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Amorphous Ga-Sb-Se thin films fabricated by co-sputtering

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Ternary chalcogenides of Ga-Sb-Se system are prospective materials for potential applications in the field of infrared optics. This letter deals with the optical properties and photosensitivity of Ga-Sb-Se thin films deposited by co-sputtering, enabling to fabricate amorphous thin films outside the glass-forming region. The optical bandgap range 1.92-1.35 eV with corresponding refractive index at 1.55 μm ranging from 2.47-3.33 can be reliably covered using Ga_2Se_3 and Sb_2Se_3 targets. Furthermore, the prolonged irradiation by the near-bandgap light under the pure argon atmosphere leads to the irreversible photo-bleaching effect in fabricated films. The magnitude of this effect decreases monotonically with an increasing antimony content.

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Amorphous chalcogenides, which are non-crystalline materials based on the elements of chalcogens (*i.e.* S, Se and Te), are of a great interest in various fields since 1950s.

Specifically, the ternary systems consisting of chalcogens accompanied by different elements from 13-15 group of the periodic table of elements have attracted the attention of large number of researchers throughout the world [1-4].

Gallium-containing chalcogenide glasses, in the form of thin films and optical fibers have become important materials for the photoluminescence studies due to the suitable solubility of rare earth elements in such matrices [5-7]. Moreover, glasses from Ga-Sb-Se ternary system have been investigated by Lecomte *et al.* for the potential night-vision applications [8]. Furthermore, Sb-rich Ga-Sb-Se thin films can be considered as a potential phase-change materials having higher thermal stability, smaller density change and higher crystallization speed when compared to classical Ge-Sb-Te compositions [2]. It should be also noted, that co-sputtered thin films of this system were recently investigated by mass spectrometry by Mawale *et al.* [9].

Undeniable advantage of co-sputtering deposition method lies in the easy-process and cost-efficient possibility to fabricate thin films of wide range of chemical compositions. This physical vapor

deposition technique is an efficient deposition technique to fabricate amorphous thin films whose composition is out of the glass-forming region of the system under study. Within the context, fabrication and properties of Ga-Sb-Se thin films prepared *via* co-sputtering using Ga_2Se_3 and Sb_2Se_3 targets is reported in this work.

The co-sputtering of Ga-Sb-Se films was performed at a room temperature using MPE600 multi-chamber deposition system (Plassys-Bestek, Marolles-en-Hurepoix, France) with symmetrically arranged confocal deposition cluster consisting of three cathodes. Two polycrystalline targets with the composition of Ga_2Se_3 and Sb_2Se_3 were used. The experimental conditions of RF (13.56 MHz) magnetron co-sputtering were held constant throughout all the depositions, *i.e.* background pressure of $\leq 5.10^{-4}$ Pa, argon working pressure of 0.5 Pa maintained by 75 sscm flow rate and substrate-target distance of about 8 cm with substrate holder rotation. The chemical composition of the co-sputtered films was adjusted by varying the electrical power ratio between the two cathodes. The maximum power on cathode with Ga_2Se_3 target was 25 W while, for Sb_2Se_3 , it was only 15 W. These experimental conditions were chosen with respect to the film thickness and the difference in the deposition rate between the two individual target materials.

The morphology and the chemical composition of films was checked by scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS). Furthermore, amorphous state of fabricated layers was confirmed by X-ray diffraction (XRD). Surface topography was examined by atomic force microscopy (AFM) Solver Next (NT-MDT Co., Moscow, Russia).

Optical properties were investigated using spectroscopic ellipsometry (J. A. Woollam Co., Inc., Lincoln, NE, USA) in the wavelength region of 300-2300 nm. Among all the fitted parameters, particularly the thickness, optical bandgap energy E_g , parameter E_D and refractive index n were determined from the ellipsometry data using Cody-Lorentz oscillator model [10]. Transmission spectra were collected using spectrometer UV-3600 Plus (Shimadzu Co., Kyoto, Japan) in the range of 180-3300 nm.

It should be noted that two different substrates were used for the depositions – crown glass (Schott BK7) for the optical

characterization and single crystalline silicon wafers <100> for SEM, EDS and AFM measurements.

