JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 13, No. 11-12 , November – December 2011, p. 1487 - 1492

High density optical recording in thin chalcogenide films

A. A. KRYUCHYN, V. V. PETROV[*], S. O. KOSTYUKEVYCH[a]
Institute for Information Recording of NAS of Ukraine, 2 Shpak Str., 03113, Kyiv, Ukraine
[a]*V. Ye. Lashkaryov Institute of Semiconductor Physics of NAS of Ukraine, 41 Prospect Nauky, 03028, Kiev, Ukraine*

Presented in this work are the results of investigations aimed at recording information with focused laser radiation in thin films of chalcogenide vitreous semiconductors (ChVS). Over all the stages in creation of systems for optical recording, there widely used were thin films of ChVS. The first optical disc carriers were designed using thermo-sensitive materials based on tellurium alloys. Shown is perspective to use thin ChVS films for creation of optical carriers for long-term information storage. The high density of recorded information in them is achieved when using the thermo-lithographic methods. Non-organic photoresists based on ChVS can be also efficiently used for manufacturing master discs. Obtaining the needed minimal sizes of pits in master discs (used in manufacturing compact-discs) is promoted by a non-linear dependence of the exposure characteristics on the intensity of exposing radiation. When using non-organic resists of the As-S, As-S-Se systems, there obtained are pits of 0.25 – 0.3 μm width. Information was recorded using the focusing objective with the numeric aperture 0.85 and radiation from a semiconductor laser with the wavelength 405 nm. The metal adhesive layer deposited on the glass substrate strongly influences on the recording process. We chose the recording regime in such a manner that enabled us to prevent local photo-thermal destruction of resist in the center of irradiated area. Presented in the work are the results of studying optical recording in thin ChVS films prepared recently in labs of Institute for Information Recording and V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine. One of the obtained results is technology for manufacturing stamps for copying CD based on non-organic photoresists.

(Received June 22, 2011; accepted November 23, 2011)

Keywords: Thin chalcogenide films, Optical recording, Thermolithography

1. Introduction

The complex of unique physical-and-chemical properties of chalcogenide vitreous semiconductors (ChVS) allows considering them as promising materials for creation high-resolution photo-sensitive materials for information carriers and registering media for long-term information storage. Development of characteristics inherent to optical and magnetic information carriers, flash-memory, diversity of optoelectronic devices is related with creation of technologies for manufacturing nano-sized relief structures on the surface of substrates made from various materials. In many cases, it is very interesting to make relief structures in surface layers of these substrates themselves.

For a long time, enhancement of the resolving power in photo-lithographic processes was provided by a decrease in the wavelength of exposing radiation and increase in the numeric aperture of focusing systems.

In the systems for information optical recording on master discs, possibilities to further increase the resolving power in diffraction-limited optical systems are practically exhausted. These systems allow focusing the radiation with the wavelength 265 nm into a spot of 0.35 μm diameter. Only application of photo-sensitive materials with non-linear exposure characteristics (in the best case, with the threshold ones) allow to obtain pits with geometrical sizes corresponding to currently standards for modern carriers (for instance, Blu-ray discs).

Non-organic resists possess resolution providing to record elements with geometrical sizes of the order of 100 nm. As it can be seen from the results of interferential photo-lithography with using non-organic resists based on ChVS, one can make gratings with the spatial frequencies 5350 mm^{-1} [1]. The minimal width of prints $d_{\min}$ obtained in the course of laser recording by using focused laser radiation is defined by the Rayleigh criterion

$$d_{min}=K\left(\frac{\lambda}{NA}\right)$$

where λ is the wavelength, NA – numeric aperture, K – proportionality coefficient depending on photoresist characteristics and technological regime for processing it.

To record information on master discs in currently formats by using radiation with the wavelength 405 nm, it is necessary to reach the coefficient K value within the range 0.26-0.30.

A strong dependence of light sensitivity for registering media based on ChVS on the intensity of exposing radiation was found in investigations performed during 70-80-th years of the last century [2, 3].

