

Electrochemical Nanostructuring of CuInS₂ Bulk Crystals

Eduard MONAICO¹, Veaceslav URSAKI², Victor ZALAMAI², Alisa MASNIK¹, Nicolae SYRBU¹, Alexandru BURLACU³

¹Technical University of Moldova, Stefan cel Mare av. 168, Chisinau MD-2004, Republic of Moldova, e-mail: Eduard_m@mail.utm.md

²Institute of Applied Physics, Academy of Sciences of Moldova, Academy str. 5, Chisinau MD-2028, Moldova

³Institute of Electronic Engineering and Nanotechnologies, Academy of Sciences of Moldova, Academy str. 3/3, Chisinau MD-2028, Republic of Moldova

Abstract — We show that chalcopyrite CuInS₂ crystals can be nanostructured by electrochemical treatment in an aqueous HCl solution. In order the crystals to become suitable for electrochemical nanostructuring they are subjected to thermal treatment either in vacuum or in Zn vapors. The morphology of the produced material and the diameter of pores are found to be a function of the resistivity of samples attained after thermal treatment. The pore diameter can vary in the range from 50 nm to 1 µm. The influence of thermal treatment and electrochemical etching on the photoluminescence spectra is analyzed. It is shown that nanopatterned surfaces can be produced either by short duration electrochemical etching, or by longer treatment followed by sonication.

Index Terms — chalcopyrite crystals, electrical conductivity, electrochemical treatment, nanostructuring, luminescence.

I. INTRODUCTION

Solar cell technologies, using I-III-VI₂ direct band-gap chalcopyrite semiconductors as the absorber layer, have attracted great interest [1]. Copper indium disulphide (CuInS₂) is a promising absorber material for thin film photovoltaics. CuInS₂ has an ideal direct band gap for efficient photo-conversion ($E_g=1.55$ eV), a large absorption coefficient (10^5 cm⁻¹) and in addition, does not contain any toxic components. However, the cost-effectiveness of commercial solar cells still does not meet the market requirements. The large difference between the record conversion efficiency of 13% of CuInS₂-based solar [2,3] and the theoretical limit for a one-junction solar cell of 30% [4] is an indicative of the importance of further technological improvements.

One way of boosting the performance of solar cells consists in coating them with a textured layer. The idea is to traps more light so that it bounces around inside the cell instead of reflecting back out, since reflection means the loss of the light, which is absorbed to solar cell and generates electric power. Light trapping regimes were realized in thin-film silicon solar cells with a photonic pattern [5], in textured multicrystalline silicon [6], in GaAs solar cells textured with dielectric 1D and 2D nanopatterns [7] etc. Nanopatterning of solar cells was produced by nano-imprint lithography [8,9], by surface etching processes [10], or by the formation of a porous silicon layers on the textured silicon wafer [11]. The porous layer can be produced by anodization [11]. Electrochemical treatment proved to be a powerful tool for the preparation

of a variety of porous morphologies also in III-V [12] and II-VI [13,14] materials. As demonstrated [12], two types of pores can be introduced in III-V semiconductor compounds, namely crystallographically oriented or ‘crysto’ pores, and current-line oriented or ‘curro’ pores. Crysto pores are usually generated at low anodic current densities due to direct dissolution of the material. They exhibit a triangular-prism like shape reflecting the anisotropy of anodic etching inherent to semiconductor compounds. As to curro pores, they are generated at relatively high anodic current densities, their growth being mediated by oxide formation and its dissolution at the pore tip [12]. Curro pores show usually circular shape, independent on the crystallographic orientation of the substrate.

The goal of this paper is to demonstrate that electrochemical treatment can be also applied for nanostructuring of CuInS₂ crystals, particularly for patterning the surface of the samples to reduce the reflection at the surface in the case of their implementation in solar cells.