The photoinduced phenomena in co-sputtered Ga-Sb-Se thin films was studied via prolonged irradiation with continuous-wave lasers working at different wavelengths but at a constant laser beam power density of $\sim 150 \text{ mW.cm}^{-2}$ ($\pm 10\%$). Appropriate laser wavelength for each film was chosen taking in account the optical bandgap and the penetration depth. Light sources operating at 593.5 nm (2.09 eV), 635 nm (1.95 eV), 656 nm (1.89 eV), 690 nm (1.80 eV), 730 nm (1.70 eV), 785 nm (1.58 eV) and 808 nm (1.53 eV) were used for this purpose. The sample is placed in a photo-kinetic cell under pure argon atmosphere in order to minimize the effect of surface oxidation of the samples. All the samples were irradiated at room temperature for 180 minutes. Spectroscopic ellipsometry was used for the determination of E_g and n before (in as-deposited films) and after irradiation. Photoinduced changes by means of E_g change and n change are defined as $\Delta E_g = E_g$ (irradiated) - E_g (as-deposited) and $\Delta n = n$ (irradiated) - n (as-deposited) respectively. Moreover, direct transmission measurements using the portable spectrophotometer EPP2000 (StellarNet Inc., Tampa, FL, USA) working in the range of 400-1100 nm were carried out for the quick control of the absorption edge shift during the irradiation. Tungsten-halogen light source was used as the probe light.

Co-sputtered thin films of Ga-Sb-Se system were fabricated in order to achieve a reasonable thickness for the characterization of optical properties (at least 500 nm). The morphology studied *via* SEM showed a smooth surface of deposited films without any significant large particles, cracks or holes. The amorphous state was confirmed by the XRD measurements. The good optical quality of thin films was confirmed by the presence of clear interference fringes in their transmission spectra illustrated in Figure 1, reaching maximum transmission of $\sim 92\%$.

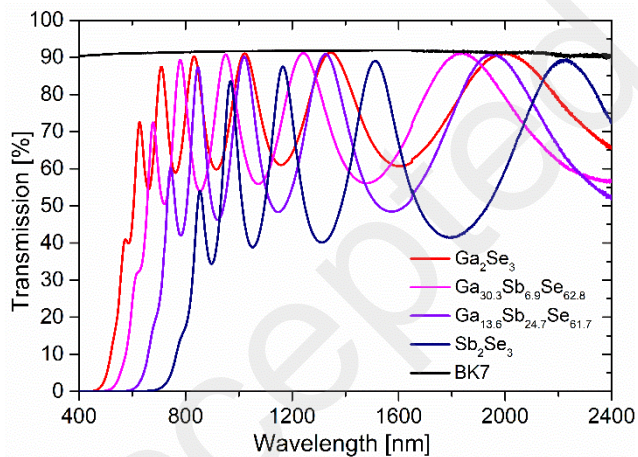


Fig. 1 Transmission spectra of Ga_2Se_3 , $\text{Ga}_{30.3}\text{Sb}_{6.9}\text{Se}_{62.8}$, $\text{Ga}_{13.6}\text{Sb}_{24.7}\text{Se}_{61.7}$ and Sb_2Se_3 thin films and BK7 glass substrate.

An overview of co-sputtered Ga-Sb-Se thin films together with their chemical compositions, thicknesses and optical parameters are summarized in **Table 1**. Furthermore, the chemical composition of fabricated Ga-Sb-Se films together with the glass-forming region of Ga-Sb-Se system is depicted in the ternary diagram in Figure 2.

Table 1

Summary of co-sputtered Ga-Sb-Se thin films with their chemical composition (± 1 at. %) evaluated by EDS, thickness l (± 2 nm) / wavelength of irradiation (λ_{irr} in nanometres), optical bandgap energy (± 0.01 eV) / photoinduced change in optical bandgap $\Delta E_g = E_g$ (irradiated) - E_g (as-deposited), refractive index at $1.55 \mu\text{m}$ (± 0.01) / photoinduced change in refractive index at $1.55 \mu\text{m}$ $\Delta n = n$ (irradiated) - n (as-deposited) and parameter E_u (± 20 meV).

