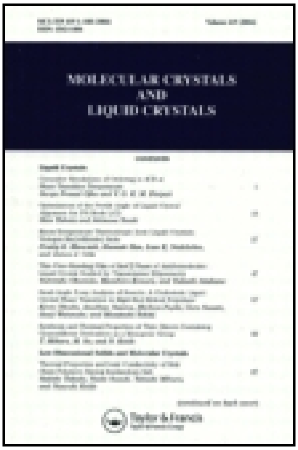

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Effect of Composite Layers Based on Dyes with Different Types of Conductivity on Photovoltaic Properties of CIS Films

A. Verbitsky [a] , Ya. Vertsimakha [a] , S. Studzinsky [b] , S. Bereznev [c] & J. Kois [c]

[a] Institute of Physics of the NAS of Ukraine, Kyiv, Ukraine
[b] Taras Shevchenko Kyiv National University, Kyiv, Ukraine
[c] Tallinn University of Technology, Tallinn, Estonia

To cite this article: A. Verbitsky, Ya. Vertsimakha, S. Studzinsky, S. Bereznev & J. Kois (2007): Effect of Composite Layers Based on Dyes with Different Types of Conductivity on Photovoltaic Properties of CIS Films, Molecular Crystals and Liquid Crystals, 467:1, 123-133

To link to this article: http://dx.doi.org/10.1080/15421400701221245

Mol. Cryst. Liq. Cryst., Vol. 467, pp. 123–133, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701221245

Effect of Composite Layers Based on Dyes with Different Types of Conductivity on Photovoltaic Properties of CIS Films

A. Verbitsky
Ya. Vertsimakha
Institute of Physics of the NAS of Ukraine, Kyiv, Ukraine

S. Studzinsky
Taras Shevchenko Kyiv National University, Kyiv, Ukraine

S. Bereznev
J. Kois
Tallinn University of Technology, Tallinn, Estonia

The effect of the deposition of layers "polymer-dye" with different types of conductivity on the surface photovoltage (V) of $CuInS_2$ (CIS) has been studied. The influence of composite layers depends on the molecular structure of a polymer, the type of conductivity and photosensitivity of a dye. The photovoltage growth mainly in the region of strong absorption of a dye was observed after the deposition of the composite consisted of the p-type polymethine dye and the carbazole I-contained polymer on the CIS surface. The spectral dependence of this composite in the low-absorption region is only weakly changed. On the contrary, the deposition of the composite consisted of the perylene n-type dye in polymer on CIS leads to a decrease of V, especially in the dye absorption region. A decrease of the short-wavelength slope is caused by the presence of surface recombination centers in CIS films. The above-mentioned results can be explained by the presence of a few concurrent processes, the efficiency of which strongly depends on the used polymer and the type of conductivity of a dye.

Keywords: $CuInS_2$; organic dyes; polymer composites; surface photovoltage

The authors thank Prof. Dieter Meissner, Prof. A. A. Ishchenko, and Dr. J. Penndorf for the gift of DiMe-PTCDI and HITC dyes and CISCuT layers, respectively. This work is supported by INTAS Grant N 03-51-4561.

Address correspondence to A. Verbitsky, Institute of Physics of the NAS of Ukraine, 46, Nauky Ave, Kyiv, 03028 Ukraine. E-mail: avsky@iop.kiev.ua

INTRODUCTION

We considered polymers and organic semiconductors as perspective materials for the replacement of CdS because of the presence of toxic Cd in heterostructures $CdS/CuInS_2$ (CIS), for which the efficiency of a transformation, being more than 17%, was obtained [1].

However, preliminary studies have shown that, after the deposition of polymeric layers on a free surface of n-type CIS, there are simultaneously a small decrease of the surface photovoltage (V) and an essential increase of the short-circuit photocurrent (I_{sc}) [2,3].

