DAUGAVPILS UNIVERSITY
THE FACULTY OF NATURAL SCIENCES AND MATHEMATICS
G.LIBERTS INNOVATIVE MICROSCOPY CENTER

Mag.phys. Eriks Sledevskis

The photoinduced processes in chalcogenide films by continuous and pulse laser exposure

Summary of Promotion Thesis

Daugavpils University
Daugavpils, 2010

The paper has been written in G.Liberts Innovative Microscopy centre of Daugavpils University during period of 2005 till 2010.

Scientific supervisor: Dr.phys. J.Teteris
Scientific adviser: Dr.phys. V.Gerbreders

The Outline of Paper

The promotion thesis consists of an introduction, its aims and objectives, description of methods of research objects and experimental equipment, results of research, theses and references, as well as list of author's published works. The appendix of thesis contains copies of published articles issued in international publications on promotion theme.
The paper contains 53 pages, 36 pictures. The list of references contains 70 titles.

The Topicality of Research

During last ten years amorphous semiconductor compounds have been drawing a greater scientists' attention. The reason for this concerns the interests in applied and fundamental sciences. Amorphous chalcogenide materials are widely used in holographic data recording and as media for the storage of bit data on CDs and DVDs. Media with changeable phases states is the most perspective material which is assigned to be used in data optical technologies. There can already be found recordable optical discs (DVD-DW), in which phase transition between amorphous and crystalline states is used for data storage. The class of chalcogenide materials with its photoinduced transition of phases, that may form a considerable alternative to flash memory, is in prospect.

Response speed of optical systems of information has a great importance. Response speed is to a great extent caused by properties of media, its speed of crystallization and amorphization as a result of laser impulses exposure. Therefore search of new perspective materials for a pulse optical recording is essential. For this purpose are used chalcogenide with Ge, Se, Bi, Sb and others in its structure, which raise the crystallization tendency of material. The task to use $Sb_{20}Se_{80}$ glassy semiconductor as the carrier of optical information was put in this work. The light affect on films with intensity higher than threshold intensity causes the formation of sub-micron sizes polycrystalline areas. An intensive laser affect on films Sb-Se creates their crystallization. With the help of photo-crystallization, the changes of optical properties of the films $Sb_{20}Se_{80}$ have become a topical subject for investigations, owing to the application of these properties to the realization of data optical recording.

Holographic recording in amorphous chalcogenide films is the subject of investigations for many scientists. Not only search of new materials for an optical recording, but ways of increase of their photosensitivity is conducted. As_2S_3 films are the well investigated medium for classical hologram recording. Owing to low sensitivity E=30-40 J/cm^2, their use in pixel hologram recording is troublesome. This was the reason for the investigation of the possibility of sensitivity increase of the films As_2S_3 in As_2S_3-Al system. Taking into consideration the selective dissolution capacity of the films As_2S_3, As_2S_3-Al system is a perspective in acquisition of relief-phase holograms.

Modern optical discs achieve the recording density up to 10^8 bit/cm^2. Optical recording usually is performed on film surface without beam focusing. Micro hologram recording on film surface and deep in the film layer is an interesting matter in practical application. This fact can increase fundamentally the total capacity of a data carrier. Therefore, there is a necessity in investigation of the feasibility of the recording in the layer depth of As_2S_3 chalcogenide.

Recently there has been a growing interest in development of optical materials with large nonlinear optical coefficients aimed for applications in electro-optic and integrated optic devices. It is of great importance to develop materials with small size and relatively simple and not expansive fabrication technology allowing their easy integration in optical applications. Chalcogenide and chalcohalide glasses may be promising in this respect and, therefore, are potentially perspective for applications in different areas of quantum electronics: infrared (IR) optoelectronics, holography and integrated optics, particularly as materials for IR fibres. Varying their content one can improve the technological parameters, particularly optical and nonlinear optical coefficients.

Aims and Objectives of Promotion Thesis

Aims:

The aim of the promotion thesis is research of influence of continuous and pulse laser radiation on As_2S_3 and $Sb_{20}Se_{80}$ thin films for increase of photosensitivity and optical recording density.

Also it was put aim to investigate of nonlinear optical processes in Se thin films and systems Se-metal at femtosecond laser exposure.

