JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 11, No. 12, December 2009, p. 2083 - 2087

Second harmonic generation in selenium-copper structures

I. MIHAILOVA[a*], V. GERBREDERS[a], E. TAMANIS[a], E. SLEDEVSKIS[a,b], V. KOLBJONOKS[a]
[a]*Innovation Centre of Microscopy, Daugavpils University, 1 Parades St., Daugavpils, LV-5401, Latvia*
[b]*Institute of Solid State Physics, University of Latvia, 8 Kengaraga St., Riga, LV-1063, Latvia*

Optical second harmonic generation (SHG) observations and precise X-ray diffraction experiments have been performed on selenium-copper film structures. Selenium-copper structures were obtained by successive thermal evaporation of selenium and ion evaporation of copper onto the glass substrate in vacuum. To determine what compounds have emerged and if the material is crystalline x-ray diffraction (XRD) analysis was performed. The SHG experiment was performed by confocal microscope where the femtosecond radiation from femtosecond laser (180 fs, 80 MHz) was injected. Second harmonic intensity dependence on wavelength of the exciting radiation and on thickness of Cu layer was observed. We found out that adding small amount of Cu increases reflected SH intensity.

(Received July 5, 2009; accepted November 12, 2009)

Keywords: Second harmonic generation (SHG); Chalcogenides, Copper, Semiconductor, Thin films

1. Introduction

Thin films of chalcogenides have been investigated by numerous authors as new optical materials with high optical nonlinearity, perspective for applications in quantum electronics, optoelectronics and integrated optical devices. Semiconducting metal chalcogenide thin films are of considerable interest in the field of solar selective coating, optoelectronic devices, electronics and electrical devices, etc. For example, copper selenide (CuSe) is a semiconducting material, which has electrical and optical properties suitable for photovoltaic application. [1, 2, 3]. Nowadays semiconducting chalcogenide glasses have been widely used as low-power media for reverse optical recording with ultrahigh density. It is being considered that unique properties of these materials (high transparency in wide range of wavelength in infrared diapason; the possibility of changing refraction coefficient in wide diapason, low interaction energy of phonons, adaptability to manufacture, etc.) allow to find an application for these materials in different devices in telecommunication and integral optics [4]. Photoinduced stable second harmonic generation has also been reported in chalcogenide glasses [5, 6, 7].

Interesting research of second harmonic generation was also performed on copper surface under the influence of femtosecond laser radiation [8, 9].

In the theory, the second harmonic (SH) can be induced only in anisotropic media without inversion symmetry. However, the experiment shows that SHG is possible also in isotropic matter with centre of symmetry. Different possibilities exist: 1) initial film already has anisotropy after deposition (is not completely amorphous); 2) initial film has a weak anisotropy which is enhanced by incident radiation; 3) initial film has no anisotropy, it is somehow produced by the incident radiation, for example, additional nonlinear polarization may occur due to electrical field gradient of laser [10]. On the other hand film with thickness of few interatomic distances is always non-centrosymmetrical, because operation of inversion is no longer an operation of symmetry in the direction of normal to surface (in other words, direction „up" un „down" are not equivalent). That means that surface layer always has non linear quadratic susceptibility $\chi^{(2)}$, which is the only source of reflected SHG in centrosymmetrical media. SHG generation from surface is not cloaked by non linear response from the volume of the film and it carries information only about properties of surface. Consequently, surface SHG is possible even for materials which do not exhibit SHG in bulk. Furthermore, intensity of SH generated on surface depends on the shape and size of asperities, electrostatical field and additional illumination [11]. We assumed that deposition of thin copper layer on a selenium film leads to appearance of some anisotropy in the film and on the surface and at certain conditions may increase the intensity of SH. In this paper we mainly report results of reflected second harmonic generation measurements on Se and Se-Cu thin films with different Cu concentration. Just evaporated as well as annealed thin films were explored.

2. Experimental details

Selenium films were obtained by thermal evaporation in vacuum 10^{-5} Torr onto amorphous BK-7 glass substrates. Selenium-copper structures were obtained by successive thermal evaporation of selenium and ion evaporation of copper onto the BK-7 glass substrate in vacuum 10^{-5} Torr. Obtained films looked homogeneous,

bright and without defects. Thickness of Se was controlled during evaporation by means of interference technique at wavelength of 650 nm [12]. Selenium films of 0.5 μm thickness have been obtained. Thickness of copper layers onto selenium was about 0.5 nm to 100 nm, it was calculated before evaporation. Films of various copper and selenium concentration have been used in experiments.