It is possible to explain this fact by a decrease of the potential barrier height and an increase of the efficiency of the transport of charge carriers through the CIS-polymer interface. The changes of V and I_{sc} depend on the molecular structure of a polymeric compound. However, this does not result in changes of the spectral dependence of V and I_{sc}. Hence, a great concentration of trap centers and a high rate of the surface recombination of charge carriers in the CIS layer, which gives an essential decrease of the photosensitivity of heterostructures at $h\nu > 2.4\,\text{eV}$, are maintained on the CISCuT/polymer interface [3]. At the same time, at the deposition of the organic dye lead phthalocyanine on the free surface of the CIS layer, there are a partial neutralization of trap centers and a decrease of the recombination rate of charge carriers at the interface with CIS [2].

The above-mentioned data allow us to consider that the introduction of a dye in a polymeric compound can lead both to an increase of V stimulated by the photogeneration of charge carriers in the composite layer and to the neutralization of centers of the recombination of charge carriers at the interface owing to the interaction of molecules of the dye and CIS.

Therefore the aim of the present work was to study the influence of composite layers polymer/dye with different conductivity types on the photovoltaic properties of CIS-based structures.

EXPERIMENTAL

The CIS film deposition on a copper tape (CIS Cu Tape–so-called CISCuT) by the method In electrodeposition with successive sulfurization and vacuum annealing was described in [4].

To create composite layers, we used carbazole polymers and organic dyes: polymethine and perylene derivative. Namely, we selected the following polymer compounds: polyepoxypropylcarbazole (PEPC) and poly(3-iodo-9-vinylcarbazole co-octyl methacrylate (P-3I-9VC:OMA). PEPC was produced by the “Azot” plant (Severodonetsk, Ukraine) and has a molecular weight of 900–1000. P-3I-9VC:OMA was synthesized as described in [3]. This polymer has a molecular weight of 5000–7000, the contents of 3I-9VC monomer in co-polymers were 70 mol% [3].

The 1,3,3,1′,3′,3′-hexamethylindotricarbocyanine tetrafluoroborate polymethine p-type dye (HITC) and the N, N′-dimethyl perylene-tetracarboxylic acid diimide (DiMe-PTCDI) n-type pigment were also used as the components of composites.

Composite films were prepared by the spin casting method from a dichloroethane solution for the HITC-based composite and from a mixture of dichloroethane and dimethylformamide (1:4) in the case DiMe-PTCDI-based composites. The concentration of the dye in the composite was 50 wt%. Composite films deposited onto CISCuT of 1 × 1 cm in size and control samples on transparent glass substrates coated by a conductive ITO layer were made. The thicknesses of composite layers were c.a. 1 μm.

We prepared also samples, where DiMe-PTCDI was deposited onto CISCuT by the method of vacuum deposition at room temperature.

The techniques, as well as the experimental setup used in measurements of the surface photovoltage (*V*), were described elsewhere [2,3].

RESULTS AND DISCUSSION

The spectra of *V* for a CISCuT film (curve 1), structures of composite HITC + P-3I-9VC:OMA on CISCuT (curve 2), and composite HITC + PEPK/CISCuT (curve 3) are shown in Figure 1.

The maximum at 1.6 eV and the drastic decrease with increase in hν, which is typical of chalcogenides, were observed in the spectra of *V* for CISCuT films [5]. This decrease is caused by the great recombination rate of charge carriers near the free surfaces of the studied films.

The effect of (p-type) HITC-based composite layers strongly depends on the type of the used polymer. The increase of *V* in the region of strong dye absorption (1.5–2.0 eV) is predominant for the I-contained polymer, while the deposition of the PEPK-based composite leads to some decrease of *V* in this region. *V* practically is not changed in the region of weak absorption of the dye (2.5–3.2 eV). A small increase of *V* at ~2.25 eV (Fig. 1, curve 3) can be caused by the aggregation of the dye displaying in this polymer [6,7].