Using the optical pulses with duration of 10 ns for information recording allows to realize heating the registering media in the regime close to the adiabatic one and initiate considerable structural transformations in illuminated material owing to non-linear processes developed under the influence of highly intense laser radiation. ChVS can be considered as promising light-sensitive material for thermo-lithographic recording, which provides making the prints with an essentially lower (3 to 5 times) size than that of illuminated area [4], if using focused radiation with strongly non-homogeneous distribution of light in the latter. The main way to record master discs in the Blu-ray format is now based on the recording process with using phase transitions in composite materials (PTM-processes) [5, 6].

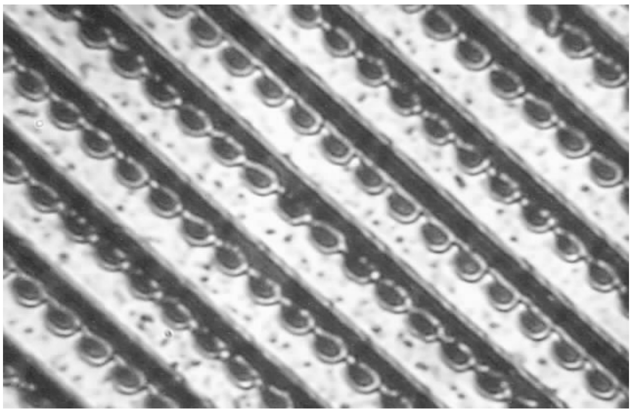
It seemed in recent years that registering materials with ablation recording mechanism could not find their application in up-to-date systems of information recording as caused by limited resolution of these materials and their low photo-sensitivity. However, the perfortmed complex investigations of information carriers for long-term data storage showed that the carriers with micro- or nano-relief form of data representation provide the highest terms of information storage [7-9]. The process of ablation recording is now considered as one of the promising methods to realize thermo-lithographic recording. Application of modern systems for optical recording enables to obtain pits with the diameter close to 40 nm in regime of ablation recording [10]. Therefore, investigation and development of highly stable materials for ablation recording are of considerable interest.

2. Experimental

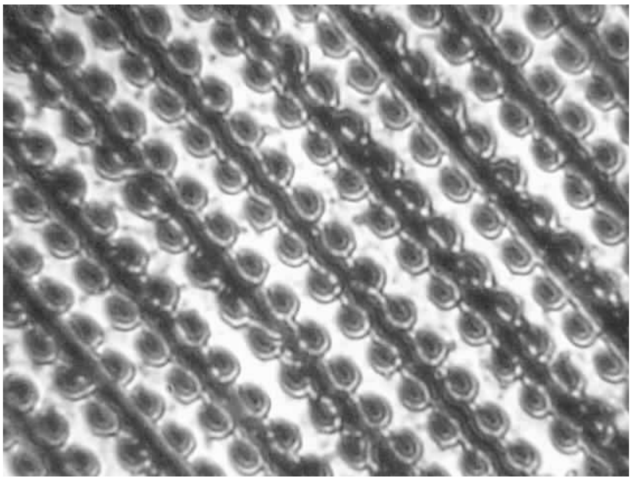
Our investigations of optical recording in thin ChVS films were performed using experimental samples of disc optical storing facility and laser station for master discs. In detail, the description of the optical system used for experiments with the laser station was carried out in [11]. To record master discs in the DVD format and investigate data recording in the Blu-ray format, we changed argon laser for the gallium nitride one. The numeric aperture of focusing objective was 0.85. To increase accuracy in operation and fast response, we used a piezoelectric actuator in the system for automated focusing the recording laser radiation.

The process of exposing the ChVS thin films deposited on disc substrates has a number of features related with the high power density and inhomogeneous intensity distribution within the illuminated area as well as application of pulsed irradiation. In detail, this process was investigated by several authors that found a decrease in the width of recorded lines as compared with the diameter of exposing beam and increase in the sensitivity of the power density of exposing radiation. The attempts to considerably increase the power of exposing beam resulted in local photo-thermal destruction of ChVS films in the center of irradiated area [12]. These investigations were multiply repeated using more short-wave lasers (from He-Ne to argon and, recently, to the gallium nitride ones). Further processing the exposed substrates in selective etchants provided creation both negative and positive images [13-15]. The shape of pits (for positive resists) and bumps (for the negative ones) depends on the recording radiation wavelength, intensity, irradiation time and etch time [13, 16-18].