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

Single phase CuInS₂ crystals were grown by chemical transport. Stoichiometric amounts of the constituents were sealed in silica tubes under high vacuum. Due to the high vapour pressure of sulfur and to avoid explosion, the samples were heated at 600 °C for 1 day (to have the sulfur reacted with Cu and In completely) and held at 1100 °C for another 2 days (to produce homogeneous materials). The single phase CuInS₂ powders, together with iodine as the

transport agent were sealed in silica tubes under high vacuum (10^{-6} torr). Chemical transport was done in a horizontal furnace. The charge end was held at 800 °C while the optimal growth zone was determined to be in the range of 740-760 °C. The system was cooled down slowly at a rate of 10 °C/h to avoid straining of the crystals after crystal growth.

Electrochemical treatment for nanostructuring was performed in an electrochemical cell as described elsewhere [15]. A four Pt electrode configuration was used: a reference electrode in the electrolyte, a reference electrode on the sample, a counter electrode and a working electrode. The area of the sample exposed to the electrolyte solution was 0.1 cm². The anodic etching was carried out in a 5% HCl:H₂O electrolyte in the potentiostatic regime at room temperature. The resulting morphology of the etched samples was studied using a TESCAN scanning electron microscope (SEM). The photoluminescence (PL) was excited by a 325 nm line of a He-Cd Melles Griot laser and analyzed through a double spectrometer. The resolution was better than 0.5 meV. The samples were mounted on the cold station of a LTS-22-C-330 cryogenic system.

III. RESULTS AND DISCUSSIONS

The as-grown CuInS₂ crystals are n-type with resistivity in the order of 10^6 - 10^7 Ω·cm. It is known that low resistivity crystals are required for nanostructuring by electrochemical treatment. For decreasing the resistivity of the as-grown CuInS₂ crystals several types of thermal treatment has been applied. Crystals with the resistivity down to 0.3 Ω·cm were produced by annealing of crystals in vacuum. For a further decrease of resistivity, the samples were subjected to annealing in Zn vapors. The samples were subjected to annealing during 30 hours. The parameters of samples as a function of the technological conditions are presented in Table 1.

TABLE I. ELECTRICAL PARAMETERS OF CuInS₂ CRYSTALS SUBJECTED TO DIFFERENT THERMAL TREATMENT

Sample treatment conditions	ρ (Ω·cm)	n (cm ⁻³)	μ (cm ² /V·s)
As grown, #1	$10^6 \div 10^7$	-	-
Annealed in vacuum at 500°C, #2	20	10^{15}	300
Annealed in vacuum at 600°C, #3	1	$3 \cdot 10^{16}$	200
Annealed in vacuum at 700°C, #4	0.3	$1.4 \cdot 10^{17}$	140
Annealed in Zn vapours at 600°C, #5	0.1	$6 \cdot 10^{17}$	100
Annealed in Zn vapours at 700°C, #6	0.05	$3 \cdot 10^{18}$	40

The PL spectra of the samples #1 to #6 with parameters from Table 1 are presented in Fig. 1. The spectrum of the as-grown sample consists of several near-band-edge lines and a deeper PL band at 1.4 eV followed by unresolved phonon replicas. Among the near-band-edge lines, two most intensive lines at 1.52 eV and 1.53 eV are attributed to the recombination of bound excitons [16,17], while the band at higher photon energies (1.537 eV) is due to the recombination of free excitons [16,17]. The band at 1.4 eV was previously attributed to a free-to-bound optical transition with In interstitial (In_i) as a donor center involved in this transition. Annealing of crystals in vacuum at 500

°C leads to the decrease of the luminescence intensity by a factor of 10, to broadening of the lines related to the recombination of bound excitons, and to the disappearance of the band associated with the recombination of free excitons. The increase of the annealing temperature to 600 °C leads to the quenching of the exciton lines and the emergence of a new broad and asymmetric PL band in the near-band-edge region (at 1.555 eV). The intensity of this band decreases with the increase of the annealing temperature to 700 °C, while it is broadened and its maximum shifts to higher energies. This PL band is attributed to the band-to-band transitions, since the shift of the maximum and its broadening correlates with the shift of the equilibrium Fermi level. A similar behavior was observed for the near-band-edge PL band in ZnSe single crystals annealed in Zn melt containing Al impurity [18].