Objectives:

Realisation of aims of the promotion thesis demands performance of following research problems:

1. To study change of optical parameters of As_2S_3 and $Sb_{20}Se_{80}$ thin films at influence of continuous and pulse laser radiation at bit-by-bit and holographic recording;
2. To investigate optical properties of reflective system As_2S_3-Al and realisation possibility of optical recording in it;
3. To study the possibility of confocal system for recording micropoints by the focused radiation on surface and inside thin films;
4. To achieve registration of the second optical harmonic in Se thin films and Se-metal systems. To find out dependence of intensity of second optical harmonic on parameters of film and wave length of exciting radiation.

Contents

The description of investigation results and experiments contains 5 parts which are dedicated to the pulsed light holographic recording in amorphous As_2S_3 thin films (5), to the optical properties of and holographic recording in the $Sb_{20}Se_{80}$ thin films (6), to the photoinduced reflection changes and to the holographic recording in the As_2S_3-Al system (7), to the optical recording on surface and inside As_2S_3 thin films (8) and to the photoinduced second harmonic generation in selenium-metal structures (9).

1. Diffraction grating recording in amorphous As_2S_3 films by means of pulse laser QUANTEL (YG980 Q-Switched Nd:YAD Laser, pulse duration ~ 8 ns, beam diameter 5 mm, λ – 532 nm, polarisation – vertical) and continuous Nd:YAD laser VERDI (λ – 532 nm) is studied. The sharp increase in a photosensitivity of films (~100) is shown for exposure by nanosecond pulses in comparison with recording by continuous radiation.
2. The process of optical recording in the $Sb_{20}Se_{80}$ films, as a result of which photocrystallization of amorphous material takes place, is considered. The experimental setup, allowing by laser exposure photocrystallize Sb-Se films with the subsequent studying of crystallization process in a scanning electronic microscope has been collected. The definition has been done for the minimum range of light quantum power that makes photocrystallization possible, and its threshold value required for the

real-time initiation of photocrystallization. Such photocrystallization in $Sb_{20}Se_{80}$ films proceeded under continuous and pulsed laser irradiation. The increase (~10^2) of film sensitivity has been observed, operating with impulses of picosecond range.

3. The investigation of optical recording in As_2S_3 thin films allowed increasing their sensitivity in As_2S_3-Al system more than two times. The methods of obtaining the As_2S_3-Al thin films with minimal radiation coefficient (~15% wavelength λ=532 nm) are developed. Taking into consideration the possibilities of selective etching, the practical application of the As_2S_3-Al system in holography is in perspective.

4. To increase a capacity of the information storage material the recording of holograms should be performed both on the surface and inside the film. At present this method of non-holographic recording by bit is realized in DVD-s. In thesis it is shown, that optical recording in the As_2S_3 films by bit can be realized on the surface and in the depth of the film with good resolution of the signals coming from the surface and the depth of film during readout. Since holographic recording with high diffraction efficiency is possible in $A_{S2}S_3$ films, the next step in research will be the implementation of dot holographic recording on the surface and inside of the film.

5. Results of photoinduced second harmonic (SH) generation in amorphous and crystalline selenium films and selenium-metal (Ga, Zn, In, Sb, Bi) sandwich structures induced by titanium-sapphire femtosecond laser Chameleon Ultra (180 fsec. pulse width, 80 MHz repetition rate, λ - 690-1040 nm, linear polarization) are presented. The experiment was performed by confocal microscope LEICA where the femtosecond radiation from laser was injected. In work possibilities of increase in intensity of the second harmonic are considered at increase of a thickness of selenium films. Generation processes in amorphous and a crystalline state depending on energy of quanta of exciting radiation are investigated. Life times of excited state for amorphous and crystalline selenium films are received.

The Novelty of the Research

It is established that exposure of As_2S_3 films by pulse laser light of the nanosecond range raises photosensitivity of films on two orders (~10^2) in comparison with exposure by the continuous laser. Recording of holographic grating in As_2S_3 films is executed by one impulse of the nanosecond laser.

It is established that exposure of $Sb_{20}Se_{80}$ films by pulse laser light picosecond range raises photosensitivity of films on two orders (~10^2) in comparison with exposure by the continuous

laser. Recording of holographic grating on phase transition amorphous-crystalline state is executed.

Recording of holographic grating in system As2S3-Al is investigated. It is shown that use of As_2S_3 films in system As_2S_3-Al raises their photosensitivity more than two times at optical recording.

It is shown that in system As2S3-Al the bit-by-bit optical recording both on surface and inside of film layer is possible.

It is established that exposure of amorphous both crystalline Se films and structure metal-Se by pulse laser light of the femtosecond range produce generation of the second optical harmonic in them.