The products as-obtained were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and confocal laser scanning microscope LEICA SP5. To determine exact amount of copper in obtained structures, microanalysis of thin films was performed with module of X-ray spectroscopy "INCA x-stream and mics" (Oxford Instruments Analytical), which was assembled on bases of "TESCAN-VEGA VGU" scanning electron microscope. The sample was placed in chamber with 11.088 mPa pressure and exposed of an electron beam focused to 914 nm diameter. An electron beam was scanned over a defined area of the sample at 30 keV accelerating voltage and 47.1 μA emission current.

Some of amorphous films were annealed in nitrogen atmosphere at temperature 85°C. Crystallisation was supervised by reduction of light transmission of He-Ne laser (λ= 650 nm) to saturation [12].

X-ray diffraction (XRD) measurements were performed at room temperature on diffractometer RIGAKU operated at 45kV and 200mA. Bragg-Brentano focusing optics with Cu-Kα radiation wavelength (λ=1.543 Á) from a 9kW rotating anode generator without primary monochromator has been used. Continuous scan mode with K beta filter method for monochromatization had been used during measurements. Automatic recording of the intensity has been made. Data were collected within the range $10° < 2\vartheta < 80°$ from 3 x 5 mm area. The X-ray pattern (diffractogram) peaks were compared to ones from data base [13] to identify different crystalline phases or deduce elementary compositions of compound materials.

Second harmonic generation in thin films has been investigated by titan-sapphire ($Ti:Al_2O_3$) femtosecond laser CHAMELEON ULTRA (linearly polarized, 180 fsec pulse duration, 80 MHz repetition rate, λ - 690-1040 nm) in a unified complex with confocal microscope LEICA SP5 (Fig. 1), which allowed measurements of transmitted (4) and reflected (5) light intensity. Photo multiplier tubes (PMT) helped to collect weak emitted light, multiple fluorescent signals.

Ti:Saphire laser beam of certain wavelength from 800 nm to 1000 nm and power of 2–20 kW/cm^2 was focused up to diametre 2 μm on thin film surface via objective lens 10x (2) and 193.75 μm length line was scanned for certain time. Reflected light is detected by the detector which is adjusted to certain wavelength – correspondent to second harmonic. As-evaporated and annealed thin films were investigated.

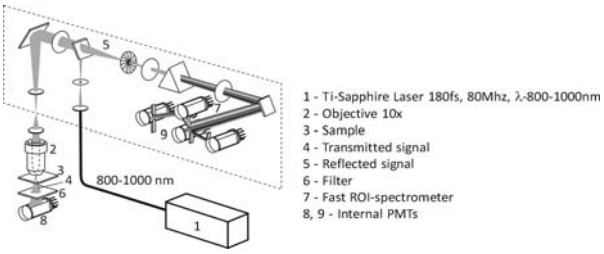


Fig.1. Schematic illustration of equipment for SHG measurements

.

3. Experimental results and discussion

Exposing as-evaporated and annealed Se and Se-Cu thin films at femtosecond laser radiation at wavelength 800-1000 nm leads to appearance SH at wavelength 400 - 500 nm. Intensity of second harmonic depends on wavelength of the exciting radiation. To determine this dependence, we provided some measurements of reflected SH intensity versus excited wavelength at a constant intensity of exciting radiation 9.34 kW/cm^2. It was found out that the highest intensity of reflected SH is provided by laser radiation at wavelengths 950 - 1000 nm (Fig. 2).

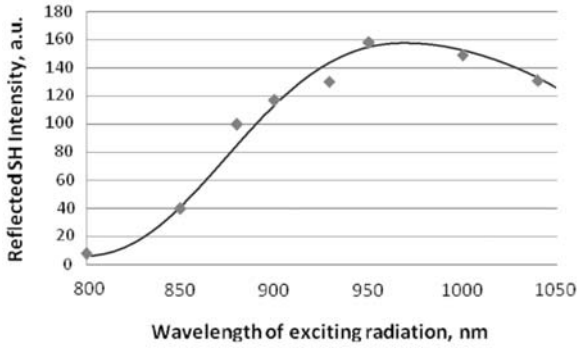


Fig.2. The dependence of SH intensity on the wavelength of exciting radiation for annealed thin film with 0.46 atomic % Cu.

