a wide transparency in the infrared range (≈1-12 μm for sulfides, ≈1-16 μm for selenides and ≈2-20 μm for tellurides)[1, 2], photosensitivity[3, 4, 5, 6], high linear- and non-linear refractive index[7, 8, 9, 10, 11] and a suitable shaping ability (to fabricate fibers[12, 13] or thin films[14, 15, 16]). Thereby various applications were developed using chalcogenide glasses: chemical and biochemical sensors[17, 18, 19], components for high speed

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all-optical processing of telecommunications signals[20, 21] or phase change materials for rewritable data storage[22].

Amorphous chalcogenides are commonly used as thin films, which can be fabricated from a solid material through different physical vapor deposition methods: RF magnetron sputtering[23, 24, 25], pulsed laser deposition (PLD)[6, 24, 26], thermal evaporation[23, 26] or electron beam deposition[27]. Among mentioned methods, PLD seems to be promising for chalcogenide thin films fabrication due to its flexibility, easy control of the deposition process, possibility to fabricate multilayered structures and often stoichiometric material transfer from the target to the films[5, 6].

From a wide variety of chalcogenide glass-forming systems, Ge-Sb-Se one, especially in thin films form, already proved to offer a great potential for photonic devices such as chemical sensors[25, 28, 29] because it does not contain arsenic, which is environmentally improper due to its high toxicity in elemental form[23]. This system has a large glass-forming region[30] which gives the possibility to adjust the chemical composition of the glasses according to required physical characteristics. The optical properties and structure of chalcogenide glasses within the pseudo-binary $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ ($5 \leq x \leq 70$) system have previously been characterized[7, 31]. Reported structural analyses of $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ glasses based on Raman scattering spectroscopy reveal a progressive change in the glassy network structure with the introduction of Sb_2Se_3 into $GeSe_2$ amorphous matrix. In order to allow the insertion of $[SbSe_{3/2}]$ entities, it is first favoring edge-shared $[GeSe_{4/2}]$ entities to the detriment of $[GeSe_{4/2}]$ tetrahedra linked by the corners. At intermediate Sb_2Se_3 content, glassy network contains significant number of $[SbSe_{3/2}]$ trigonal pyramids. Finally, Sb_2Se_3 rich glasses seem to contain slightly higher number of homopolar Sb-Sb, Ge-Ge and Se-Se bonds[7]. When studying Raman spectra of corresponding thin films prepared by pulsed laser deposition in as-deposited state[6], a higher proportion of homopolar Sb-Sb and Ge-Ge bonds

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has been evidenced in comparison with parent bulk glasses. Consequently, in this paper we aim at studying the bonding arrangement at the surface of $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ ($0 \leq x \leq 60$) as-deposited PLD thin films using X-ray photoelectron spectroscopy (XPS) to understand better PLD films' structural organization.

II. Experimental Procedure

Chalcogenide glasses with the $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ ($0 \leq x \leq 60$) nominal composition were prepared using the conventional melting and quenching method[7]. Glasses were synthesized from high purity (5N) commercial elements. Selenium was pre-purified by a static distillation. Elements were weighted in appropriate amounts and introduced in silica ampoules. The ampoules were then evacuated and sealed. The elements were melted in a rocking furnace at 800 °C; ampoules with the melt were quenched in water and finally annealed at 20 °C below glass transition temperature (T_g). Chalcogenide glasses with a diameter of 25 mm and a thickness of 3 mm used as PLD targets were obtained after slicing and polishing the glass rods.

Thin films were obtained by PLD. In detail, Ge-Sb-Se targets were ablated with a KrF excimer laser emitting at 248 nm (Compex 102, Lambda Physik) using 300 $\pm$3 mJ output pulse energy, pulses duration of 30 ns and 20 Hz repetition rate. Laser fluency was set at 2.6 J.cm^{-2}. Background pressure in the vacuum chamber before deposition was about 3-4.10^{-4} Pa. In order to obtain films with uniform thickness ($\pm$2%), off-axis PLD technique with rotating substrates and targets was used. Substrates were silicon wafers (10 $\times$ 15 mm) which were positioned parallel to the target surface at a distance of 5 cm. After the deposition, thin film samples around 0.7-1.2 μm were kept under vacuum (5.10^{-5} mbars), thus limiting any further surface contamination or chemical degradation (such as oxidation) until XPS surface analysis was carried out. The glass targets used for PLD originate from the glass-forming domain. The

