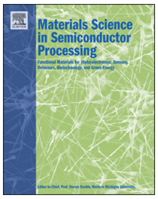
Materials Science in Semiconductor Processing 86 (2018) 101–110

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp



Photoconductivity and laser operated piezoelectricity the Ag-Ga-Ge-(S,Se) crystals and solid solutions

A.M. El-Naggar[a,*], A.A. Albassam[a], G.L. Myronchuk[b,*], O.V. Zamuruyeva[b], I.V. Kityk[b,c], P. Rakus[c], O.V. Parasyuk[d], J. Jędryka[c], V. Pavlyuk[e,f], M. Piasecki[b,g,**]

[a] *Research Chair of Exploitation of Renewable Energy Applications in Saudi Arabia, Physics & Astronomy, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia*
[b] *Department of Physics, Lesya Ukrainka Eastern European National University, 13 Voli Avenue, Lutsk 43025, Ukraine*
[c] *Institute of Optoelectronics and Measuring Systems, Faculty of Electrical Engineering, Czestochowa University Technology, Armii Krajowej 17, PL-42-201 Czestochowa, Poland*
[d] *Department of Inorganic and Physical Chemistry, Lesya Ukrainka Eastern European National University, 13 Voli Avenue, 43025 Lutsk, Ukraine*
[e] *Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine*
[f] *Institute of Chemistry, Environmental Protection and Biotechnology, Jan Długosz University of Częstochowa, al. Armii Krajowej 13/15, 42200 Częstochowa, Poland*
[g] *Institute of Physics, Jan Długosz University of Częstochowa, Armii Krajowej 13/15, 42-200 Czestochowa, Poland*

ARTICLE INFO

Keywords:
Chalcogenides
Photoelectricity
Piezoelectricity
Photoinduced effects

ABSTRACT

A new type of chalcogenide semiconductors possessing different laser operated optoelectronic features is studied for the $AgGaGeS_4$–$AgGaGe_3Se_8$ crystalline system give a rare opportunity to form continuous solid solution series based on the substrate compounds. This one allow to perform efficient operation by their optical and electronic features using an external laser light due to presence of huge number of intrinsic defects and high electron-phonon anharmonicities [1].

With accordance to previously reported method were prepared specimens of high quality and homogenous in centimeter range (confirmed by SEM and EPMA) $AgGaGeS_4$ and $AgGaGe_3Se_8$ single crystals and the series of intermediate solid solution, in particular $AgGaGe_{1.8}S_{2.4}Se_{3.2}$, $AgGaGe_2S_2Se_4$ and $AgGaGe_{2.2}S_{1.6}Se_{4.8}$. The investigated Ag-Ga-Ge-(S,Se) crystals and solid solutions posses high non-linear optical efficiencies as well as high birefringence that make them efficient for coherent laser frequency conversion in the near-infrared spectral range. So they may be promising for the coherent laser frequency convertors. To expand the possibilities of applications as pressure sensors, optical triggers, modulators or radiation detectors and for better understanding of relation between composition-structure-properties for these materials we perform the complex investigation of temperature dependences of the transparency, photoconductivity, rise and decreasing photocurrent relaxation for determination parameters of localized states and temperature dependent, photoinduced piezoelectric properties.

1. Introduction

Recently one can observe an enhanced interest to semiconductor chalcogenide materials for optoelectronics. Particular interest cause metal chalcogenides and halide compounds forming a very large and versatile group of materials, that are widely used in production of different optoelectronic and photonic devices [2]. For these compounds all ions are four-fold coordinated and the chemical bonds between them are usually strongly covalent. The crystal structure of the chalcogenide compounds offers a possibility for partial or complete substitution of cation or anion groups, i.e. formation of solid state solutions, whose properties can be significantly different from those of pure compounds [3,4]. Especially the introduction of controlled imperfection into crystals opens a promising opportunity for desire tuning of properties with particular various applications [5]. The existence of the intrinsic defect levels situated intra the energy gap allows to use them to operation by external lasers. The important field of applications chalcogenides and halide compounds is existence of nonlinear optical effects in infrared spectral range (IR NLO) [2–5]. Unfortunately optical applications require high quality single crystals possessing at least centimeter sizes. The syntheses of the such crystals is a serious technological problem [3]. Moreover, chalcogenide materials have other opportunities for

---

* Corresponding authors.
** Corresponding author at: Institute of Physics, Jan Długosz University of Częstochowa, Armii Krajowej 13/15, 42-200 Czestochowa, Poland.
E-mail addresses: elnaggar@ksu.edu.sa (A.M. El-Naggar), g_muronchuk@ukr.net (G.L. Myronchuk), m.piasecki@ajd.czest.pl (M. Piasecki).

https://doi.org/10.1016/j.mssp.2018.06.019
Received 7 March 2018; Received in revised form 26 May 2018; Accepted 21 June 2018

applications as solar cells, pressure sensors or thermoelectric devices where polycrystalline and defected states are often sufficient [6,7].