In parallel, we performed investigations concerning formation of micro-relief structures directly in the process of exposure with pulsed focused radiation [19]. Ar-laser radiation provided formation of micro-pits with the diameter 0.5 – 0.6 μm on the surface of optical discs. Beside pits that coded the registered information, we recorded ordering information as well as control tracks. The latter were recorded in the process of marking the disc carriers, while information bits were recorded near them. Fig. 1 shows a record in this carrier.



(a)



(b)

Fig. 1. External view of the recording zone on the optical carrier: (a) data recording is realized from one side of the guide track; (b) and from both sides.

This location of information data relatively to ordering information is realized rather simply when using the only recording beam, however, it cannot be recommended for creation of carriers in the field of long-term data storage. In the latter case, the control tracks and ordering information should be formatted in another layer or in the information carrier substrate. Light-sensitive layers of ChVS were deposited on disc substrates by using thermal evaporation in vacuum from silica evaporators with indirect heating or from metal boats with heated screens. The thickness of layers in the disc operation area was kept with the accuracy 2 to 3 nm, which was provided by placing the substrates at the distance not less than 350 mm from evaporators and their planetary rotation in the course of sputtering.

To enhance adhesion of non-organic photoresist layers, the substrates were covered with a special adhesive layer. As this layer, we used chromium layers or ChVS layers containing germanium. Use of germanium-containing ChVS layers to enhance adhesion of non-organic resists *x AsS – y AsSe* was also offered by the authors of [20].

The thickness of chromium adhesive layers should not exceed 20 – 30 nm, since a further increase in it results in increase of the energy for recording information bits.

When these adhesive layers are absent, one can observe layer separation from the substrate in the process of selective etching.

3. Results

The longest terms for information storage are predicted in the case of optical carriers with micro(nano)-relief presentation of information bits. It is assumed here that the relief is formed from the film of highly stable photo-thermo-sensitive resist by focused laser radiation [9, 21]. Relevant storage terms in these carriers are essentially different. One of the ways for making such photo-thermo-sensitive layer is deposition of thin (120 – 200 nm) ChVS layers. As it was mentioned in many investigations (see, for instance [19, 22]), choice of these resists is reasonable due to their low thermal conductivity, high chemical stability, high optical absorption and reflection. A particular interest is caused by investigation of thin ChVS films where information records were made many years ago. After 30-year storage of disc carriers, registering layer of which was made of $Te_{14}Sb_{10}Se_{61}Ge_{15}$ (quaternary compact eutectic alloy)[23], the recorded pits have kept their shape and sizes. The reflection coefficient of the registering layer has been changed insignificantly (by 10 to 12%, which is related with growth of the oxygen concentration in ChVS film up to10 -13%) [24].

Exposure of non-organic resist based on *As-S-Se* layer with focused (numeric aperture 0.8) Ar laser beam (λ = 488 nm) enabled us to obtain prints of the width 250 to 300 nm after following selective etching. The width of prints was changed in dependence on power of exposing radiation. The power was varied within the range 0.23 up to 0.82 mW (Table 1). Etching the photoresist was made in selective etchant based on ethylenediamine [14, 15, 25].