Composition (at. %)	l λ_{irr} (nm)	E_g ΔE_g (eV)	n_0 Δn_0	E_u (meV)
$\text{Ga}_{38}\text{Se}_{62}$	790 593.5	1.92 0.10	2.47 -0.01	160
$\text{Ga}_{32}\text{Sb}_5\text{Se}_{63}$	610 635	1.80 0.06	2.59 -0.01	140
$\text{Ga}_{30}\text{Sb}_7\text{Se}_{63}$	700 656	1.74 0.06	2.62 0.00	120
$\text{Ga}_{19}\text{Sb}_{18}\text{Se}_{63}$	790 690	1.65 -0.01	2.80 0.03	90
$\text{Ga}_{16}\text{Sb}_{22}\text{Se}_{62}$	560 730	1.58 0.02	2.87 0.01	96
$\text{Ga}_{14}\text{Sb}_{25}\text{Se}_{62}$	670 730	1.56 0.00	2.94 0.00	85
$\text{Ga}_{11}\text{Sb}_{27}\text{Se}_{62}$	670 785	1.53 -0.01	3.02 0.02	79
$\text{Ga}_8\text{Sb}_{31}\text{Se}_{61}$	620 808	1.48 0.00	3.11 0.02	76
$\text{Sb}_{38}\text{Se}_{61}$	730 808	1.35 0.01	3.33 0.02	70

The chemical composition of films sputtered from individual targets (*i.e.* Ga_2Se_3 and Sb_2Se_3) is in a good accordance with nominal composition. Only a small loss of gallium (~ 2.4 at. %) and antimony (~ 1.5 at. %) was observed.

AFM images were taken for both, $5 \mu\text{m} \times 5 \mu\text{m}$ and $1 \mu\text{m} \times 1 \mu\text{m}$ area. Measured data were edited by means of rows alignment using polynomial function of the third order. AFM scans ($5 \mu\text{m} \times 5 \mu\text{m}$) of selected samples together with the values of root-mean squared roughness (S_q) are shown as inserts in the Figure 2. As seen, sputtered film from Ga_2Se_3 target only contains particles ranging in size of 35-60 nm (Figure 2a). As seen, only sputtered films from Ga_2Se_3 target contains few particles ranging in size of 35-60 nm (Figure 2a). The presence of these particles increases the S_q value significantly. Their likely origin could be Ga_2Se_3 crystallites even if they cannot be detected by XRD because of their small proportion and size. However, AFM scans performed on the area of $1 \mu\text{m} \times 1 \mu\text{m}$ showed no deviation in topography (and S_q) when compared to other films where Sb_2Se_3 target was used for co-sputtering. For co-sputtering depositions above mentioned particles were not observed and the values of S_q are typically $\sim 0.2 \pm 0.1$ nm for Ga-Sb-Se film thicknesses of about 600-800 nm. Moreover, it seems that the S_q values drops down when Sb_2Se_3 cathode is used in any proportion.

The values of optical bandgap energies vary from 1.92 eV for sputtered Ga_2Se_3 down to 1.35 eV for gallium-free Sb_2Se_3 thin film (Table 1). It is noteworthy that Afifi *et al.* [11] reported somewhat larger optical bandgap energy value of 2.06 eV for thermally evaporated amorphous Ga_2Se_3 (E_g extracted from ellipsometry data by Tauc extrapolation). The refractive index at the telecommunication wavelength of $1.55 \mu\text{m}$ varies from 2.47 (Ga_2Se_3) up to 3.33 (Sb_2Se_3) in corresponding films (Table 1).

As could be expected when one compares the E_g of Ga_2Se_3 to Sb_2Se_3 related to their electronic structure, the introduction of antimony selenide shifts the absorption edge towards the lower energies reducing the optical bandgap energy (and increasing n).