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PLD process typically exhibits a cooling rate during the film growth much higher than conventional cooling for glass fabrication increasing the vitreous domain for the PLD films. However, to be sure about amorphous state of the films, XRD measurements for PLD films (in particular for $GeSe_2$ and Se7 targets) were recorded with a D8-Advance diffractometer (Bruker AXS, Germany) with Bragg–Brentano θ–θ geometry (40 kV, 40 mA) using CuKα radiation with secondary graphite monochromator. The XRD patterns were measured at room temperature from 5 to 65° (2θ) within 0.02° steps with a counting time of 5 s per step.

A Kratos Axis Ultra X-ray photoelectron spectrometer was employed to characterize the top surface of as-deposited Ge-Sb-Se thin films using monochromatic Al Kα X-rays (1486.6 eV, 15 kV – 15 mA). Survey scans were recorded in the [+1250, -5 eV] binding energy (BE) range using the constant pass energy of 80 eV and energy steps of 0.5 eV. High resolution spectra were further acquired within Sb 3d – O 1s, Se 3d, Sb 4d – Ge 3d core levels, using pass energy of 20 eV and an energy step of 0.1 eV. The analysis was made at 0° take off angle with respect to the normal to the sample surface. Data analysis of the core levels (Ge $2p_{3/2}$, Sb 3d – O 1s, Se 3d, Sb 4d – Ge 3d) was carried out with standard CASA-XPS software [32]. Each 3d (Ge, Sb, Se) and 4d (Sb) core-level spectrum is constituted of $3d_{5/2}$, $3d_{3/2}$ and $4d_{5/2}$, $4d_{3/2}$ spin orbits doublets. The binding energy scale has been calibrated on the Se $3d_{5/2}$ peak of chalcogenide thin film with the nominal composition $Ge_{28.1}Sb_{6.3}Se_{65.6}$ (x = 10) positioned at 53.75 eV. Afterwards, other samples have been calibrated by aligning the Sb $3d_{5/2}$ peak onto those obtained for previous sample (i.e. 528.85 ± 0.08 eV). An "Offset Shirley" background was used for determining the spectral areas, in which the Linear to Shirley blend ratio was fixed to 1. Line shapes for curve ftting were determined thanks to the analysis of a freshly fractured bulk glass $Ge_{25}Sb_{10}Se_{65}$, whose structure presents almost only Ge-$(Se)_4$ and Sb-$(Se)_3$ environments. For the Sb 4d and Ge 3d spectra an Lorentzian Finite (LF) profile was used, in which the asymmetry parameters were set to unity to achieve a

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symmetric line shape; the tail damping and the width of the Gaussian were adjusted to the experimental spectrum, leading to LF(1,1,20,200) and LF(1,1,30,400) for the Sb 4d and Ge 3d components respectively. For the Se3d spectrum a Gaussian-Lorentzian (GL(30)) profile was used. Concerning the fitting parameters, BE were free, Full Width at Half Maximum (FWHM) were free but constraint to be identical for all components of the same element, finally spin-orbit parameters (intensity ratio and BE separation) are fixed to (0.667 − 0.57 eV), (0.667 − 1.25 eV) and (0.667 − 0.87 eV) for the Ge3d, Sb4d and Se3d spectrum respectively.

The chemical composition of $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ glassy targets and PLD thin films was measured using a scanning electron microscope with an energy-dispersive X-ray analyzer (EDS, JSM 6400-OXFORD Link INCA). A ZAF (effects of atomic number (Z), absorption within the sample and detector (A), and X-ray-induced fluorescence within the sample (F)) correction was used for the quantitative microanalysis. A $Ge_{25}Sb_{10}Se_{65}$ commercial bulk glass was used to validate the quantification procedure for Ge-Sb-Se glass samples. Atomic percentage of each element (±0.5 and ±1 % for the targets and the films, respectively) was extracted exploiting LLL lines of Ge, Sb and Se element working at 20 kV for the targets and at 10 kV for the films.