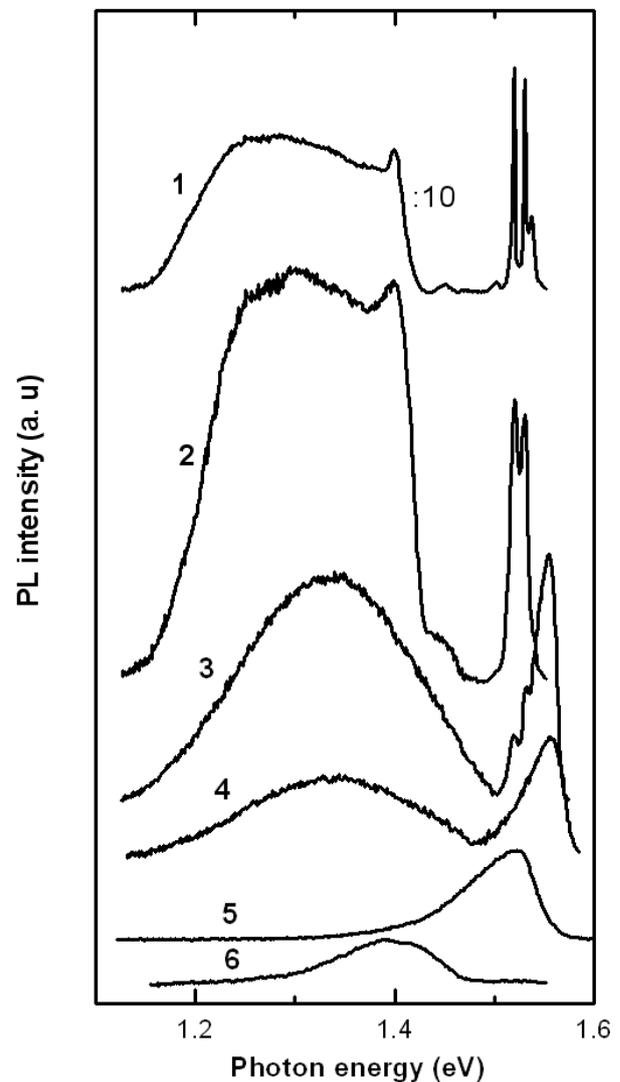


Fig. 1. PL spectra of CuInS₂ crystals measured at T = 10 K. The numbers of curves correspond to the number of samples in Table 1.

The annealing of crystals in Zn vapors instead of vacuum leads to a further increase of the carrier concentration. At the same time, taking into account the decrease of carrier mobility, one can suggest that a partial compensation of conductivity occurs due to the formation

of acceptor centers in addition to donors. As a result, the near-band-edge PL band is shifted to lower photon energies in samples annealed in Zn vapors as compared to samples annealed in vacuum (compare curves 4 and 5 in Fig. 1). This behavior is explained in terms of the theory of heavily doped semiconductors developed by Shklovskij, Efros, Levanyuk and Osipov in the early 1970s [19,20]. According to this theory, the asymmetric shape of PL bands is caused by the potential fluctuations in the material. These fluctuations are probably caused by high concentrations of charged defects. It should be mentioned that in ternaries compositional fluctuations can also give rise to disorder and cause very similar fluctuations of the bandgap energy.

In the case of heavy doping, the defects do not constitute a discrete distribution of defect levels inside the bandgap. Instead, the energy levels form a continuous distribution function. Consequently, the distribution function of shallow states overlaps the distribution function of conduction and valence band states. As a result, the so-called band tails are developed. Therefore, the PL band on the curve 5 in Fig. 5 can be attributed to band-to-tail (BT) electronic transitions.