The spectral dependence of the difference between *V* of samples HITC + P-3I-9VC:OMA/CISCuT (curve 2, Fig. 1) and CISCuT (curve 1, Fig. 1) correlates well with the spectral dependence of *V* for the control sample, HITC + P-3I-9VC:OMA, deposited onto the ITO-coated

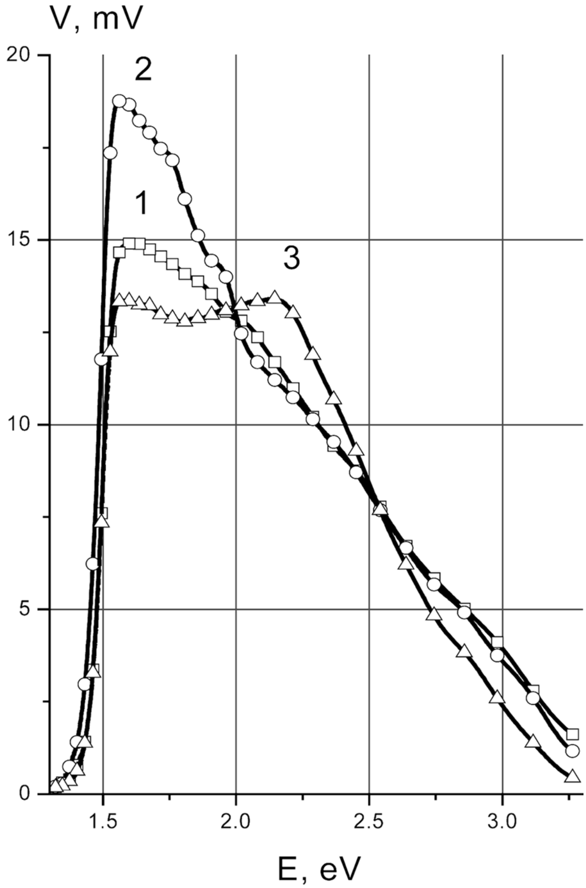

FIGURE 1 Spectra of V for CISCuT film (curve 1), and for the structures of composite HITC + P-3I-9VC:OMA/CISCuT (curve 2) and HITC + PEPK/CISCuT (curve 3).

substrate (Fig. 2, curve 2). This fact evidences for that the increase of V for samples HITC + P-3I-9VC:OMA/CISCuT in the region 1.5–2.0 eV after the deposition of a composite layer onto the CISCuT surface can be associated with the effective photogeneration in the composite layer.

The decrease of V for a HITC + PEPK/CISCuT sample in the region 1.5–2.0 eV after the deposition of a composite layer also corresponds to the spectral dependence of V for the control film of the HITC + PEPK composite deposited onto the ITO-coated glass substrate under the same conditions (Fig. 2, curve 1). Probably, the decrease of V for

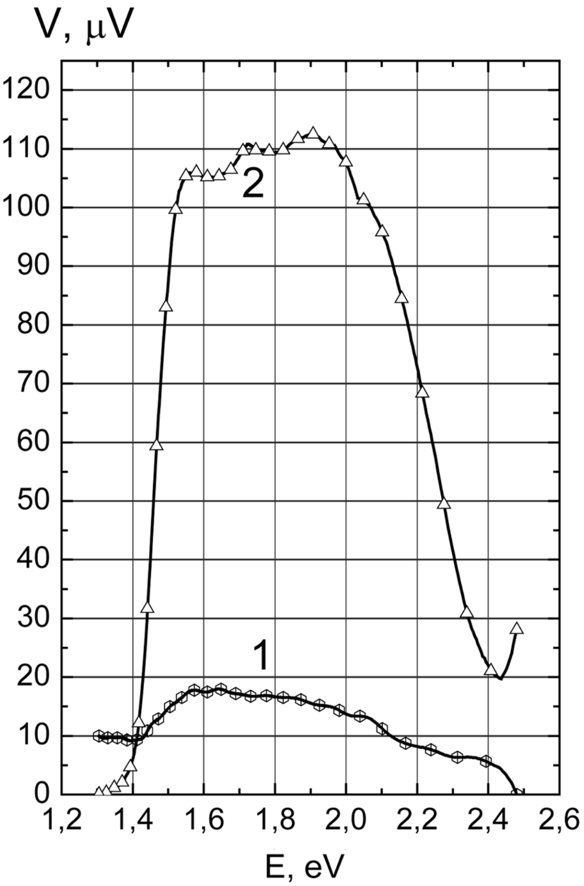

FIGURE 2 Spectra of *V* for the films of HITC dye composites in PEPK (1), and P-3I-9VC:OMA (2).