III.   Results and Discussion

In order to compare the local structural units present in as-deposited $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ PLD thin films, XPS was used to describe bonding arrangement at the surface of the layers. Moreover, surface chemical composition was also studied by XPS and the obtained results were compared to EDS data. Fig. 1 shows an example of typical XPS survey spectrum of as-deposited thin film ($Ge_{23.5}Sb_{11.8}Se_{64.7}$, i.e. x=20). The well-defined peaks are visible for Ge, Sb and Se core level as well as Auger lines (Ge LMM, Sb MNN and Se LMM). No elements

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other than the thin films' components and residual oxygen were observed in all the $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ thin films' XPS survey spectra.

Table I presents the chemical composition data of the as-deposited thin films from $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ system determined by EDS in comparison with parent glass targets. Consequently, the chemical composition of PLD films was studied by XPS and compared to EDS values (Fig. 2). For all the Ge-Sb-Se compositions under study, the agreement between these two methods is fine and very similar general behavior is observed. Thereby, a deficiency in chalcogen content (lower than 4 at. %) and an excess of antimony were observed in comparison with glass targets real composition. The loss of selenium is probably caused by its high volatility compared to germanium and antimony. In the case of germanium, when its content is lower than $\approx$ 25 at. %, the agreement between the composition of the films and theoretical one is very good as shown in Fig. 2. For higher Ge content, small excess of this element in the films is observed.

The bonding characteristics of as-deposited $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ (x values varying from 0 to 60) thin films were studied by analyzing the core level XPS spectra taking into account earlier papers[25, 33, 34]. Fig. 3 (a, b, c) shows the Sb 4d and Ge 3d core level spectra for films with x=5, x=20 and x=60. The binding energy (BE, eV), the full width at half maximum (FWHM, eV) and the proportion of bonds (%) of the different components used for the fitting of core level spectra of as-deposited thin films are presented in Table II. As expected due to the chemical composition, the Sb core-level spectra area increases with the introduction of antimony (or increase of x value) and a corresponding decrease in the area of Ge core-level spectra is observed.

The Ge 3d core-level spectra presents a primary component at $\approx$ 30.30 eV ($\pm$0.05 eV). Additional doublets have to be introduced to correctly fit the Ge 3d core-level spectra, one with lower BE value (from 29.57 to 30.04 eV) and one with higher BE value (from 31.40 to

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31.64 eV). The different BE of each structural units is determined by the neighboring atom electronegativity. Accordingly, the binding energy downshift will be larger when the difference of neighboring atom electronegativity is larger. From the electronegativities of Ge, Sb and Se (2.01, 2.05 and 2.55 respectively in view of Pauling scale), the chemical environments can be deduced. The primary component at ≈30.30 eV is assigned to the regular **Ge**-(Se)$_4$ environment corresponding to [GeSe$_{4/2}$] tetrahedra. The doublet observed at lower BE (from 29.57 to 30.04 eV) should be attributed to the (Ge,Sb)-**Ge**-(Se)$_3$ environment i.e. to a distorted tetrahedra where one Se atom is substituted with Ge or Sb atom (because of their very similar electronegativities) forming M-M bonds. Finally, the doublet at higher BE value (from 31.40 to 31.64 eV) is attributed to the oxide (Se$_y$)-**Ge**-O$_x$ because of the high electronegativity of O (3.44)[25].

In analogy, three doublets are used to describe the Sb 4d core-level spectra. The primary component is located from 32.66 to 32.78 eV and is attributed to the regular Sb-(Se)$_3$ arrangement of [SbSe$_{3/2}$] trigonal pyramid. M-M bonds are also observed with the second doublet located at lower BE (from 32.23 to 32.65 eV) and attributed to (Ge,Sb)-**Sb**-(Se)$_2$ environment. As in the case of Ge 3d core-level spectra, a third doublet is used to correctly fit the Sb 4d core-level spectra of as-deposited thin films and it is attributed to (Se$_y$)-**Sb**-Ox (at 34.02 eV)[25, 34]. However, (Se$_y$)-**Sb**-Ox is clearly observed for only (GeSe$_2$)$_{70}$(Sb$_2$Se$_3$)$_{30}$ as-deposited thin film (Table II).