The increase of the annealing temperature in Zn vapors from 600 °C to 700 °C leads to a further shift of the PL band to lower photon energy and its splitting into two bands (see curve 6 in Fig. 1). This splitting is explained by the fact that in heavily doped semiconductors the recombination between the conduction band and an impurity level can occur via two channels. The first so called tail-to-impurity (TI) recombination takes place between the electrons that are localized in the conduction band tails and the holes that are localized at the acceptor state (the PL band at 1.39 eV on the curve 6 in Fig. 1). The second so-called band-to-impurity (BI) recombination takes place between the free electrons in the conduction band and the holes that are localized at the acceptor state (the PL band at 1.42 eV on the curve 6 in Fig. 1). Similar electronic transitions have been observed in other heavily doped chalcopyrite materials [21-23].

The conductivity of samples directly influences the processes of electrochemical etching. The morphology of samples # 3, #4, and #6 from Table 1 in cross section after electrochemical treatment under the applied voltage of 0.8V in aqueous HCl electrolyte is shown in Fig. 2. One can realize the formation of porous layers with various diameters of pores, it being around 1 µm for sample #3, 250-300 nm for sample #3, and around 50 nm for sample #6. Therefore, the diameter of pores sharply decreases with increasing the conductivity of the material.

One should mention also the possibility of producing multilayer porous structures with various porosities as illustrated in Fig. 3b. The change of the applied voltage during electrochemical etching from 0.8V to 1.5V indicated by the horizontal line in Fig. 3b leads to the decrease of the mean diameter of pores from 250-300 nm to 100-150 nm.

Fig. 4 illustrates a porous CuInS₂ template produced on the sample #4 with removing the surface nucleation layer after electrochemical treatment at 0.8V. One can note that the morphology of this template is similar to the typical morphologies produced previously in GaP wafers anodized in a H₂SO₄ electrolyte.

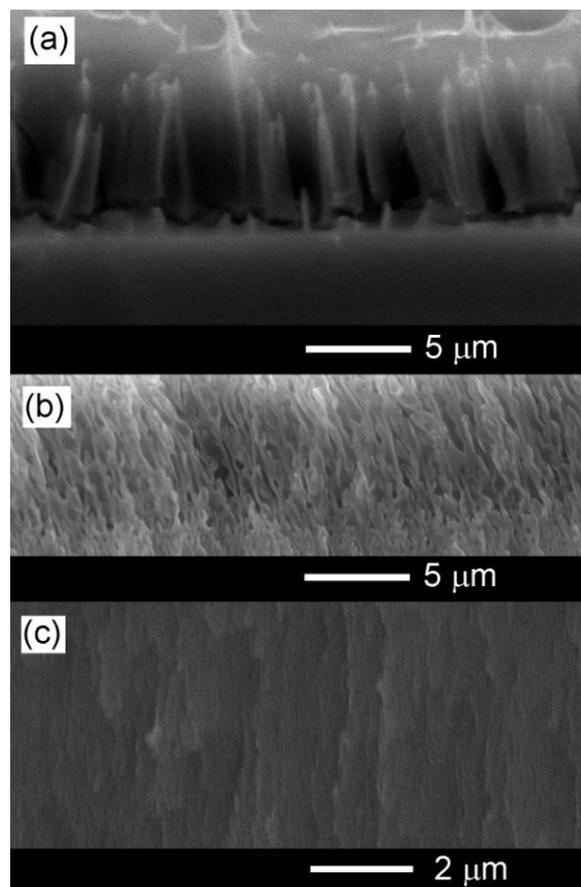


Fig. 2. SEM image of CuInS₂ crystals with numbers #3 (a) #4 (b) and #6 (c) in Table 1 subjected to electrochemical treatment at 0.8 V in an aqueous HCl electrolyte.