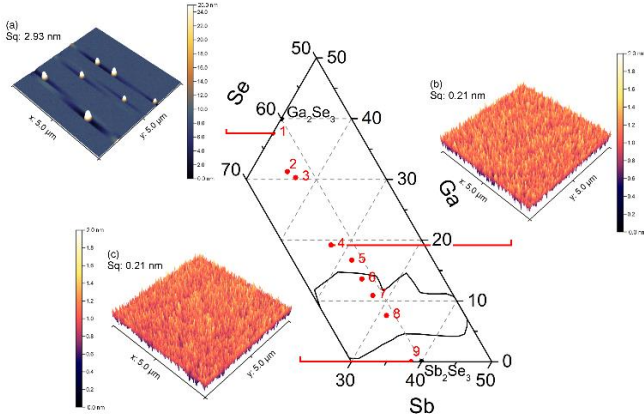


Fig. 2 Ternary Ga-Sb-Se diagram with indicated positions of co-sputtered thin films' composition (red points), targets' composition (black points) and glass-forming region when quenched by fast cooling taken from ref. [8] (black curve). Inserts of AFM scans (5 μm×5 μm) with indicated RMS roughness values Sq of (a) Ga_{37.6}Se_{62.4} (b) Ga_{19.2}Sb_{17.5}Se_{63.3} and (c) Sb_{38.5}Se_{61.5} film.

The proposed band structure of Ga-Sb-Se film is based on the assumption that the gallium atoms in the crystalline polymorphs of Ga₂Se₃ are 4-fold coordinated leaving the 2- and 3-fold coordinated selenium atoms in the ratio of about 1:2. This structure, called as vacancy ordering, leaves the dangling bond states of anion atoms near the vacant sites which appear at the valence band maxima (VBM) [12]. Another contribution to VBM is coming from *p* orbitals of 2-fold coordinated selenium. On the other hand, the conduction band minima (CBM) is formed by antibonding states of gallium and selenium *s* orbitals [13]. An observed drop in the optical bandgap energy induced by the introduction of antimony may be of the similar origin as in Ge-Sb-Se films, *i.e.* Sb *5p* bonding electrons are contributing to the very top of VBM [14].

Furthermore, the value of E_g decreases from 160 ± 20 meV in Ga₂Se₃ film down to 70 ± 20 meV in case of Sb₂Se₃ (Table 1). This may indicate that the local order (represented here by E_g values) is increased with the introduction of antimony. Such variation in composition of Ga-Sb-Se co-sputtered layers possibly reduces the number of defects such as Se-Se of dimers or selenium chains and Ga(Sb)-Ga(Sb) bonds.

Estimated photoinduced changes in Ga-Sb-Se co-sputtered films are summarized in Table 1. Largest photobleaching (PB) effect was found in the sample deposited from Ga₂Se₃ where the change ΔE_g is 0.1 eV. The magnitude of PB decreases monotonically with an increasing antimony content. Such behavior is similar to that observed in Ge-Sb-Se bulk glasses and thin films [15-17]. Effectively, Halenkovič *et al.* [14] reported ΔE_g change of 0.1 eV in sputtered GeSe₂ and 0.09 eV in co-sputtered Ge-Sb-Se film with composition of Ge_{32.5}Sb₁₂Se_{66.3}. While the magnitude of PB in Ge-Sb-Se thin films is comparable with Ga-Sb-Se ones, these changes occur at a lower concentration of germanium with respect to gallium (at 33 at. % of Ge and 40 at. % of Ga). Thus, it is reasonable to assume, that the photosensitivity of Ga-Sb-Se thin films is slightly less efficient when compared to Ge-Sb-Se.

In situ transmission measurements during the irradiation using the setup depicted in fig. 3a revealed that the PB is preceded by a fast transient photodarkening (PD) process. This phenomenon was already observed in evaporated Ge-As-Se thin films by Khan *et al.*, who have combined the two stretched exponential functions to

describe the coexisting transient PD and metastable PB (eq. 1) [1] giving total transmission change ΔT :

$$\Delta T = A \left[\exp \left\{ - \left(\frac{t}{\tau_d} \right)^{\beta_d} \right\} \right] + \Delta T_{sd} + \Delta T_{sb} \left[1 - \exp \left\{ - \left(\frac{t}{\tau_b} \right)^{\beta_b} \right\} \right] \quad (1)$$

where A is the total amount of transient changes, τ is the effective response time, t is irradiation time, β refers to dispersion parameter of photoinduced change which defines the slope of PD and PB. ΔT_s is the metastable part and its value is slightly higher than the actual transmission change of PD and PB effects. The subscripts 'd' and 'b' correspond to the PD and PB [1].

