

PACS: 66.30.Jt, 66.30.Qa, 61.72.Vv, 61.72.Ff, 61.72.Yx

Silver-related local centres in cadmium sulfide

L.V. Borkovskaya, B.M. Bulakh, L.Yu. Khomenkova, I.V. Markevich

*Institute of Semiconductor Physics, NAS Ukraine, 45 prospect Nauki, Kyiv, 03028, Ukraine,
Tel: (044) 265-72-34, Fax: (044) 265-83-44, E-mail: bork@lumin.semicond.kiev.ua*

Abstract. Silver-related defects and their diffusion in CdS crystals were investigated. The impurity was introduced in the crystal and extracted from it under electric field $E_d = 10^2$ V/cm at $T = 300\text{--}450^\circ\text{C}$ both parallel and perpendicular to the c -axis. The only local centre that was proved to appear after Ag introduction and to disappear after its extraction was deep acceptor responsible for emission band $\lambda_m = 610$ nm. Photo-enhanced defect reaction resulting in photosensitivity degradation was shown to occur after Ag incorporation. It was found that diffusion anisotropy took place, Ag diffusion being some times faster parallel to the c -axis.

Keywords: local centres, diffusion.

Paper received 07.06.01; revised manuscript received 18.06.01; accepted for publication 13.07.01.

1. Introduction

To get information about impurity-related local centres in crystal lattice of any semiconductor an impurity is introduced in it and then characteristics of doped material and undoped one are compared. As a rule, doping is carried out under growing or by diffusion from the surface at rather high temperatures. Under these conditions creation of native defects and their complexes is highly probable, the types of these defects and their densities depending on temperature, ambient atmosphere and type of impurity [1]. The presence of such «outside» defects makes difficulties for identification of defects related to introduced impurity. At the same time, it is known that diffusion of some impurities, particularly, copper and silver can be accelerated in many semiconductors, including CdS, by external electric field [2-4]. In this case application of electric field allows to lower the temperature of the doping process and so to reduce the probability of outside defect creation. Besides, one can introduce the impurity in the sample and then extract that from it changing the polarity of the electric field [4]. These procedures can be made over and over again, which facilitates the identification of the impurity-related centres. In the present work Ag-related local centres in CdS crystals were investigated by this technique.

2. Experimental procedure and results

Nominally undoped high-resistivity ($\rho > 10^8 \Omega\text{-cm}$) bulk and platelet CdS crystals were used. Initial crystals have bright yellow colour. The impurity was introduced in the sample from electrode containing Ag, the other electrode being pure In. The sample was fastened horizontally on the heater, heated to the temperature T_d from 300-450 °C range and then direct electric field $E_d = 100\text{--}300\text{V/cm}$ was applied to it so that the electrode containing Ag was the anode [3]. After time interval $\Delta t = 5\text{--}45$ min the electric field was switched off and the sample was cooled to room temperature. Similar procedure was also made with some CdS:Ag crystals doped under growing, both electrodes being pure In. These crystals have bright brown colour.

Soon after the electric field was switched on, in initially undoped crystals a dark region appeared near the anode and then spread to the cathode. After cooling to room temperature the dark region acquired bright brown colour like CdS:Ag crystals while the rest sample remained bright yellow. When the sample was heated again to T_d and electric field of opposite direction was applied to it, the brown region shortened with time and the yellow one spread to the new cathode. In previously doped crystals after electric field switching on a light region appeared