Fig. 4a shows normalized core level band of Sb 4d – Ge 3d for (GeSe$_2$)$_{100-x}$(Sb$_2$Se$_3$)$_x$ thin films, dashed lines correspond to the binding energies associated to the different entities considered of x=10 sample which was used for the calibration. A slight shift towards higher energies can be observed with the introduction of antimony. In detail, in Ge 3d core level spectra, the doublet attributed to (Ge,Sb)-**Ge**-(Se)$_3$ binding arrangement is shifted from 29.57 eV (x=5) to 29.99 eV (x=60). Likewise the doublet in the Sb 4d core level spectra, which is

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attributed to (Ge,Sb)-**Sb**-$(Se)_2$ binding arrangement, is shifted from 32.23 eV (x=5) to 32.65 eV (x=60).

The presence of M-M bonds (M = Ge, Sb) was also demonstrated for bulk Ge-Sb-Se glasses[7, 31, 34] and thin films[6, 23, 33]. Sati et al[34] used an additional doublet to fit Sb 4d core level (at $\approx$ 32.20 $\pm$ 0.05 eV) which was attributed to a distorted Sb-based trigonal pyramid with substitution of two and more Se atoms by Ge or Sb atoms[34]. Further, an additional doublet was used to fit the Ge 3d core level spectra at $\approx$ 29.90 $\pm$ 0.05 eV in $Ge_{28}Sb_{12}Se_{60}$ and $Ge_{32}Sb_8Se_{60}$ glasses; this doublet was assigned to $(Ge,Sb)_2$-Ge-$(Se)_2$ bonding arrangement[34]. In contrast with this XPS analysis of Ge-rich $Sb_xGe_{40-x}Se_{60}$ glasses[34], the mentioned additional doublet associated to Sb and Ge entities with a substitution of two and more Se atoms by Ge or Sb atoms were not required for the description of Sb 4d – Ge 3d core level spectra in this work.

As results from XPS data analysis performed in this study, the proportion of Sb-$(Se)_3$ arrangements increases from 3.9 at.% (for x=5) to 28.4 at.% (for x=60) and the proportion of Ge-$(Se)_4$ arrangements decreases from 33.1 at.% (for x=0) to 7.9 at.% (for x=60) (Table 2). These values confirm that the amorphous network of as-deposited thin films slowly evolves from a $[GeSe_{4/2}]$ tetrahedra dominated structure to a $[SbSe_{3/2}]$ trigonal pyramidal one. Furthermore, the proportion of (Ge,Sb)-**Sb**-$(Se)_2$ bonds ranges from 6.5 to 21 % (from x=5 to 20) and then this proportion decreases to 7.5 % (x=60) (Table II). Similarly, the proportion of (Ge,Sb)-**Ge**-$(Se)_3$ bonds increases from 10.3 to 29.5 % from x=0 to 50 and then decreases to 16.6 % for x=60 (Table II). The lower value observed for x=30 film could be related to more important amount of (Se_y)-**Sb**-O_x (11.7 %) and (Se_y)-**Ge**-O_x (5.8 %) bonds at the surface of the films. Fig. 5 presents the M-M bonds proportions (at. %) i.e. Ge-Ge, Sb-Sb and Ge-Sb bonds observed in Ge3d and Sb4d core level spectra. Introduction of antimony in thin films' network leads to M-M bonds increase first due to (Ge,Sb)-**Ge**-$(Se)_3$ and then to (Ge,Sb)-**Sb**-

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(Se)$_2$. The decrease of M-M bonds observed for x > 30 can be explained by the glass network character which evolves to a network dominated by [SbSe$_3$] pyramids (Table 2). Raman analysis of PLD as-deposited thin film is somewhat different[6]. In fact, a decrease of Ge-Ge bonds (at $\approx$ 170 and $\approx$ 270 cm^{-1}) is observed with the introduction of antimony in thin films network. Furthermore, proportion of Sb-Sb bonds (at $\approx$ 155 cm^{-1}) seems to slightly increase with x values and Raman spectra are dominated by Sb-Se ($\approx$ 190 cm^{-1}) bonds for as-deposited thin films with x>50.