It can be assumed that eq. 1 can be used to describe the kinetics of photoinduced phenomena in other amorphous chalcogenide thin films. This assumption is confirmed in this work for Ga-Sb-Se co-sputtered thin films (fig. 3b). For Ga-Sb-Se layers, the dispersion parameter of metastable PB β_b tends to increase with an increasing antimony content. Simultaneously ΔT_{sb} , which defines the magnitude of the PB, decreases. These two trends are responsible for the stretching of nonlinear curve in the part which defines the PB. It should be noted that τ and β , found in the simple stretched exponential function used for the description of the PD kinetics, are thickness dependent [18].

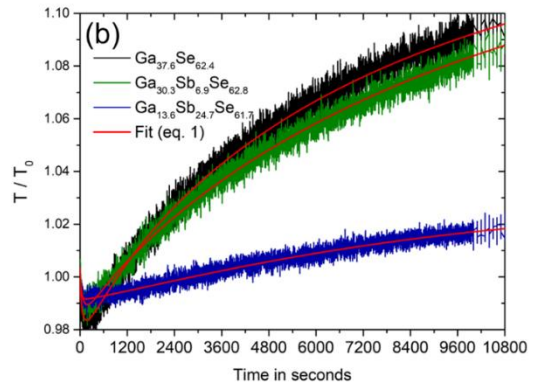
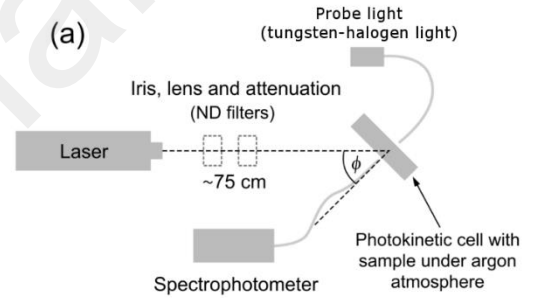


Fig. 3 (a) Experimental setup for irradiations of co-sputtered Ga-Sb-Se thin films (b) Time evolution of normalized transmission at the wavelength where the initial transmission $T_0 = 20$ % for Ga_{37.6}Se_{62.4}, Ga_{30.3}Sb_{6.9}Se_{62.8} and Ga_{13.6}Sb_{24.7}Se_{61.5} thin films.

Therefore, it is expected that the shape of the nonlinear curve described by eq. 1 is also affected by the thickness diversity of fabricated films. Unlike the changes in optical bandgap no clear trends can be explained in the refractive index changes Δn . The largest magnitude of Δn was observed in sample with the composition Ga_{19.2}Sb_{17.5}Se_{63.3} with Δn of 0.03. This value of Δn is

comparable with $\text{Ge}_{16.4}\text{Sb}_{19.4}\text{Se}_{64.2}$ and $\text{Ge}_{12.3}\text{Sb}_{24.8}\text{Se}_{62.9}$ reported in co-sputtered Ge-Sb-Se thin films (Δn of 0.02 and 0.04 respectively) [14].

The possible origin of observed photoinduced changes in the Ga-Sb-Se thin films may be similar to that in the Ge-Sb-Se system [19, 20]. Nonetheless, despite the fact that the experiments were performed under pure argon atmosphere, the influence of humidity (and oxygen) should not be completely ruled out [21]. Photo-enhanced oxidation in crystalline Ga_2Se_3 under Ar^+ laser irradiation ($\lambda = 514.5$ nm) on air leads to the replacement of selenium by oxygen as reported by Nobuaki *et al.* [22] resulting in an increase in optical transparency of the thin film.