We provided experiments to determine SH intensity dependence on the thickness of Cu layer. We assumed that deposition of thin copper layer on a selenium film leads to a diffusion of metal inside the selenium with subsequent formation of compound copper-selenium. This may lead to appearance of some anisotropy in the film and films surface and at certain conditions may increase the intensity of SH. Both as-evaporated and annealed thin films were exposed to femtosecond laser radiation for 300 seconds and reflected SH intensity vs time diagrams were obtained for films with different thickness of Cu layer (0.5-50 nm). Intensity of exciting radiation was approximately 8.8 kW/cm^2.

In third figure reflected SH intensity vs time is shown in some annealed thin films. It is obvious that in films with 0.46 atomic % Cu concentration SH is the highest. After maximum intensity is reached, SH intensity attenuates probably because of destruction of structure of matter under the influence of laser radiation. In most cases the SH yield also dropped with increasing adsorbate coverage for adsorbates like O_2 and CO. Qualitatively the strong reduction of the surface SHG by strongly bound molecules like oxygen is explained by the reduced polarizability on the conduction electrons of the metal substrate [14]. However, slightly decreasing exciting irradiation (about 7 kW/cm^2) SH intensity after reaching its maximum doesn't change anymore. Similar curves were also obtained for amorphous samples, SH is observed after longer time than in annealed films. That could be explained by a diffusion and crystallization processes starting in thin film.

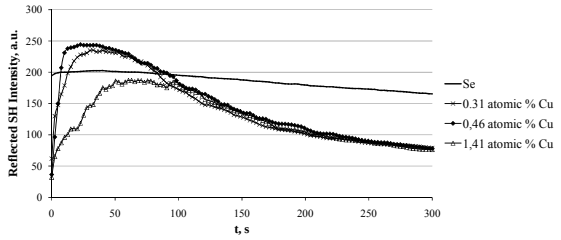


Fig. 3. Reflected SH Intensity of some annealed samples as a function of time.

In Fig.4 the time necessary to reach maximum intensity of reflected SH is shown. So, SH maximum intensity is reached faster and is higher (Fig.5) in annealed films rather than as-evaporated films with corresponding Cu concentration. For both as-evaporated and annealed thin films the fastest maximum intensity reaching time and highest SH intensity was observed at little concentration of Cu 0.46 atomic % (corresponding to 15 Å of Cu layer thickness). That brings to a conclusion that adding small amount of Cu increases anisotropy of the film surface and, herewith, also increases SH intensity. However, increasing of the amount of Cu > 2% leads to decreasing SH intensity [15].

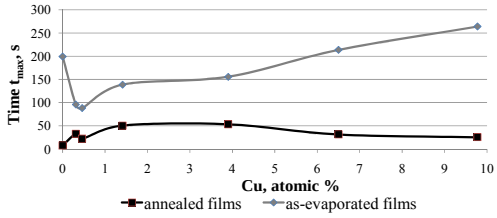


Fig. 4.The time necessary to reach maximum intensity of reflected SH.

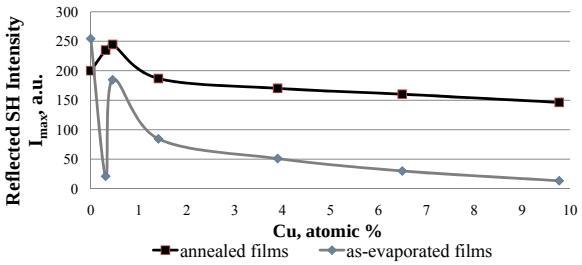
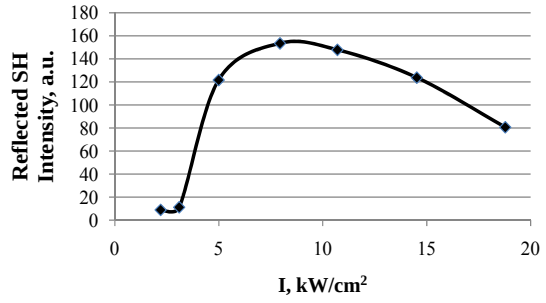
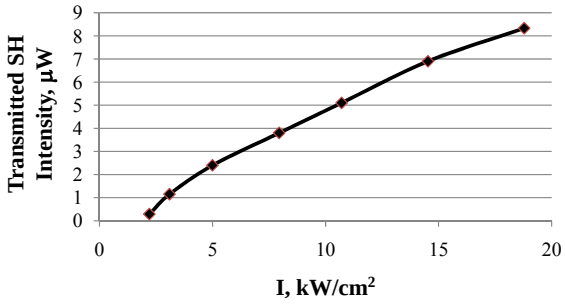


Fig.5. Dependence of SH maximum intensity on the amount of Cu in thin film.