The Theses of the Promotion Thesis

1. The photosensitivity of As_2S_3 and $Sb_{20}Se_{80}$ thin films increases at transition from continuous to pulse laser irradiation.
2. Using the interference system As_2S_3-Al for optical recording allows increasing photosensitivity of As_2S_3 films.
3. Using confocal systems allows carrying out optical recording and reading both on surface, and inside the As_2S_3 thin film.
4. Influence of femtosecond laser radiation on selenium and selenium-metal films leads to generation of the second optical harmonic in them.

Conclusions

1. Diffraction grating recording in amorphous As_2S_3 films by one impulse of pulse laser QUANTEL (λ=532nm) has been investigated. It was established that after the termination of exposure of laser radiation (8 ns), diffraction efficiency continued growing during 150-200 ns. Whereupon relaxation processes in films (till 12 μs), accompanied by recession of diffraction efficiency, has happened. Relaxation time depends both on an exposition dose, and thickness of the sample. On films As_2S_3 with the thickness 6 μm has been received the diffraction grating with the greatest diffraction efficiency (DE=12 %) at smaller relaxation time (τ=2μs) and exposition dose - 250 mJ/cm^2, in comparison with films of other thickness. Measurements indicate an increase in photosensitivity by a factor of about 100 times for exposure with pulsed light as compared to continuous wave recording.

2. The influence of light and thermal treatment on the amorphous $Sb_{20}Se_{80}$ thin films leads to their crystallization. The energy of light quantum minimal value for photocrystallization is 1.85 eV. The light quanta 1.96 eV and 2.41 eV have limit intensity value (3.5 W/cm^2 and 0.2 W/cm^2, respectively) starting from which the crystallization process takes place. The light quanta 2.54 eV and 2.72 eV have no intensity limit. Comparing with the impact of continuous laser, light pulse impact (λ=532 nm, f = 50 kHz, T_{imp}=30 ps) increases $Sb_{20}Se_{80}$ films light sensitivity two order (from ~10^{-3} cm$^2 \cdot J^{-1}$ to ~10^{-1} cm$^2 \cdot J^{-1}$). The $Sb_{20}Se_{80}$ films light sensitivity increases in their bases with lower thermal conductivity. Diffraction grating recording with diffraction efficiency 1% has been obtained on the $Sb_{20}Se_{80}$ films. As the result of the formation of tiny polycrystalline area, the grating periodic structure takes shape, owing to the spatial position of interference line intensity.

3. Optical recording has been investigated in the As_2S_3-Al system. The thickness of the As_2S_3 layer of the As_2S_3-Al system influences the amplitude of reflection coefficient changes and the system sensitivity against laser radiation. The maximum changes ~45% of the reflected signal have been obtained on the 2,2 – 3,5 μm As_2S_3 thick films. The maximum light sensitivity ~0,08 cm^2/J corresponds to the films of 3.6 μm thickness. The recording of the holographic grating was performed in As_2S_3-Al system. Its diffraction efficiency depends on both film thickness and initial conditions of reflectivity in the system. Maximal diffraction efficiency 1.2% and 1.5% in the second maximum of reflectivity was achieved for film thickness of 2.2 μm and 6.8 μm respectively, provided the recording was made in the point with minimal initial reflectivity.

4. Application possibility of confocal microscope TCSP-5 (Leica) for a bit-by-bit optical recording in system As_2S_3-Al is studied. Optimal value of exposure for optical recording E=0.4 J/cm^2 will be defined at which change of reflection of system was maximal. In the present work we find out that optical recording in the As_2S_3 films by bit can be realized on the surface and in the depth of the film with good resolution of the signals coming from the surface and the depth of film during readout.

5. Exposure of femtosecond radiations on films of selenium and structure selenium-metal (Ga, Sb, Bi, Zn, In) are studied. Illumination of amorphous and crystalline Se and Se-metal films with powerful femtosecond laser radiation λ – 800-1000 nm leads to appearance of second harmonic generation (SHG) λ – 400-500 nm. It is established that