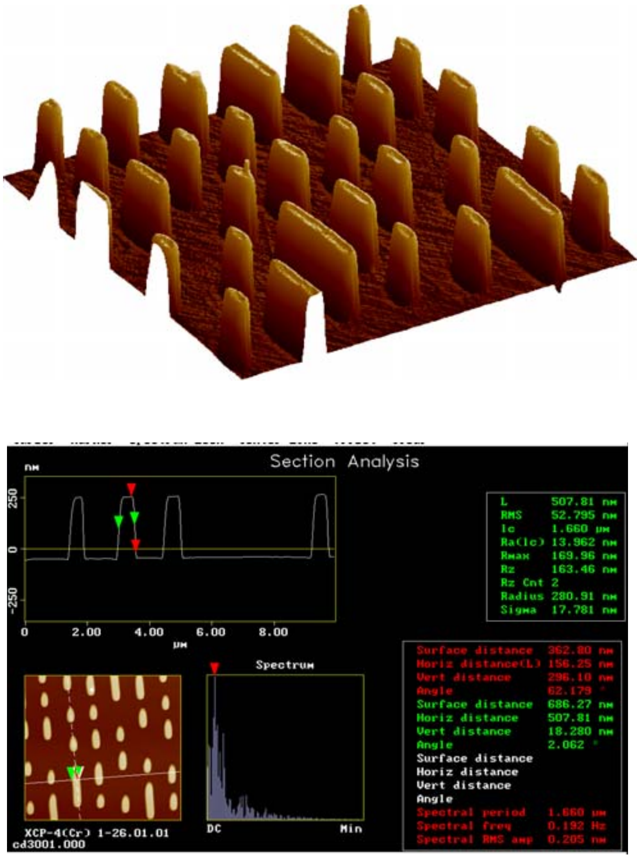
The data summarized in Table 1 show that with increasing the radiation power at the micro-objective output the track width is gradually increased. When using the negative etching process, one can observe a more sharp dependence of the width on the intensity of recording radiation.

Table 1. Dependence of track widths for negative and positive etching on the power of recording radiation in the layer $As_{40}S_{40}Se_{20}$ (λ = 488 nm).

Power of recording radiation, mW	Track width for negative etching, nm	Track width for positive etching, nm
0.25	230	250
0.35	500	300
0.45	600	350
0.55	700	400
0.65	780	440
0.75	880	490

Investigations of topology for the obtained relief micro-structures performed using the atomic force microscope Nanoscope IIIa Dimension 3000 have shown that the tracks possess a shape close to that of isosceles trapezium with the slope angle of side faces, the value of which does not depend on power of exposing radiation and is approximately 30 - 35° [11].