In Fig.6 reflected (a) and transmitted (b) SH intensity vs intensity of exciting radiation is shown for annealed film with 0.46 atomic % Cu. At intensities of exciting radiation higher than 10 kW/cm² intensity of reflected SH for amorphous and crystalline Se-Cu films decreases due to changes of film structure. Intensity of transmitted SH keep growing. Though considering dependence of transmitted SH on irradiation time, e.g., at intensity of 19 kW/cm^2, when a maximal value of transmitted SH intensity is reached, it rapidly decreases afterwards. At intensities lower than 1kW/cm² the generation of SH in amorphous films is not observable at all. Optimal exciting radiation intensity for SHG in Se-Cu thin films is approximately 7 kW/cm².



a



b

Fig.6. Reflected (a) and transmitted (b) SH intensity vs intensity of exciting radiation for annealed film with 0.46 atomic % Cu.

The XRD measurement results of the as-evaporated and annealed Se films are shown in Fig.7 (a) and (b), respectively. As-evaporated film is amorphous, but after annealing at 85 C it crystallizes and peaks corresponding hexagonal and monoclinic Se phase appear.

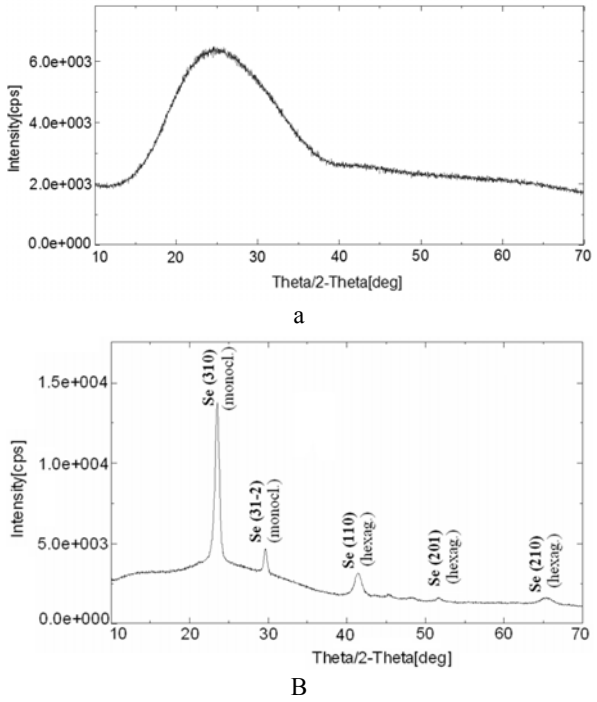


Fig. 7. XRD pattern of as deposited (a) and annealed (b) Se thin film.

X-ray diffraction study reveals that in as-evaporated Se-Cu thin films some crystalline phases of Se and Cu-Se compounds were observed. When increasing thickness of Cu layer, level of crystallization also increases. Obviously, when evaporating Cu layer, the temperature was reached at which crystallization of Se and formation of crystalline Cu-Se compounds was possible. Probably this partial crystallization allowed to observe SH in as-evaporated thin films. Later crystallization level was increased by annealing and stabilizing the films. The diffused background was observed because of the amorphous glass substrate and presence of some amorphous phase in the Se-Cu thin film sample.

X-ray diffraction pattern reveals that the annealed films are polycrystalline in nature. Furthermore, for thin films with 5 Å copper layer (0.31 atomic% Cu) all peaks correspond to selenium. No peaks correspondent to Cu or its compounds with Se were observed. From that we infere that at too small thickness of Cu layer it is not homogenous and a structure of islands of Cu or Cu-Se compounds has developed, and X-ray diffractometr cannot detect the presence of Cu in thin film. In films with 0.46 atomic % Cu a little peak of Cu (2.061) appears. Peaks correspondent to hexagonal phase of Cu-Se compounds already can be observed in film with 1.41 atomic % Cu. The (h k l) indices are shown above the reflections in Fig. 8. The conclusion is that Cu diffuses good and forms coumpuonds with Se.