there is a threshold of intensity ~0.5 kW/cm ² since which, generation of SH is observed in amorphous films. For crystalline films such threshold of intensity it is not revealed. Moreover, at intensities of exciting radiation higher than 7.5 kW/cm², we did not observe differences in the intensity of SH for amorphous and crystalline selenium films. It is established that the intensity of transmitted SH depends on film thickness. For selenium films of thickness 1.5 μm it is approximately 4 times higher than for those of thickness 0.5 μm. At equal parameters of exciting radiation in films of both thicknesses (0.5 μm and 1.5 μm) no differences were found in intensities of reflected SH. Intensity of the second harmonic depends on pulse duration of exciting radiation. The increase of pulse duration of exciting radiation from 180 up to 800 fs leads to a sharp reduction of SH intensity (approximately in 10 times). From all metals used in experiments (Ga, Zn, In, Sb, Bi) better results (higher intensities) were achieved with Ga and Zn. The SH intensity of Se-Ga and Se-Zn compounds were close to that of pure selenium films (Fig.4). At the same time the threshold of destruction of Se-Ga, Se-Zn compounds at illumination with powerful femtosecond radiation is higher than that of pure selenium films. Therefore, the exploitation time of these selenium-metal sandwich structures should be higher than that of pure selenium films. Life times of excited state (radiation time of SH) for films of selenium and system selenium-metal (t – 100-200ps) are received.

The results of the promotion thesis are published in 8 international generally established reviewed publications. The obtained results have been presented in 11 conferences, which are reflected in 18 conference theses.

The List of Published Works

Publications

To perform these tasks, experiments have been conducted, which results are reflected in the publications [1st publ. – 8th publ.] included into the promotion thesis:

[1.publ.] I.Mihailova, V.Gerbreders, E.Tamanis, **E.Sledevskis**, V.Kolbjonoks. Second harmonic generation in selenium-copper structures. Journal of Optoelectronics and Advanced Materials, Vol.11, No.12, 2083–2087 (2009).

[2.publ.] V.Gerbreders, **E.Sledevskis**, V.Kolbjonoks, J.Teteris, A.Gulbis. Second harmonic generation in selenium-metal structures. Journal of Non-Crystalline Solids, Vol.355, 1959-1961 (2009).

[3.publ.] A.Bulanovs, V.Gerbreders, **E.Sledevskis**, Investigation As_2S_3-Al films for dot-matrix holographic recording. Proc. of SPIE, 2.12.2008, Vol. 7142, 714211 (2008).

[4.publ.] I.Mihailova, V.Gerbreders, **E.Sledevskis**, V.Kolbjonoks, E.Tamanis, Second harmonic generation in selenium-metal structures. Proc. of SPIE, Vol. 7142, 71420D (2008).

[5.publ.] **E.Sledevskis**, V.Gerbreders, V.Kolbjonoks, J.Teteris, A.Gulbis. Second harmonic generation in selenium thin films. Proc. of SPIE, Vol. 7142, 71420F (2008).

[6.publ.] Vj.Gerbreder, **E.Sledevskis**, G.Liberts, J.Teteris, V.Pashkevich. Optical recording on surface and inside As_2S_3 thin films, Journal of Optoelectronics and Advanced Materials, Vol. 9, No. 10, 3161-3163 (2007).

[7.publ.] V.Gerbreders, J.Teteris, **E. Sledevskis**, A.Bulanovs. Photoinduced changes of optical reflectivity in As_2S_3-Al system, Journal of Optoelectronics and Advanced Materials, Vol.9, No.10, 3153-3156 (2007).

[8.publ.] **E.Sledevskis**, Vj.Gerbreders, J.Teteris, A.Bulanovs. Photoinduced processes in $Sb_{20}Se_{80}$ thin films, Latvijas Fizikas un Tehnisko Zinātņu Žurnals, Nr 3-2007, 51-59 (2007).

Conferences:

The results have been presented in several conferences that are reflected in the following conference theses:

1. V.Gerbreders, **E.Sledevskis**, O.Shimane, A.Bulanovs, V.Pashkevichs. Photostimulated crystallization of Sb-Se thin films. 4-th International Conference on Amorphous and Nanostructured Chalcogenides (ANC-4), (Constanta, Romania, 29.06 – 3.07.2009), p.45

2. I.Mihailova, V.Gerbreders, E.Tamanis, **E.Sledevskis**, V.Kolbjonoks. Second harmonic generation in selenium-copper structures. 4-th International Conference on Amorphous and Nanostructured Chalcogenides (ANC-4), (Constanta, Romania, 29.06 – 3.07.2009), p.45.

3. O.Šimane, V.Gerbreders, **E.Sledevskis**, A.Bulanovs, V.Paškevičs, Fotostimulēta plāno Sb-Se kārtiņu kristalizācija. Daugavpils Universitātes 51. Starptautiskā zinātniskā conference, (Daugavpils, Latvija 15.-18.aprīlis, 2009), p.7.

4. I.Mihailova, V.Gerbreders, **E.Sļedevskis**, V.Kolbjonoks, Otrās harmonikas ģenerācija struktūrās selēns-varš. Daugavpils Universitātes 51. Starptautiskā zinātniskā conference, (Daugavpils, Latvija 15.-18.aprīlis, 2009), p.6.