The study of various properties of co-sputtered amorphous Ga-Sb-Se thin films was presented. The used deposition technique allows to fabricate amorphous thin films with compositions fairly far away from glass-forming region in Ga-Sb-Se ternary system. It was shown that broad range of thin films' optical bandgap energies (1.92-1.35 eV) with corresponding refractive index range 2.47-3.33 may be covered by co-sputtering technique exploiting Ga_2Se_3 and Sb_2Se_3 polycrystalline targets. The studies of photosensitivity that the behavior of Ga-Sb-Se thin films is similar to that of Ge-Sb-Se system supporting the assumption of 4-fold coordinated gallium atoms in the amorphous matrices. Photoinduced changes have revealed that the antimony-free Ga_2Se_3 film undergo the highest magnitude of photobleaching (*i.e.* increase in E_g by 0.1 eV) which is gradually reduced by the introduction of antimony in Ga-Sb-Se co-sputtered films.

Changes in parameter E_U of fabricated films indicate that the introduction of 3-fold coordinated antimony induces the lower disorder in amorphous films, possibly reducing the number of homopolar bonds such as Se-Se, Ga-Ga and short selenium chains in Ga-Sb-Se co-sputtered layers.

Thin films of Ga-Sb-Se system seem to be prospective materials for the potential applications in infrared optics and nonlinear applications due to their low photosensitivity.

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References

- [1] P. Khan, A.R. Barik, E.M. Vinod, K.S. Sangunni, H. Jain, K.V. Adarsh, Coexistence of fast photodarkening and slow photobleaching in $\text{Ge}_{19}\text{As}_{21}\text{Se}_{60}$ thin films, *Opt. Express* 20(11) (2012) 12416-12421.
- [2] Y. Lu, S. Song, X. Shen, G. Wang, L. Wu, Z. Song, B. Liu, S. Dai, Phase change characteristics of Sb-rich Ga-Sb-Se materials, *Journal of Alloys and Compounds* 586 (2014) 669-673.
- [3] P. Němec, S. Zhang, V. Nazabal, K. Fedus, G. Boudebs, A. Moreac, M. Cathelin, X.H. Zhang, Photo-stability of pulsed laser deposited $\text{Ge}_{100-x}\text{As}_x$ amorphous thin films, *Opt. Express* 18(22) (2010) 22944-22957.
- [4] T. Wang, X. Gai, W. Wei, R. Wang, Z. Yang, X. Shen, S. Madden, B. Luther-Davies, Systematic z-scan measurements of the third order nonlinearity of chalcogenide glasses, *Opt. Mater. Express* 4(5) (2014) 1011-1022.
- [5] R. Chahal, F. Starecki, J.L. Doualan, P. Němec, A. Trapananti, C. Prestipino, G. Tricot, C. Boussard-Pledel, K. Michel, A. Braud, P. Camy, J.L. Adam, B. Bureau, V. Nazabal, Nd^{3+} :Ga-Ge-Sb-S glasses and fibers for luminescence in mid-IR: synthesis,