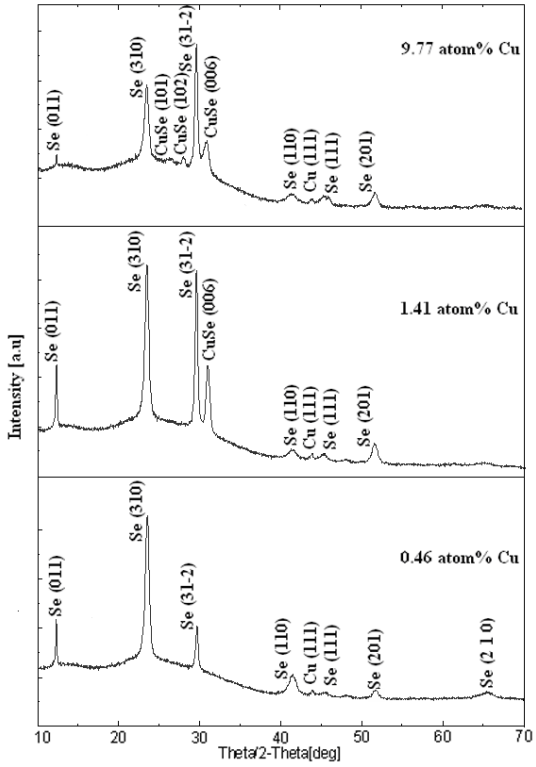


Fig. 8. The XRD measurement results of some Se-Cu thin films.

Very small grain sizes and lattice strain effects may be reasons for the broad peak profiles in the observed patterns. Due to these effects, in some cases neighboring peaks merge and can no longer be resolved experimentally. As a consequence it can lead to mistakes in identification of different crystalline phases or deduce elementary compositions of compound materials, especially if intensity of peaks is small.

4. Conclusion

Irradiating as-evaporated and annealed Se and Se-Cu thin films with femtosecond laser beam at wavelength 800-1000 nm SHG at wavelength 400-500 nm was observed. The highest intensity of reflected SH is provided by laser radiation at wavelength 950 -1000 nm. Amorphous films have the threshold for SHG and intensity of exciting radiation should be higher than 1 kW/cm². Intensity of reflected SH depends also on the amount of Cu in structures Se-Cu. It was found out that adding small amount of Cu increases anisotropy of the film and, herewith, increases also SH intensity. However, increasing of the amount of Cu > 2% leads to formation of crystalline

CuSe compound and that lead to reducing of generated second harmonic intensity.

References

[1] Gosavi S.R., Deshpande N.G., Gudagea Y.G., Sharma Ramphal, Journal of Alloys and Compounds **448**, 344 (2008).

[2] Mellikov E., Meissner D., Varema T., Altosaar M., Kauk M., Volobujeva O., Raudoja J., Timmo K., Danilson M., Solar Energy Materials & Solar Cells **93**, 65 (2009).

[3] Hankare P.P., Khomaneb A.S., Chate P.A., Rathod K.C., Garadkar K.M., Journal of Alloys and Compounds **469**, 478 (2009).

[4] Sanghera J.S. and Aggarwal I.D., J. Optolectron. Adv. Mater. **4**(3), 665 (2002).

[5] Qiu J., Hirao K., Si J., Opt. Lett. **26** (12), 914 (2001).

[6] Gruhn W., Optica Applicata, Vol.XXXV, No.3, 2005.

[7] Zakery A. and Elliott S.R., '', J. Non-Cryst. Solids **330**(1-3), 1 (2003).

[8] Ishida H., Mizoguchi R., Onda K., Hirose C., Kano S.S., Wada A., Surface Science **526**, 201(2003).

[9] Locharoenrat, K; Sano, H; Mizutani, G., J. Phys.: Conf. Ser. **100**, 052050 (2008).

[10] Fedyanin A.A., Dolgova T.V., Aktsipetrov O. A., Schuhmacher D., Marowsky G. Thin Solid Films **364**, 91 (2000);

[11] Akcipetrov O.A., Priroda (in Russian), No. 7., 9—17 (2005);

[12] Sledevskis E., Gerbreders V., Teteris J., Bulanovs A., Latvian J. Phys. Techn. Sc. **6**(3), 51(2007).

[13] Crystallographic and Crystallochemical Database for Minerals and their Structural Analogues, http://database.iem.ac.ru/mincryst/

[14] Bennemann K.H., [Nonlinear Optics in Metals], Clarendon Press, Oxford, 49 (1998).

[15] I.Mihailova, V.Gerbreders, E.Sledevskis, V.Kolbjonoks, E.Tamanis Proc. of SPIE, Vol. **7142**, 71420D (2008).

* Corresponding author: Irena.mihailova@du.lv