5. Vj.Gerbreders, **Ē.Sļedevskis**, A.Bulanovs, O.Šimane, J.Teteris, Optiskās, elektriskās īpašības un kristalizācijas procesi Sb-Se planas kārtiņās, 25. zinātniskā konference, LU Cietvielu fizikas institūts, (Rīga, Latvija, 11.-13.02.2009), p.48.

6. V.Gerbreders, A.Gerbreders, G.Kirilovs, J.Teteris, **E.Sledevskis**, A.Bulanovs, Planar waveguides based on organic polymer – As_2S_3 films, The 6^{TH} International Conference on Advanced Optical Materials and Devices (AOMD-6), (Riga, Latvia, 24 – 27 August 2008), p.65.

7. A.Bulanovs, V.Gerbreders, **E.Sledevskis**, Investigation As_2S_3-Al films for dot-matrix holographic recording, The 6^{TH} International Conference on Advanced Optical Materials and Devices (AOMD-6), (Riga, Latvia, 24 – 27 August 2008), p.82.

8. I.Mihailova, V.Gerbreders, **E.Sledevskis**, V.Kolbjonoks, E.Tamanis, Second harmonic generation in selenium-metal structures, The 6^{TH} International Conference on Advanced Optical Materials and Devices (AOMD-6), (Riga, Latvia, 24 – 27 August 2008), p.55.

9. **E.Sledevskis**, V.Gerbreders, V.Kolbjonoks, J.Teteris, A.Gulbis, Second harmonic generation in selenium thin films, The 6^{TH} International Conference on Advanced Optical Materials and Devices (AOMD-6), (Riga, Latvia, 24 – 27 August 2008), p.57.

10. **Ē.Sļedevskis**, Fotoinducētie procesi sistēmā metāls-selens, Daugavpils Universitātes 50. Starptautiskās zinātniskā konference, (Daugavpils, 15.-17.05.2008), p.38.

11. A.Bulanovs, V.Gerbreders, **E.Sledevskis**, V. Pashkevich, J.Teteris. Dot matrix holographic recording in As_2S_3-Al films, XVI^{th} International Symposium on Non-Oxide and New Optical Glasses. (Montpellier, France, April 20-25, 2008), p. 53.

12. V.Gerbreders, **E.Sledevskis**, V.Kolbjonoks, J.Teteris, A.Gulbis, Second harmonic generation in selenium-metal structures, XVI^{th} International Symposium on Non-Oxide and New Optical Glasses. (Montpellier, France, April 20-25, 2008), p.49.

13. **Ē. Sļedevskis**, Vj. Gerbreders, J. Teteris, Fotoinducētie procesi sistēmā metāls-selens, 24. zinātniskā konference, LU Cietvielu fizikas institūts, (Rīga, Latvija, 22.-27.02.2008), p.48.

14. Vj.Gerbreder, **E.Sledevskis**, G.Liberts, J.Teteris, V.Pashkevich, Optical recording on surface and inside As_2S_3 thin films, Third International Conference on Amorphous and Nanostructured Chalcogenides (ANC-3), (Brasov, Romania, 02-06.06.2007), p.42.

15. V.Gerbreders, J.Teteris, **E.Sledevskis**, A.Bulanovs, Photoinduced changes of optical reflectivity in As_2S_3-Al system, Third International Conference on Amorphous and Nanostructured Chalcogenides (ANC-3), (Brasov, Romania, 02-06.07. 2007), p.36.

16. V.Gerbreders, G.Liberts, **Ē.Sļedevskis**, A.Bulanovs, I.Mihailova, Konfokālā mikroskopa TCSP-5 (LEICA) izmantošana optiskā ieraksta eksperementos halkogenīdu stiklos. 1.Latvijas Inovatīvās Mikroskopijas Seminārs (Daugavpils, Latvija, 29-30.03.2007).

17. **Ē.Sļedevskis**, Vj.Gerbreders, J.Teteris, Fotoinducēti procesi amorfās Sb-Se kārtiņās, 23. zinātniskā konference, LU Cietvielu fizikas institūts, (Rīga, Latvija, 13.-15.02.2007), p.46.

18. **E.Sledevskis**, J.Teteris, Vj.Gerbreders, Pulsed light holographic recording in amorphous As_2S_3 thin films, The 5^{TH} International Conference on Advanced Optical Materials and Devices, (Vilnius, Lithuania, 27-30.08. 2006), p.73.

The theses have been accepted for publication.