Among other, ternary compounds $AgGaS_2$ and especially $AgGaSe_2$ have high non-linear optical coefficients that are suitable for achievement of coherent frequency conversion in the near-infrared spectral range [8,9]. However, in recent years it is increasingly sought to replace them with more complex analogs $AgGaGeS_4$ and $Ag_xGa_xGe_{1-x}Se_2$ which can create real competition due to higher values of laser damage threshold, band gap energy, birefringence, as well as a greater variety of phase matching schemes [10–15]. $AgGaGeS_4$ formed in the $AgGaS_2$–GeS_2 system as an intermediate phase with a homogeneity region 48–57 mol.% GeS_2 (at 720 K) and congruent melting at 1136 K [16]. It crystallizes in a noncentrosymmetric space group *Fdd*2, with unit cell parameters equal to $a = 1.2028$, $b = 2.2918$, $c = 0.6874$ nm (for the stoichiometric composition). The quaternary phase $Ag_xGa_xGe_{1-x}Se_2$ formed in the $AgGaSe_2$–$GeSe_2$ system exists within the range of 65–88 mol.% (at 720 K). It is congruent as well, and is isostructural with the above sulfide [17]. The maximum melting point observed at 995 K corresponds to the composition of $AgGaGe_3Se_8$. The physical properties of $AgGaGeS_4$ and $AgGaGe_3Se_8$ single crystals are well investigated and presented in the works [18–22].

Phase diagram of the $AgGaGeS_4$–$AgGaGe_3Se_8$ system belongs to Type 1 of Roozeboom classification with the formation of a continuous solid solution series for the substrate compounds [23]. The refinement of the crystal structure of the equimolar composition ($AgGaGe_2S_2Se_4$) possessed six crystallographic sites: one of them (*16b*) is occupied by about half by Ag atoms. Other possess sites *8a* and 16*b* containing statistically mixed Ga and Ge atoms, and three more *16b* local sites belonging to the statistical mixture of chalcogens. Four crystals of intermediate compositions with 20 mol.% step were grown, and their band gap energy was determined from the principal spectral position of the absorption edge.

Therefore, to expand the possibilities of applications as well as better understanding of relation between composition-structure-properties and checking opportunities of the adapting the paraments to individual requirements for these materials, we studied the optical, photoelectrical and piezoelectric features of the $AgGaGeS_4$ and $AgGaGe_3Se_8$ crystals together with some the solid solution $AgGaGe_{1.8}S_{2.4}Se_{3.2}$, $AgGaGe_2S_2Se_4$ and $AgGaGe_{2.2}S_{1.6}Se_{4.8}$ with the content of 40, 50 and 60 mol.% $AgGaGeS_4$, respectively.

The discovered features are principally different with respect to the traditional oxide materials. All the mentioned allow to design multifunctional materials possessing high efficient photosensitivity, laser operated optoelectronics features possessed by a one sample. Principal role for the applications for the laser operation play intrinsic defect states forming a huge number of trapping levels. Additionally these levels form active canters participating in the transport properties. In the present work we perform complex studies of photoconductivity, laser stimulated piezoelectricity for the $AgGaGeS_4$–$AgGaGe_3Se_8$ crystalline system.

2. Materials and methods

The single crystals of $AgGaGe_{1.8}S_{2.4}Se_{3.2}$, $AgGaGe_{2.2}S_{1.6}Se_{4.8}$ and $AgGaGe_2S_2Se_4$ were grown by Bridgman-Stokbarger method. The technique of syntheses crystal and solid solutions is described in details in [23].

The specimens for piezoelectric measurements were cut as parallelepipeds with $4 \times 5 \times 3\,mm^3$ dimensions. Optical investigations were performed on parallel-plane parallelepiped plates of 0.06–0.08 mm thickness with optical-quality surfaces.