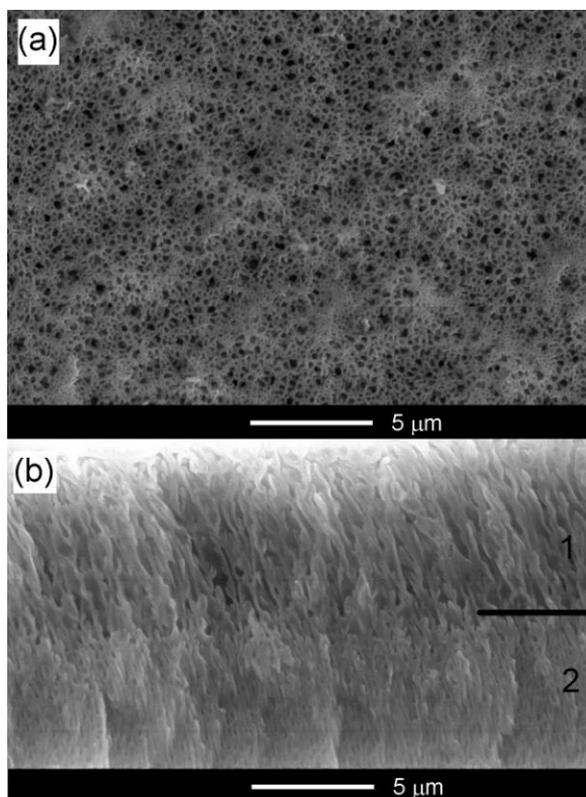


Fig. 3. Top view SEM image of the sample #4 (a) and the cross-section resulting from the increase of the applied voltage from 0.8V to 1.5V during the etching.

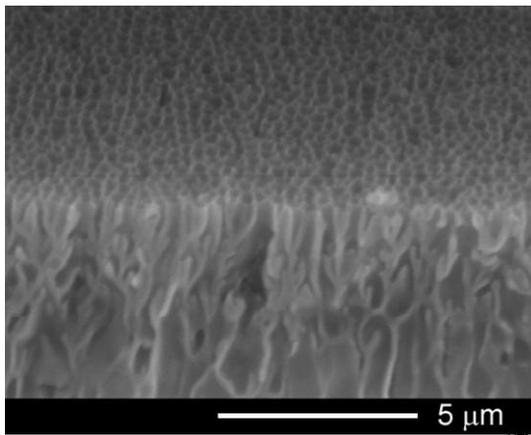


Fig. 4. SEM image a porous CuInS₂ template produced on the sample #4 with removing the surface nucleation layer after electrochemical treatment at 0.8V.

Figure 5 compares the PL spectra of CuInS₂ samples before and after electrochemical treatment. One can see that electrochemical etching leads to the increase of the PL intensity. Apart from that, in sample #3 the electrochemical treatment leads to narrowing the band-to-band emission and the increase of the intensity of lines related to the recombination of bound excitons. This suggests a good passivation of the porous skeleton surface and the increase of the material quality as a result of treatment.