HITC + PEPK/CISCuT samples in this region can be associated with a significantly smaller (5-6 times) efficiency of the photogeneration of charge carriers in the PEPK composite layer by comparing the photosensitivity of the P-3I-9VC:OMA composite layer (Fig. 2, curve 2).

The effect of DiMe-PTCDI-based composites onto CISCuT also depends strongly on the polymer type used to create a composite, although the decrease of *V* only was observed for all the studied composite samples. This decrease is markedly greater for PEPK-based composites (Fig. 3, curves 1, 2). The peculiarities of these structures are also a decrease of the *V* drop rate (that characterizes the degree of surface recombination) with increase in the energy of quanta and

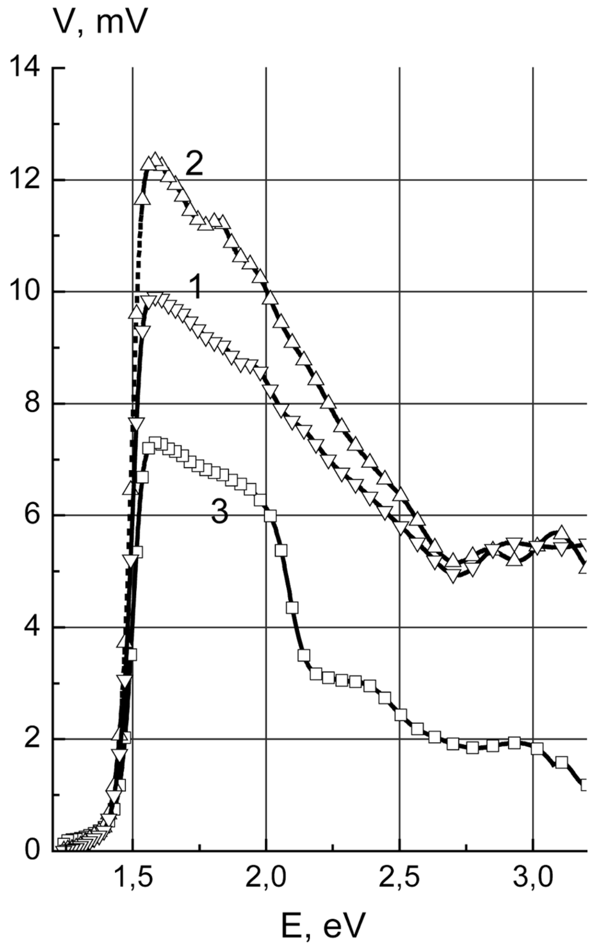

FIGURE 3 Spectra of *V* for the structures of composites DiMe-PTCDI + PEPK/CISCuT (1), and DiMe-PTCDI + 3I-9VC:OMA/CISCuT (2), and a vacuum deposited layer DiMe-PTCDI on CISCuT (3).

a selective decrease of *V* in the region of strong absorption of composites (2.4–2.75 eV). This range is the region of the displaying of dimer aggregates in DiMe-PTCDI [8].