TESCAN scanning electron microscope (SEM) equipped with WDS/EDX detectors for electron probe micro analyses (EPMA) were used to phases control and determining of chemical compositions of crystals.

The IR transmittance spectra in the spectral range up to 20 μm were studied using Spectrum Two FTIR Spectrometer (PerkinElmer).

Optical properties were investigated within the temperature range 100–300 K using a Utreks K41-3 thermostat with ± 0.02 K thermostabilizing). An MDR-206 monochromator with silicon photosensor was used as a spectrophotometer (with spectral resolution 0.2 nm). The computation of the absorption coefficient is presented in [24].

Photoconductivity spectra were measured by MDR-206 monochromator with 0.5 nm spectral resolution. The current sensitivity of the experimental set-up (Keithley 6514) was higher than 1 pA + 5%. This set-up allowed to perform at least 500 measurements/s. The current contacts were made by sticking of metallic In and were Ohmic for all the considered conditions. The temperature was stabilized using Utrex K 41-3 temperature regulator with accuracy equal to about 0.2 K. A 100 W halogen lamp was used as a light source. The excitation of non-equilibrium conductivity was carried out by 808 nm cw laser with power about 300 mW.

Piezoelectric investigations were performed using a d_{33}-meter (APC International, Ltd.) suitable for the measurements of the piezoelectric modulus in the 1–200 pQ/V range with 0.1 pC/V resolution and ± 2% error. Temperature dependence of the piezoelectric modulus was measured in a thermal chamber suitable for the range of 293–357 K, with ± 002 K accuracy. Investigations of laser-induced piezoelectric effect used a 400 mW laser with 532 nm wavelength.

Nonlinear optical studies were performed using Er: glass nanosecond laser with a wavelength of 1.64 μm and power density of up to 1 GW/cm^2.

3. Results and discussion

The brownish-reddish plates that have been cut off from crystals (Fig. 1a) were used to phase control and determining of chemical compositions by means TESCAN scanning electron microscope (SEM) equipped with WDS/EDXS detectors for electron probe micro analyses (EPMA). The SEM micrograph (Fig. 1b) of the fragment of a $AgGaGe_2S_2Se_4$ crystal confirms single phase morphology.

Figs. 2a, 3a and 4a depict the cross sectional view of the $AgGaGe_{2.2}S_{1.6}Se_{4.8}$, $AgGaGe_{1.8}S_{2.4}Se_{3.2}$ and $AgGaGe_2S_2Se_4$ crystals. One can clearly see that all the crystals show single phase morphology, although for all crystals there are visible dark spots, lighter and darker areas resulting from the heterogeneous roughness of the surface caused by cutting and grinding. A chemical compositions determined by EPMA agree well with starting composition of samples and are in a form: $Ag_{1.1(1)}Ga_{0.9(2)}Ge_{2.2(2)}S_{1.7(3)}Se_{4.7(2)}$, $Ag_{1.2(1)}Ga_{0.9(2)}Ge_{1.6(2)}S_{2.2(4)}Se_{3.4(3)}$ and $Ag_{1.1(1)}Ga_{1.0(1)}Ge_{1.9(2)}S_{1.9(3)}Se_{4.1(2)}$. The EDS mapped area and element distribution images for all the crystals are shown in Fig. 2b-f, Fig. 3b-f and Fig. 4b-f. This method confirms a qualitative assessment of the elemental composition and homogeneity of all samples at the scale of the selected scanning area.

To determine transparence windows of Ag-Ga-Ge-(S,Se) crystals of the solid solutions in the middle IR spectral range, required by CO_2 lasers (10.6 μm), the FTIR (Fig. 5) and absorbance spectral (Fig. 6) measurements were performed.

Fig. 5 shows the transmission spectra of the investigated crystals. All single crystals have the distinctive minimum transmittance situated within 12–16 μm wavelengths [25]. For the $AgGaGe_3Se_8$, the transmission window is wider −1 to 15 μm [11], and with an increase of silver content the transmission window has been reduced up to 1–11 μm for the $AgGaGeS_4$ single crystal.

The additional spectral peaks observed at spectral range between 2.5 and 8 μm are originated from intrinsic defect centers levels situated within the energy gap. They identification cannot be unambiguously performed due to superposition of different defects. This clarification requires to perform additional quantum chemical and molecular dynamics simulation which may be a separate work in a future.

Localized electronic states in the band gap region lead to the appearance of exponential decline (Urbach tail region) in the spectral dependence of absorption. Fig. 6 presents typical spectral dependences