In the case of XPS analysis of selenium, two doublets ($3d_{5/2}$ and $3d_{3/2}$) were used to fit correctly Se 3d core level spectra. Fig. 3 (d, e and f) illustrates fitting of Se 3d core level spectra for x=5, 20 and 60. The Se 3d core level spectra presents a main component located from 53.47 to 53.78 eV depending on composition which can be attributed to the (Ge,Sb)-**Se**-(Ge,Sb) entities (Table 2). The second doublet, located from 54.02 to 54.35 eV, is assigned to the Se-**Se**-(Ge,Sb) entities[33, 34, 35]. A very slight shift towards lower energies was observed for PLD films with the introduction of antimony as shown in Fig. 4b. Therefore Se-**Se**-(Ge,Sb) and **Se**-(Ge,Sb)$_2$ arrangements are shifted from 54.35 to 54.02 eV (from x=0 to x=40) and from 53.75 to 53.47 eV (from x=5 to x=40) (Table 2). The content of (Ge,Sb)-**Se**-(Ge,Sb) (80.8 – 89.9 %) and Se-**Se**-(Ge,Sb) (10.1 – 19.2 %) bonds is almost independent of composition for all (GeSe$_2$)$_{100-x}$(Sb$_2$Se$_3$)$_x$ thin films (Table 2). Due to the comparable electronegativities of Ge and Sb, the contributions from Ge and Sb are similar but not exactly the same. Indeed, Sati et al.[34] reported higher FWHM values for the two doublets attributed to (Ge,Sb)-**Se**-(Ge,Sb) and Se-**Se**-(Ge,Sb) environments (0.8–0.9 eV) in comparison to doublets of binary Ge-Se chalcogenide glasses (0.6-0.7 eV). In the case of Ge-Sb-Se sputtered thin films, FWHM values of those doublets are also higher (0.9-1.0 eV)[33]. In the line with mentioned data, XPS bands of as-deposited PLD thin films present also higher FWHM values (0.8-1.0 eV, Table 2), similar to Ge-Sb-Se bulk glasses and sputtered thin films.

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Our previous XPS analysis[33] performed with RF sputtered thin films with the nominal composition $Ge_{28.1}Sb_{6.3}Se_{65.6}$ (x=10) presents comparable proportion of M-M bonds as follows. Considering the closest chemical composition of as-deposited PLD thin films (i.e. comparison with the films sputtered at Ar pressure of 1.10^{-2} mbar), the proportion of (Ge,Sb)-**Ge**-(Se)$_3$ entities is about 14.1% (Table 2) and 12% for as-deposited PLD and sputtered thin films, respectively. In the same way, the proportion of (Ge,Sb)-**Sb**-(Se)$_2$ entities is about 11.5% (Table 2) and 9% for PLD and sputtered thin films, respectively. As mentioned above, local structure analysis of $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ bulk glasses[7], PLD[6] and sputtered thin films[33] (for x=10 and x=50) using Raman spectroscopy has been previously reported. The presence of homopolar Ge-Ge bonds in $Ge_2Se_{6/2}$ and $Ge-Ge_mSe_{4-m}$ (m = 1,2,3,4) species and Sb-Sb(Ge) bonds of $Se_2Sb-Sb(Ge)Se_{2(3)}$ structural units in PLD films was confirmed by Raman spectroscopy.

On the other hand, M-M bonds proportion seems to be to some extent overestimated by XPS analysis for as-deposited PLD thin films with the nominal composition $Ge_{12.5}Sb_{25}Se_{62.5}$ (x=50). In fact, the proportion of (Ge,Sb)-**Ge**-(Se)$_3$ entities is about 29.5% (Table II) and 7% for as-deposited PLD and sputtered thin films, respectively. Further, the proportion of (Ge,Sb)-**Sb**-(Se)$_2$ entities is about 15.0% (Table II) and 0% for PLD and sputtered thin films, respectively. This is consistent with Raman analysis of sputtered thin films[33] which demonstrates that for higher Ar pressure, the M-M bonds are almost not observed. If we consider the Raman spectroscopy data for sputtered film deposited with Ar pressure lower than 1.10^{-2} mbar, the spectrum of PLD film (x=50) looks like Raman spectra of such sputtered films. The PLD film Raman spectrum shape is between those of two sputtered films ($7.5.10^{-3}$ and 5.10^{-3} mbar). From XPS analysis, the proportion of (Ge,Sb)-Ge-(Se)$_3$ entities for these two sputtered films is 19% and 47%, respectively. The semi-quantitative analysis of Raman spectra of PLD film (x=50) compared to sputtered films let