The measurements of *V* for the structures of CISCuT and a thin (≈100 nm) vacuum deposited film of DiMe-PTCDI show a similar but more strong influence of CISCuT films on *V* (Fig. 3, curve 3) and a more clear correlation of the selective V decrease with the *V* spectrum of DiMe-PTCDI in the PEPK composite (Fig. 4, curve 4). Therefore, the

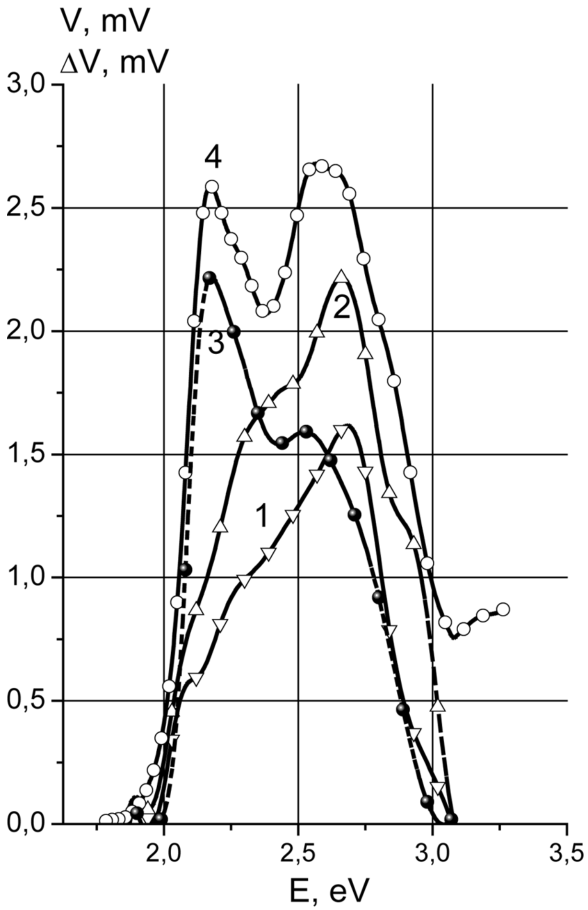

FIGURE 4 Difference ΔV for composite samples DiMe-PTCDI + PEPK/CISCuT and CISCuT (1); DiMe-PTCDI + 3I-9VC:OMA/CISCuT and CISCuT (2), ΔV for a vacuum deposited film DiMe-PTCDI/CISCuT and CISCuT (3), and the spectrum of V for DiMe-PTCDI in the PEPK composite (curve 4).

adsorption of DiMe-PTCDI molecules on the CIS surface plays the important role in a decrease of V for CIS/DiMe-PTCDI composite structures.

The selective decrease of V [the difference ΔV for samples DiMe-PTCDI + PEPK/CISCuT and CISCuT (curve 1, Fig. 4), for samples DiMe-PTCDI + 3I-9VC:OMA/CISCuT and CISCuT (curve 2, Fig. 4), and for samples of vacuum deposited DiMe-PTCDI/CISCuT and CISCuT (curve 3, Fig. 4)] correlates well with the spectral dependence of V of the control vacuum deposited film of DiMe-PTCDI and the spectral dependence of V for the polymer composite of DiMe-PTCDI (curve 4, Fig. 4). However, the ratio of the intensities of the bands with maxima at 2.15 and 2.7 eV is changed: the intensity of a band with maximum at 2.15 eV is smaller than the intensity of a band with maximum at 2.7 eV for the films of polymer composites. The opposite picture is observed for the vacuum deposited films of DiMe-PTCDI. According to [9,10], the band with maximum at 2.15 eV is predominantly caused by the formation of Frenkel excitons in DiMe-PTCDI films, while the band at 2.7 эB is caused by the formation of CT-states. Probably, the diffusion of Frenkel excitons is limited, and/or the efficiency of CT-states is higher in polymer composites. The first process leads to the limitation of the photogeneration efficiency during the capture of by surface centers, and the second one directly leads to a more effective photogeneration via CT-states. The decrease of V in the region 2,5–2.7 eV for polymer composites is caused by displaying the CT-states with high efficiency of the photogeneration of electrons [9,10].