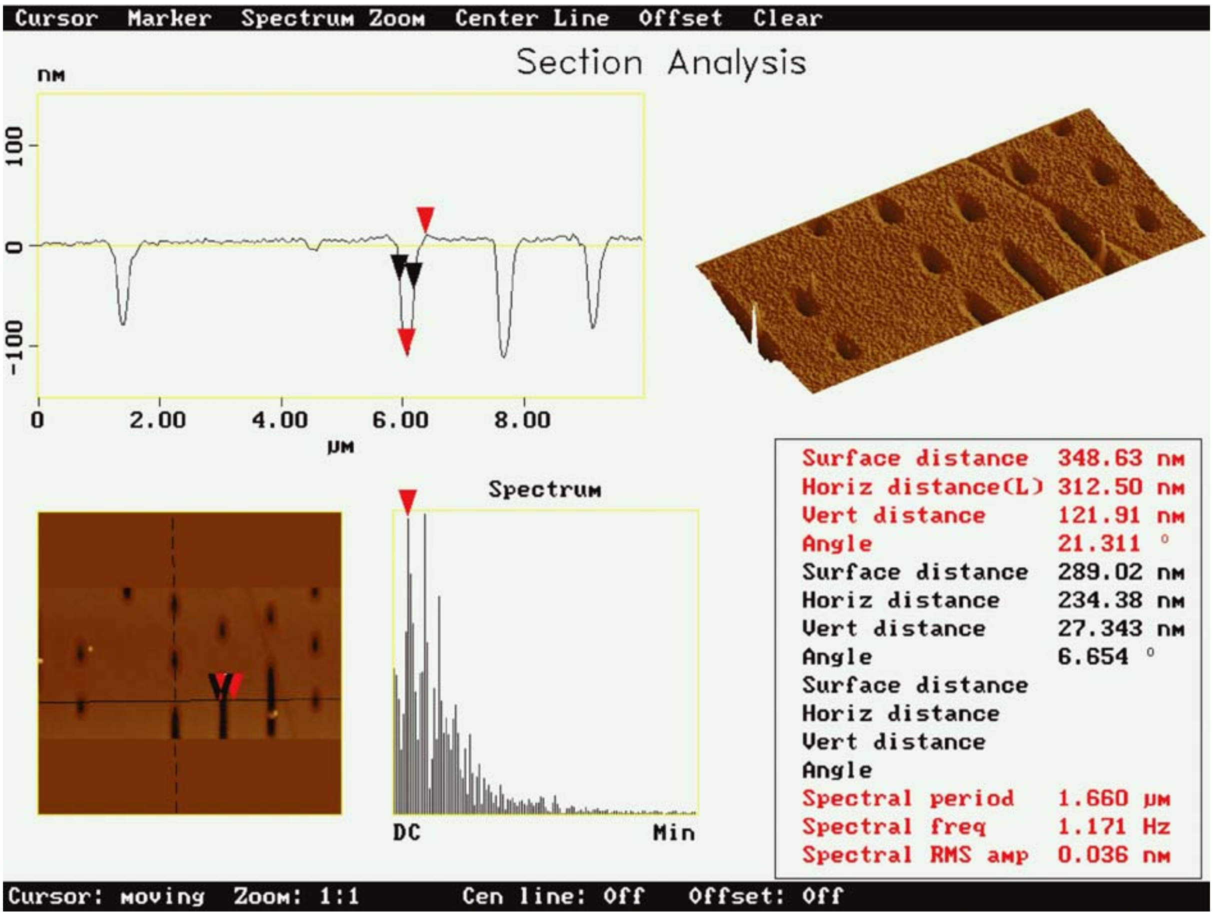
Fig. 2 shows micro-relief of a master disc surface after negative etching the photo-sensitive layer $As_{40}S_{40}Se_{20}$ with the thickness 300 nm, and Fig. 3 does that for positive etching.



```
L          507.81 nm
RMS        52.795 nm
lc         1.660 μm
Ra(lc)     13.962 nm
Rmax       169.96 nm
Rz         163.46 nm
Rz Cnt     2
Radius     280.91 nm
Sigma      17.781 nm

Surface distance     362.80 nm
Horiz distance(L)    156.25 nm
Vert distance        296.10 nm
Angle                62.179 °
Surface distance     686.27 nm
Horiz distance       507.81 nm
Vert distance        18.280 nm
Angle                2.062 °
Surface distance
Horiz distance
Vert distance
Angle
Spectral period      1.660 μm
Spectral freq        0.192 Hz
Spectral RMS amp     0.205 nm
```

Fig. 2. Micro-relief of the master disc surface after negative etching.



Surface distance 348.63 nм
Horiz distance(L) 312.50 nм
Vert distance 121.91 nм
Angle 21.311 °
Surface distance 289.02 nм
Horiz distance 234.38 nм
Vert distance 27.343 nм
Angle 6.654 °
Surface distance
Horiz distance
Vert distance
Angle
Spectral period 1.660 µм
Spectral freq 1.171 Hz
Spectral RMS aмp 0.036 nм

Cursor: мoving Zooм: 1:1 Cen line: Off Offset: Off

Fig. 3. Micro-relief of the master disc surface after positive etching.

The increase (approximately by 30%) in resolution of the optical channel in our station for laser recording (previous micro-objective was changed for that with the aperture 0.85, and the recording wavelength was chosen as 405 nm) did not enable to essentially decrease sizes of the obtained relief micro-structures. Measurements of the track width after negative etching have shown that it decreases proportionally in practice. The minimum obtained value was about 0.18 µm. In both cases, recording was carried out using laser radiation pulses with duration close to 1 µs. A further decrease in the print width can be reached by exposing with pulses of duration 10 – 15 ns. In this case, every recording pulse can consist of separate pulses with shorter duration (in dependence of the chosen recording strategy).

4. Discussion

With the transfer to wide application of shortwave ultraviolet radiation (mainly to the wavelength 405 nm) in systems of optical recording, the number of ChVS compositions suitable for usage as registering media was increased.