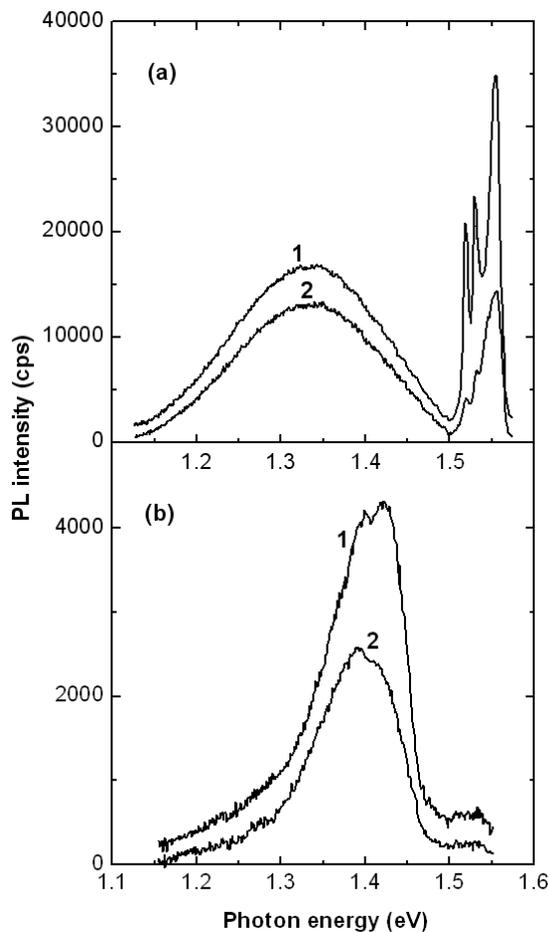


Fig. 5. PL spectra of #3 (a) and #6 (b) CuInS₂ samples before (curve1) and after (curve 2) electrochemical etching. The spectra are measured at T = 10 K.

The possibilities of producing patterned CuInS₂ surfaces which are important in reducing the reflectivity losses in solar cells are illustrated in Fig. 6, which shows the morphology of a CuInS₂ sample annealed in vacuum at 600 °C (sample #3) and subjected to a short term (1 minute) electrochemical treatment in HCl electrolyte. One can observe the formation of a nanostructured surface consisting of triangular pyramids. One can propose two technological procedures for producing patterned surfaces: (i) short term electrochemical treatment, and (ii) longer term electrochemical treatment (see the formation of a porous layer in the sample #3 after a 5 minute treatment in Fig. 2a) followed by sonication in order to remove the formed porous layer and to leave a patterned surface.

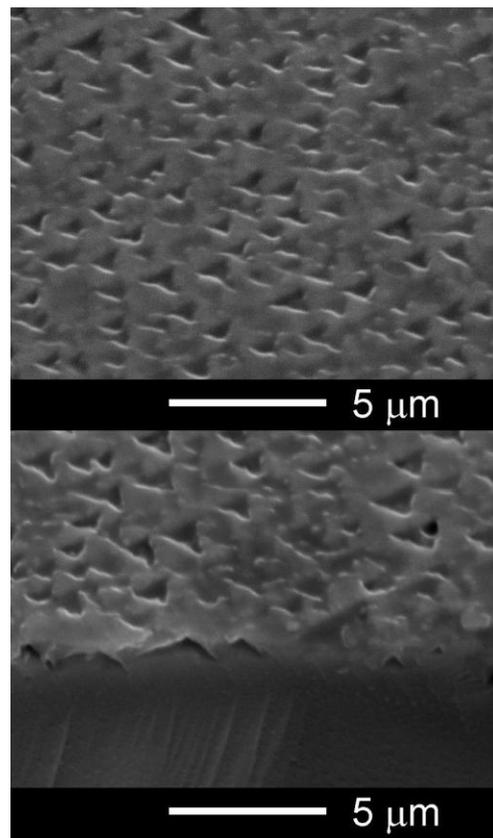


Fig. 6. Top view SEM image and an oblique view of the sample #3 subjected to a short term (1 minute) electrochemical treatment.

IV. CONCLUSION

The results of this study demonstrate possibilities of producing nanostructured layers and nanopatterned surfaces on CuInS₂ crystals. In order to reduce the resistivity of the as-grown crystals and make them suitable for electrochemical etching, they should be subjected to annealing in vacuum or in Zn vapors. The analysis of PL spectra demonstrates that passivation of the porous skeleton surface and increase of the material quality occurs as a result of electrochemical treatment which is also important in the development of solar cells.

ACKNOWLEDGMENTS

This work was supported by the Academy of Sciences of Moldova.