The observed complex effect of the deposition of polymer composites can be explained by the presence of a few following simultaneous processes, whose efficiency depends on both the molecular structure of a polymer and the type and the photosensitivity of the aggregates of dye molecules:

1. The adsorption of polymer molecules on the CIS surface leads to a decrease of the potential barrier height without change of the concentration of the recombination centers of charge carriers [3] and, consequently, should lead to a decrease of V without decrease of the drop degree of V with increase of $h\nu$.
2. The adsorption of dye molecules on the CIS surface leads, according to [2], to a decrease of the potential barrier height with a change of the concentration of the recombination centers of charge carriers and, consequently, should lead to a decrease of V with the simultaneous decrease of the drop degree of V with increase of $h\nu$.
3. The photogeneration of holes in the composite layer with their following capture on the CIS surface should lead to an increase of the potential barrier height. Therefore, V increases due to the appearance of the photovoltage with the same polarity as that of the n-CIS photovoltage [11,12].
4. The photogeneration of electrons in the composite layer with their following capture on the CIS surface should lead to a decrease of the potential barrier height. Therefore, V decreases due to the appearance of the photovoltage with the opposite polarity than that of the n-CIS photovoltage [11,12].
5. The reflectance R is changed after the composite layer deposition.

To estimate the efficiency of this process, we conduct the control measurements of *R* for the free surface of CISCuT films after the deposition of a composite layer on this surface (Fig. 5). It is obvious that the change of *R* after the deposition of a polymer or composite layers on this surface doesn't reach 0.2% ($\Delta R/R = (R_1 - R_3)/R_1$ – curve 4, Fig. 5), i.e., it is significantly smaller (~by ten times) than the observed changes of *V* (Figs. 1 and 3). This data evidence for that the change of *R* is not effective for the structures studied, and it can't be taken into the account in the analysis of changes of *V*.

The analysis of the above-mentioned processes 1–4 and their comparison with the obtained experimental data showed that processes 1 and 3 dominate in the structures HITC + 3I-9VC:OMA/CISCuT (Fig. 1, curve 2). Process 3 is more effective due to a good photosensitivity of the composite. Processes 2 and 3 are dominant in the

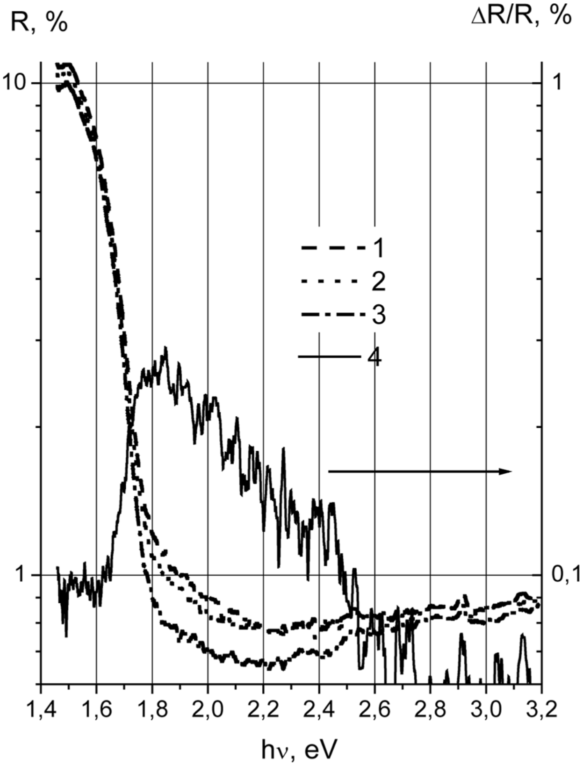

FIGURE 5 Spectra of *R* for a CISCuT film (1), structures of CISCuT with 3I-9VC:OMA polymer (2) and with the composite DiMe-PTCDI + 3I-9VC:OMA (3), and $\Delta R/R$ (4).

structures HITC + PEPK/CISCuT (Fig. 1, curve 3). Process 2 is more effective in this case due to a poor photosensitivity of the composite (we note that a decrease of *V* is observed for these structures).