- structural characterization and rare earth spectroscopy, *Opt. Mater. Express* 8(6) (2018) 1650-1671.
- [6] P. Němec, B. Frumarová, M. Frumar, Structure and properties of the pure and Pr^{3+} -doped $\text{Ge}_{25}\text{Ga}_5\text{Se}_{70}$ and $\text{Ge}_{30}\text{Ga}_5\text{Se}_{65}$ glasses, *Journal of Non-Crystalline Solids* 270(1) (2000) 137-146.
- [7] L. Strizik, S.N. Yannopoulos, V. Benekou, J. Oswald, M. Pavlista, V. Prokop, T. Wagner, J. Orava, Photoluminescence in pulsed-laser deposited GeGaSbS:Er films, *Optical Materials* 85 (2018) 246-253.
- [8] A. Lecomte, V. Nazabal, D. Le Coq, L. Calvez, Ge-free chalcogenide glasses based on Ga-Sb-Se and their stabilization by iodine incorporation, *Journal of Non-Crystalline Solids* 481 (2018) 543-547.
- [9] R. Mawale, T. Halenkovič, M. Bouška, J. Gutwirth, V. Nazabal, P.L. Bora, L. Pečinka, L. Prokeš, J. Havel, P. Němec, Mass spectrometric investigation of amorphous Ga-Sb-Se thin films, *Scientific Reports* 9(1) (2019) 10213.
- [10] A.S. Ferlauto, G.M. Ferreira, J.M. Pearce, C.R. Wronski, R.W. Collins, X. Deng, G. Ganguly, Analytical model for the optical functions of amorphous semiconductors from the near-infrared to ultraviolet: Applications in thin film photovoltaics, *Journal of Applied Physics* 92(5) (2002) 2424-2436.
- [11] M.A. Affi, A.E. Bekheet, H.T. El-Shair, I.T. Zedan, Determination and analysis of optical constants for Ga_2Se_3 films near absorption edge, *Physica B: Condensed Matter* 325 (2003) 308-318.
- [12] T. Nakayama, M. Ishikawa, Bonding and Optical Anisotropy of Vacancy-Ordered Ga₂Se₃, *Journal of the Physical Society of Japan* 66(12) (1997) 3887-3892.
- [13] G.-Y. Huang, N.M. Abdul-Jabbar, B.D. Wirth, First-principles study of the structure and band structure of Ga_2Se_3 , *Journal of Physics: Condensed Matter* 25(22) (2013) 225503.
- [14] T. Halenkovič, J. Gutwirth, P. Němec, E. Baudet, M. Specht, Y. Gueguen, J.-C. Sangleboeuf, V. Nazabal, Amorphous Ge-Sb-Se thin films fabricated by co-sputtering: Properties and photosensitivity, *Journal of the American Ceramic Society* 101(7) (2018) 2877-2887.
- [15] T. Halenkovič, P. Němec, J. Gutwirth, E. Baudet, M. Specht, Y. Gueguen, J.-C. Sangleboeuf, V. Nazabal, Co-sputtered amorphous Ge-Sb-Se thin films: optical properties and structure, *SPIE Optics + Optoelectronics, SPIE*, 2017, p. 7.
- [16] M. Olivier, P. Němec, G. Boudebs, R. Boidin, C. Focsa, V. Nazabal, Photosensitivity of pulsed laser deposited Ge-Sb-Se thin films, *Opt. Mater. Express* 5(4) (2015) 781-793.
- [17] M. Olivier, J.C. Tchahame, P. Němec, M. Chauvet, V. Besse, C. Cassagne, G. Boudebs, G. Renversez, R. Boidin, E. Baudet, V. Nazabal, Structure, nonlinear properties, and photosensitivity of $(\text{GeSe}_2)_{100-x}(\text{Sb}_2\text{Se}_3)_x$ glasses, *Opt. Mater. Express* 4(3) (2014) 525-540.
- [18] K. Shimakawa, N. Nakagawa, T. Itoh, The origin of stretched exponential function in dynamic response of photodarkening in amorphous chalcogenides, *Applied Physics Letters* 95(5) (2009) 051908.
- [19] R.A. Street, R.J. Nemanich, G.A.N. Connell, Thermally induced effects in evaporated chalcogenide films. II. Optical absorption, *Physical Review B* 18(12) (1978) 6915-6919.
- [20] Q. Yan, H. Jain, J. Ren, D. Zhao, G. Chen, Effect of Photo-Oxidation on Photobleaching of GeSe_2 and Ge_2Se_3 Films, *The Journal of Physical Chemistry C* 115(43) (2011) 21390-21395.
- [21] A. Bergeron, J. Ibrahim, R. Leonelli, S. Francoeur, Oxidation dynamics of ultrathin GaSe probed through Raman spectroscopy, *Applied Physics Letters* 110(24) (2017) 241901.
- [22] K. Nobuaki, Y. Akira, T. Kiyoshi, O. Tamotsu, K. Makoto, S. Koki, Photoinduced Oxidation of Epitaxial Ga₂Se₃ Grown by Molecular Beam Epitaxy, *Japanese Journal of Applied Physics* 32(7A) (1993) L887.
- 23.