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expect proportion of (Ge,Sb)-**Ge**-(Se)$_3$ entities around 22-25%. Thus, the general agreement between Raman and XPS analysis is good keeping in mind that only first ten nanometers are probed by XPS. Although, it seems that there is a slight overestimation of (Ge,Sb)-Ge-(Se)$_3$ entities by the XPS analysis of PLD film (x=50).

The BE values found for PLD layers are in good agreement with sputtered thin films' XPS analysis: **Ge**-(Se)$_4$ and **Sb**-(Se)$_3$ entities are located at 30.29 and 32.71 eV and 30.37 and 32.73 eV for as-deposited PLD and sputtered thin films with the nominal composition Ge$_{28.1}$Sb$_{6.3}$Se$_{65.6}$ (x=10). For Sb-rich thin films, mentioned two main entities are located at 30.32 and 32.78 eV and 30.34 and 32.71 eV for as-deposited PLD and sputtered thin films, again in very good agreement.

Likewise, Se-Se homonuclear bonds were also revealed in Raman and XPS analysis of RF sputtered thin films with the nominal chemical composition Ge$_{28.1}$Sb$_{6.3}$Se$_{65.6}$ (x=10) and Ge$_{12.5}$Sb$_{25}$Se$_{62.5}$ (x=50)[33]. The comparison of PLD and sputtered layers with x=10 gives the proportion of Se-**Se**-(Ge,Sb) entities about 13.6% (Table 2) and 14% for as-deposited PLD and sputtered thin films (at 1.10^{-2} mbar Ar)[33], respectively. In layers with x=50, the content of Se-**Se**-(Ge,Sb) entities is about 16.2% (Table 2) and 22% for as-deposited PLD and sputtered (at 1.10^{-2} mbar) thin films, respectively. Binding energies revealed for PLD thin films are also in agreement with those observed for RF sputtered thin films. For x=10 films, Se-**Se**-(Ge,Sb) entities are located at 54.30 eV (Table 2) and 54.32 eV for as-deposited PLD and sputtered (1.10^{-2} mbar Ar pressure) layers, respectively[33]. For Sb-rich thin films (x=50), these entities are situated at 54.06 eV (Table 2) and 54.10 eV for PLD and sputtered (1.10^{-2} mbar Ar pressure) layers, respectively[33]. Raman data analysis of RF sputtered thin films also revealed the presence of Se-Se bonds, especially for higher Ar pressure, with the amplitude increase of the band located at ≈265 cm^{-1} [33]. These results also agree with previous XPS data obtained for RF sputtered thin film with the nominal composition Ge$_{25}$Sb$_{10}$Se$_{65}$; the

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proportion of Se-**Se**-(Ge,Sb) is about 13% (for 5.10^{-3} mbar) and 29% (for 5.10^{-2} mbar) [25]. The proportion of Se-Se homonuclear bonds is surprisingly high in these both compositions (x=10 and x=50) close to stoichiometric composition or with deficit in chalcogen element as shown in Table I with relatively low content of M-M bonds. As it was already mentioned in previous work[25, 33], another contribution to this second Se 3d core level component spectrum might be considered: Se involved in bonds between two [GeSe$_{4/2}$] tetrahedra connected by edges could also contribute to Se-**Se**-(Ge,Sb) component.