Non-organic photoresists have no essential advantages over the traditional organic ones in technology of manufacturing master discs in CD and DVD formats. However, they can find wide application when recording information in Blu-ray and the following formats with a high density of recording. In the Blu-ray format, optical recording with visible light on non-organic photoresists can be realized using short (10 to 15 ns) and power pulses of laser radiation. Just this regime is typical for information recording in the Blu-ray format. This action provides considerable local heating the resist and generation of large amount of electron-hole pairs, which promotes recording in the very center of illuminated area. It results in diminishing the recorded print. In our experiments, we reached the print size 250 – 300 nm lower than the diameter of illuminated spot (600 nm).

Contrary to selective etching the images in manufacturing elements of optoelectronic devices (for example, gratings or micro-prisms) when used are etchants with very soft contrast characteristics [20], just contrast etchants should be used in mastering the master discs. A decrease in sizes of micro(nano)-relief structures recorded on non-organic photoresists should be promoted by using the high-contrast selective etchants. Complex use of both these factors: narrowing the print in the course of recording and processing with a high-contrast etchant, can allow 3- or 4-fold diminishing the geometric sizes of elements as compared with the diameter of exposing beam. By contrast, when recording holographic pictures, to provide a linear response of a registering system, commonly used is radiation from the range of weak resist absorption [26]. While thermolithographic recording needs high light absorption of non-organic photoresist.

As it has been shown by the performed investigations, non-organic photoresists based on ChVS with positive etching regime can be used in traditional “glass” mastering to record information on master discs with further producing the nickel stamps for copying CD. These non-organic resists with the negative etching regime can be applied in the process of direct mastering [12] when a relief image is created on the nickel substrate after exposing and selective etching. To provide production of a large number of copies (>3000-5000), it is reasonable to use non-organic photoresists with maximum possible melting temperatures. To enhance durability of stamps based on ChVS, it seems expedient to use multi-layer non-organic photoresists.

5. Conclusions

1. Thin ChVS films can be used both for creation of professional optical information carriers and in manufacturing master discs within the technological process for production CD. As it can be seen from the performed investigations, ablation recording on thin ChVS films provides long-term storage of recorded information.

2. Resolution of non-organic photoresists based on ChVS allows formation of elements with geometrical sizes of several tens nanometers. Formation of these elements by using optical radiation from the visible range is possible only due to application of non-linear non-organic photoresists that are developed under exposure with power short radiation pulses and following etching in high-contrast selective etchants.

Acknowledgments

The authors would like to express their sincere gratitude to Yu.A. Borodin, scientific researcher of the Institute for Information Recording, NAS of Ukraine, for recording information on master discs; P.Ye. Shepeliavyi, senior scientific researcher of the Institute of Semiconductor Physics, NAS of Ukraine, for processing the master discs; V.I. Min’ko, senior scientific researcher of the Institute of Semiconductor Physics, NAS of Ukraine, for vacuum deposition of the registering media; and A.A. Kudryavtsev, senior scientific researcher of the Institute of Semiconductor Physics, NAS of Ukraine, for taking part in discussion of paper materials and editing it.