REFERENCES

- [1] M. A. Green, K. Emery, D. L. King, S. Igari, and W. Warta, *Prog. Photovoltaics*, vol. 10, p. 355, 2003.
- [2] J. Klaer, J. Bruns, R. Henninger, K. Siemer, R. Klenck, K. Ellmer, and D. Braunig, *Semicond. Sci. Technol.*, vol. 13, p. 1456, 1998.
- [3] R. Klenk, J. Klaer, R. Scheer, M. Ch. Lux-Steiner, I. Luck, N. Meyer, and U. Rühle, *Thin Solid Films*, vol. 480/481, p. 509, 2005.
- [4] H. W. Schock, *Sol. Energy Mater. and Sol. Cells*, vol. 34, p. 19 (1994).
- [5] S. Zanotto, M. Liscidini, and L. C. Andreani, *Optics Express*, vol. 18, pp. 4260-4274, 2010.
- [6] Y. Ein-Eli, N. Gordon, D. Starosvetsky, *Solar Energy Materials & Solar Cells*, vol. 90, pp. 1764-1772, 2006.
- [7] K. S. Cho, P. Mandal, K. Kim, I. H. Baek, S. Lee, H. Lim, D. J. Cho, S. Kim, J. Lee, and F. Rotermund, *Optics Communications*, vol. 284, pp. 2608-2612, 2011.
- [8] K.-S. Han, J.-H. Shin, W.-Y. Yoon, and H. Lee, *Solar Energy Materials and Solar Cells*, vol. 95, pp. 288-291, 2011.
- [9] J.Y. Chen and K.W. Sun, *Solar Energy Materials and Solar Cells*, vol.94, pp. 629-633, 2010.
- [10] E. Manea, E. Budianu, M. Purica, C. Podaru, A. Popescu, C. Parvulescu, A. Dinescu, A. Coraci, I. Cernica, and F. Babarada, *Romanian J. Information Sci. and Technol.*, vol 11, pp. 337-345, 2008.
- [11] H. Kwon, J. Lee, M. Kim, and S. Lee, *ISRN Nanotechnology*, vol 2011, article ID 716409, 2011.
- [12] H. Foll, S. Langa, J. Carstensen, M. Christophersen, I. M. and Tiginyanu, *Adv. Mater.*, vol. 15, pp. 183, 2003.
- [13] E. Monaico, I. M. Tiginyanu, V. V. Ursaki, A. Sarua, M. Kuball, D. D. Nedeoglo, and V. P. Sirkeli, *Semicond. Sci. Technol.*, vol. 22, pp. 1115-1121, 2007.
- [14] E. Monaico, V. V. Ursaki, I. M. Tiginyanu, Z. Dashevsky, V. Kasiyan, and R. W. Boyd, *J. Appl. Phys.*, vol. 100, p. 053517, 2006.
- [15] S. Langa, I. M. Tiginyanu, J. Carstensen, M. Christophersen, and H. Föll, *Appl. Phys. Lett.*, vol. 82, p. 178, 2003.
- [16] I. H. Choi and D. H. Lee, *Journal of the Korean Physical Society*, vol. 44, pp. 1542-1546, 2004.
- [17] M. V. Yakushev, A. V. Mudryi, I. V. Victorov, J. Krustok and E. Mellikov, *Appl. Phys. Lett.*, vol. 88, p. 011922, 2006.
- [18] G. N. Ivanova, D. D. Nedeoglo, N. D. Nedeoglo, V. P. Sirkeli, I. M. Tiginyanu, V. V. Ursaki. *J. Appl. Phys.* vol. 101, p. 063543, 2007.
- [19] A. P. Levanyuk, V. V. Osipov, *Sov. Phys. Usp.*, vol. 133, p. 427, 1981.
- [20] B. I. Shklovskij, A. L. Efros, *Electronic Properties of Doped Semiconductors*, Springer, Berlin, 1984.
- [21] A. Jagomägi, Juri Krustok, Maarja Grossberg, Mati Danilson, and Jaan Raudoja, *Phys. Stat. Sol. (a)*, vol. 203, pp. 949-955, 2006.
- [22] M.V. Yakushev, A. Jack, I. Pettigrew, Y. Feofanov, A. V. Mudryi, and J. Krustok, *Thin Solid Films*, vol. 511 - 512, pp. 135 - 139, 2006.
- [23] A. Jagom.agi, J. Krustok, J. Raudoja, M. Grossberg, M. Danilson, and M. Yakushev, *Physica B*, vol. 337, pp. 369-374, 2003.