It is worthy to mention that other techniques were already used for the structural analysis of Ge-Sb-Se glasses, for example neutron diffraction, X-ray diffraction or extended X-ray fine structure analysis. Pethes et al.[36] used the reverse Monte-Carlo simulation technique[37] to investigate Ge$_{20}$Sb$_5$Se$_{75}$, Ge$_{20}$Sb$_{15}$Se$_{65}$ and Ge$_{20}$Sb$_{20}$Se$_{60}$ glasses. All three glass compositions show a structure mostly described by the chemically ordered network model in which Ge-Se and Sb-Se bonds are preferred. For calculations using the reverse Monte Carlo method, homopolar Se-Se bonds in Se-poor glass and M-M bonds in Se-rich glass are not needed which is distinctive to the analysis performed by XPS spectroscopy for physical vapor deposited Ge-Sb-Se films. However, the rapid quenching during the synthesis of the thin films is likely to generate more defects than parent glasses and deviate from a perfect chemically ordered network model.

IV.   Conclusion

In this paper, amorphous chalcogenide thin films with the nominal composition (GeSe$_2$)$_{100-x}$(Sb$_2$Se$_3$)$_x$ (x = 0, 5, 10, 20, 30, 40, 50 and 60) were deposited by PLD with chemical composition relatively close to the targets' composition. Nevertheless, EDX and XPS analysis, performed on glass targets and as-deposited thin films, reveals a small deficit in

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chalcogen element (Se) and an excess of Sb in the PLD films. The as-deposited thin films were characterized by X-rays photoelectron spectroscopy in order to describe bonding arrangement at the surface films. XPS investigations confirm the presence of the two main regular units **Ge**-(Se)$_4$ and **Sb**-(Se)$_3$. The Sb core level spectra amplitude increases logically with introduction of antimony so the amorphous network of as-deposited thin films slowly evolves from a [GeSe$_{4/2}$] tetrahedra dominated structure to a [SbSe$_{3/2}$] pyramidal one. The (Ge,Sb)-**Ge**-(Se)$_3$ and (Ge,Sb)-**Sb**-(Se)$_2$ environments, corresponding to distorted tetrahedra or trigonal pyramid where one chalcogen element is substituted with Ge or Sb atom(s) forming M-M bonds, were also observed. The proportion of M-M bonds increases with the introduction of antimony (from x=0 to x=40) first due to (Ge,Sb)-**Ge**-(Se)$_3$ and then thanks to (Ge,Sb)-**Sb**-(Se)$_2$ entities' appearance. The study of Se 3d core level spectra reveals the presence of two entities: (Ge,Sb)-**Se**-(Ge,Sb) and Se-**Se**-(Ge,Sb). XPS analysis of as-deposited thin films seems to overestimate Se-Se homonuclear bonds, thus this component could contain also Se involved in two [GeSe$_{4/2}$] tetrahedra connected by edges.

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Figure captions

Fig 1. Survey XPS spectrum of $Ge_{23.5}Sb_{11.8}Se_{64.7}$ (x=20) as-deposited thin film.

Fig. 2. Comparison of chemical composition of $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ PLD films determined by EDS (±1 %) and XPS (±1 %) analysis compared to theoretical composition.

Fig. 3. XPS spectra of as-deposited $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ PLD thin films. Data fitting of Ge 3d and Sb 4d core level bands: a) x=5, b) x=20 and c) x=60; data fitting of Se 3d core level bands: d) x=5, e) x=20 and f) x=60. Being very weak, the Se_y-Ge-O_x components are not shown in the curves fitting.

Fig. 4. Normalized core level band of Ge 3d – Sb 4d (a) and Se 3d (b) of $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ PLD thin films. Dashed lines correspond to the binding energy (BE, eV) of the sample used for the calibration (x=10).

Fig. 5. M-M bonds (M = Ge, Sb) proportions (at. %, ±1 %) in Ge 3d and Sb 4d core level spectra depending of x values in $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ PLD thin films (dashed curve corresponds to the overall trend of M-M bonds as a function of x values).

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Tables

Table I. Theoretical and real chemical composition (at. %) determined by EDS for chalcogenide glass targets $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ (± 0.5 %) and corresponding thin films prepared by pulsed laser deposition (± 1 %).