Processes 2 and 4 dominate in the structures DiMe-PTCDI + PEPK/CISCuT and DiMe-PTCDI + 3I-9VC:OMA/CISCuT and lead to a decrease of *V* (Fig. 3, curves 1,2). Therefore, the decrease of *V* is greater than that for the HITC + PEPK/CISCuT structures. Naturally, the observed decrease of *V* in structures with a vacuum deposited film DiMe-PTCDI/CISCuT is significantly greater, since the photosensitivity of these films is greater (more than by one order) than that of the DiMe-PTCDI polymer composites.

Thus, to enhance *V*, the n-type CISCuT structures with a photosensitive polymer composite of the p-type can be only used.

CONCLUSIONS

A few concurrent processes occur in the structures of composite films onto the CISCuT surface. The efficiency of these processes strongly depends on the type of a polymer and a dye.

The increase of *V* in the strong absorption region of a polymethine HITC p-type dye is observed for composites of this dye in the I-contained polymer. The reason for this phenomenon is mainly the photogeneration of holes in the composite layer and their capture on the CISCuT interface (the photovoltage of the same polarity arises). A change of the rate of surface recombination near the interface (the neutralization of recombination centers) isn't observed.

The decrease of *V* is observed for composites of the n-type perylene derivative dye in a polymer. The reason for this is the photogeneration of electrons in the composite layer and their capture on the CISCuT interface (the photovoltage of the opposite polarity arises). The decrease of the rate of surface recombination near the interface (the partial neutralization of recombination centers) is observed.

Thus, the deposition of photosensitive polymer composites of a p-type dye can be utilized to enhance the photovoltaic photosensitivity of CISCuT/polymer heterostructures.

REFERENCES

[1] Stolt, L., Hodstrom, J., Kessler, J., Ruch, M., Velthaus, K.-O., & Schock, H. W. (1993). *Appl. Phys. Lett.*, *62*, 597.

[2] Verbitskii, A. B., Vertsimakha, Ya., Lutsyk, P., Studzinski, S., Bereznev, S., & Kois, J. (2006). *Semiconductors*, *40*, 197.

[3] Verbitsky, A., Vertsimakha, Ya., Lutsyk, P., Studzinsky, S., Bereznev, S., Kois, J., Öpik, A., & Mellikov, E. (2006). *Proc. Estonian Acad. Sci. Chem.*, *55*, 111.

[4] Penndorf, J., Winkler, M., Tober, O., Roeser, D., & Jacobs, K. (1998). *Sol. Energy Mat. Sol. Cells*, *53*, 285.

[5] Chopra, Kasturi L. & Das, S. R. (1983). *Thin Film Solar Cells*, Kluwer Academic/ Plenum Publishers: Dordrecht.

[6] Ishchenko, A., Derevyanko, N., Piryatinskii, Yu. P., Verbitsky, A., Filonenko, D., & Studzinsky, S. (2002). *Mater. Science*, *20*, 5.

[7] Studzinsky, S., Syromyatnikov, V., Ishchenko, A., Derevyanko, N., Vertsimakha, Ya., & Verbitsky, A. (2005). *Nonlinear Optics, Quantum Optics*, *33*, 151.

[8] Lifshitz, E., Kaplan, A., Ehrenfreund, E., & Meissner, D. (1998). *J. Phys. Chem. B*, *102*, 967.

[9] Hoffmann, M. & Soos, Z. G. (2002). *Physical Review B*, *66*, 024305.

[10] Nollau, A., Hoffmann, M., Fritz, T., & Leo, K. (2000). *Thin Solid Films*, *368*, 130.

[11] Dmitruk, N. L., Kruchenko, Yu. V., Litovchenko, V. G., & Popov, V. G. (1986). *Poverkhn. Fiz., Khim., Mekh.*, *5*, 56.

[12] Dmitruk, N. L., Zuev, V. A., Kruchenko, Yu. V., & Stepanova, M. A. (1992). *Optoelectron. Polupr. Mekh.*, *23*, 78.