References

[1] V. A. Danko, I. Z. Indutniy, V. I. Minko, P. E. Shepeliavyi, Avtometry **46,** 103 (2010) [in Russian].
[2] V. V. Petrov, A. A. Kryuchyn, Quantum Electron **1,** 2618 (1974) [in Russian].
[3] M. T. Kostyshyn, S. A. Kostyukevych, Ukr. Phys. J. **26,** 1561 (1981) [in Russian].
[4] A. A. Kryuchyn, S. A. Kostyukevych, Data Recording, Storage and Processing **12,** 3 (2010) [in Russian].
[5] A. Kouchiyama, K. Aratani, Y. Takemoto et al., Jpn. J. Appl. Phys. **42,** 769 (2003).
[6] E. R. Menders, R. Rastogi. M. Van der Veer et al. Jpn. J. Appl. Phys. **46,** 3987 (2007).
[7] V. V. Petrov, V. M. Puzikov, A. A. Kryuchyn, I. V. Gorbov. Nanosystems, Nanomaterials, Nanotechnologies **7,** 825 (2009) [in Russian].
[8] E. Toppin. Digital 2 Disc. **1,** 42 (2010).
[9] Patent USA № 2008/0320205 Al. Int. cl. index G 06 F 12/00. Barry M. Lunt, Matthew R. Linford (USA), Brigham Young University (USA), Applied 20.06.2007. Published 25.12.2008.
[10] Y. Usami, T. Watanabe, Y. Kanazawa et al. Applied Physics Express **2,** 26502/1 (2009).
[11] S. A. Kostyukevych, P.E. Shepeliavyi, N. L. Moskalenko et al. Data Recording, Storage and Processing **4,** 3 (2002) [in Russian].
[12] S. A. Kostyukevych, P. E. Shepeliavyi, N. L. Moskalenko et al. Data Recording, Storage and Processing **3,** 5 (2001) [in Russian].
[13] A. M. Morozovska, S. A. Kostyukevych, L. L. Nikitenko, A. A. Kryuchyn, A. A. Kudryavtsev, P. E. Shepeliavyi, N. L. Moskalenko. Semiconductor Physics, Quantum Electronics and Optoelectronics **7,** 93 (2004).
[14] Patent 2165637 RU. Int. cl. Index G 03 H 1/18, G 02 B 5/32. E. F. Venger, S. A. Kostyukevych, P. E. Shepeliavyi, Yu. G. Goltsov, Published 20.04.2001, Bull № 11, 9 p.
[15] Patent 2008285 RU. Int. cl. Index C 03 C 15/00, 23/00. I.Z. Indutniy, S. A. Kostyukevych, P. E. Shepeliavyi, Published 28.02.1994.
[16] S. A. Kostyukevych, I. Z. Indytniy, P. E. Shepeliavyi, Data Registration, Storage and Processing **1,** 19 (1999).
[17] N. P. Eisenberg, M. Manevich, A. Arsh, M. Klebanov, V. Lyubin. Chalcogenide Let. **2, 35** (2005).
[18] J. Teteris, M. Reinfelde. J. Optoelectron. Adv. Mater **5,** 1355 (2003).
[19] V. V. Petrov, A. A. Kryuchin, S. M.Shanoilo, V. G. Kravets, I. O. Kossko, Ye. V. Belyak, A. S. Lapchuk, S. O. Kostyukevych, Kyiv, Super-dense Optical Information Recording, Institute for Information Recording, NAS of Ukraine, 2009. 282 pages [in Ukrainian].
[20] M. Veinguer, A. Feigel, B. Sfez, M. Klebanov, V. Lynbin. J. Optoelectro. Adv. Mater **5,** 1361 (2003).
[21] W. Lee, M. Chen, H. Weder, et al., Proc. SPIE **382,** 282 (1983).
[22] V. V. Petrov, A. A. Kryuchyn, A. P. Tokar et al. Kiev, Optical-and-mechanical Storage Facility, Naukova dumka, 1992. 152 pages [in Russian].

[23] A. A. Kryuchyn, V. V. Petrov, T. I. Sergiyenko, G. Yu. Yudin, Z. U. Borisova, M. D. Mikhailov, Yu. K. Lapin, A. V. Bogdanova, Applied **30**, 12 (1985).

[24] V. V. Petrov, A. A. Kryuchin, I. V. Gorbov, I. O. Kossko, S. A. Kostyukevych, Semicond. Phys. Quantum Electron and Optoelectron. **12,** 399 (2009).

[25] S. Noach, M. Manevich, M. Klebanon, V. Lynbin, N. P. Eisenberg, Proc. SPIE **3778**, 158 (1999).

[26] V. I. Minko, Y. E. Shepeliavyi. V. A. Danko. Semicond, Phys. Quantum Electron and Optoelectron. **7**, 88 (2004).

---

[*] Corresponding author: petrov@ipri.kiev.ua