	Theoretical composition			Target composition			Thin film composition		
	%Ge	%Sb	%Se	%Ge	%Sb	%Se	%Ge	%Sb	%Se
x=0	33.3	-	66.7	36.5	-	63.5	39	-	61
x=5	30.6	3.2	66.1	31.0	3.4	65.6	33	4	63
x=10	28.1	6.3	65.6	28.3	6.8	64.9	30	8	62
x=20	23.5	11.8	64.7	23.1	13.0	63.9	24	15	61
x=30	19.4	16.7	63.9	19.5	17.8	62.7	19	21	60
x=40	15.8	21.1	63.2	14.9	22.3	62.8	15	26	59
x=50	12.5	25.0	62.5	12.1	25.4	62.5	13	27	61
x=60	9.5	28.6	61.9	10.4	29.1	60.5	9	29	62

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Table II. Binding energy (BE, eV, ± 0.05eV), full width at half maximum (FWHM, eV, ± 0.05eV), proportion of bonds (%$_{bonds}$, ± 1%) and atomic ratio (%$_{at}$, ± 1%) of the different components used for the fitting of Se $3d_{5/2}$, Ge $3d_{5/2}$, Sb $4d_{5/2}$ and Sb $3d_{5/2}$ core level spectra of as-deposited $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ thin films prepared by pulsed laser deposition.

	Core Level	Se $3d_{5/2}$		Ge $3d_{5/2}$			Sb $4d_{5/2}$		
	Species	Se-(Ge,Sb)$_2$	Se-Se-(Ge,Sb)	Ge-(Se)$_4$	(Ge,Sb)-Ge-(Se)$_3$	Se$_y$-Ge-O$_x$	Sb-(Se)$_3$	(Ge,Sb)-Sb-(Se)$_2$	Se$_y$-Sb-O$_x$
x=0	BE (eV)	53.78	54.35	30.32	30.04	-	-	-	-
	FWHM	0.82	0.82	0.94	0.94	-	-	-	-
	%$_{bonds}$	84	16	90	10	-	-	-	-
	%$_{at}$	53	10	33	4	-	-	-	-
x=5	BE (eV)	53.75	54.24	30.29	29.57	31.49	32.69	32.23	-
	FWHM	0.94	0.94	1.03	1.03	1.03	1.00	1.00	-
	%$_{bonds}$	83	17	95	4	1	93	7	-
	%$_{at}$	51	11	32	1	1	4	1	
x=10	BE (eV)	53.75	54.30	30.29	29.62	31.40	32.71	32.25	-
	FWHM	0.96	0.96	0.98	0.98	0.98	1.01	1.01	-
	%$_{bonds}$	86	14	80	14	6	88	12	-
	%$_{at}$	49	8	27	5	2	9	1	-
x=20	BE (eV)	53.56	54.08	30.20	29.63	31.45	32.66	32.22	-
	FWHM	0.93	0.93	0.92	0.92	0.92	0.88	0.88	-
	%$_{bonds}$	90	10	81	18	1	79	21	-
	%$_{at}$	54	6.0	20	4	1	12	3	-
x=30	BE (eV)	53.60	54.22	30.28	29.89	31.48	32.70	32.47	34.02
	FWHM	0.93	0.93	0.85	0.85	0.85	0.86	0.86	1.28
	%$_{bonds}$	81	19	80	14	6	70	18	12
	%$_{at}$	49	12	16	3	1	14	3	2
x=40	BE (eV)	53.47	54.02	30.21	29.96	31.61	32.68	32.38	-
	FWHM	0.88	0.88	0.94	0.94	0.94	0.86	0.86	-
	%$_{bonds}$	83	17	75	24.8	0	83	17	-
	%$_{at}$	48	10	12	4	0.0	22	5	-

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x=50	BE (eV)	53.56	54.06	30.32	29.85	31.61	32.78	32.41	-
	FWHM	0.82	0.82	0.75	0.75	0.75	0.87	0.87	-
	% $_{bonds}$	84	16	60	29	11	85	15	-
	% $_{at}$	47	9	7	4	1	27	5	-
x=60	BE (eV)	53.58	54.15	30.35	29.99	31.64	32.78	32.65	-
	FWHM	0.84	0.84	0.82	0.82	0.82	0.84	0.84	-
	% $_{bonds}$	83	17	79	17	5	92	8	-
	% $_{at}$	49	10	8	2	1	28	2	-

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