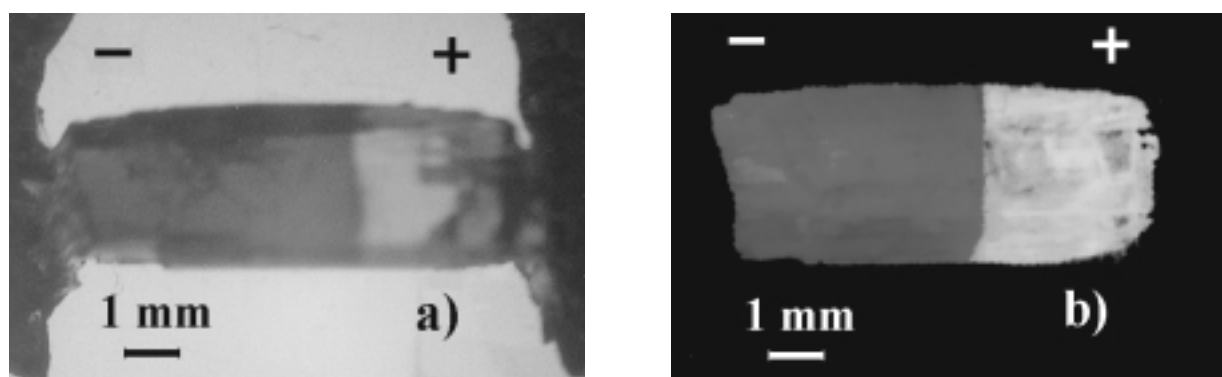


Fig. 1. a) CdS:Ag crystal partially purified at 400°C ($E_D = 200 \text{ V/cm}^2$, $\Delta t_D = 30 \text{ min}$) under visible light at 300K. b) CdS:Ag crystal partially purified at 400°C ($E_D = 200 \text{ V/cm}^2$, $Dt = 30 \text{ min}$) under excitation with $\lambda_{\text{exc}} = 365 \text{ nm}$ mercury lamp line at $T = 77 \text{ K}$.

near the anode and spread with time along the sample until only a narrow dark strip remained near the cathode. After cooling to room temperature the light region became bright yellow like undoped crystal. So, one can suppose that coloration of initially undoped crystal under electric field application is caused by Ag incorporation while bleaching of CdS:Ag crystal under electric field application is due to Ag extraction. The bleached crystal can be made bright brown again by application of opposite direction electric field. Thus, incorporation of Ag in any region of the sample and extraction of this impurity from it could be made over and over again. A sharp boundary was found to form between brown (doped with Ag) and yellow (undoped or purified) sample regions (Fig. 1, a). Transmission spectra measurements show that after Ag incorporation transparency reduced and absorption edge shifted to the long wavelength side (Fig. 2). After Ag extraction transmission spectra of undoped crystal restored.

2.1. Energy levels of Ag-related centres

Photoluminescence (PL), photocurrent (PC) and thermally stimulated current (TSC) spectra of the same crystal region were measured before and after Ag incorporation and then after its extraction. For electrical measurements additional In electrodes were applied.

The difference in PL spectra of doped and undoped regions was well conspicuous under illumination with 365 nm line of mercury lamp at 77K: the undoped region was bright green, while the doped one emitted orange light. The boundary between green and orange parts exactly coincided with that between yellow and brown regions (Fig.1, b).

PL spectra of initially undoped and doped CdS crystals measured before and after Ag incorporation or extraction are shown in Fig. 3 (a, b). It is seen that incorporation of Ag results in appearance of orange band at $\lambda_m = 610 \text{ nm}$ and quenching of edge green emission. The latter can be caused by re-absorption of the edge emis-

sion in the crystal due to the shift of absorption edge (Fig.2). After Ag extraction orange emission disappears and green band restores. The intensity of red band at $\lambda_m = 715 \text{ nm}$ that was also present in PL spectra of both doped and undoped sample regions was found to be factually independent on Ag incorporation or extraction. In some undoped crystals so-called self-activated orange emission at $\lambda_m = 590 \text{ nm}$ was observed in addition to green and red emissions. These crystals were supplied with two In electrodes and PL spectra were measured near the same electrode in the initial state and after electric field application at $T_d = 400 \text{ }^\circ\text{C}$ during $\Delta t = 30 \text{ min}$ so that this electrode was first the anode and then the cathode. Any influence of the electric field on PL spectra was not found in this case.

Incorporation of Ag was accompanied with the increase of crystal photosensitivity in the whole wavelength range, the most increase being observed in extrinsic «or-

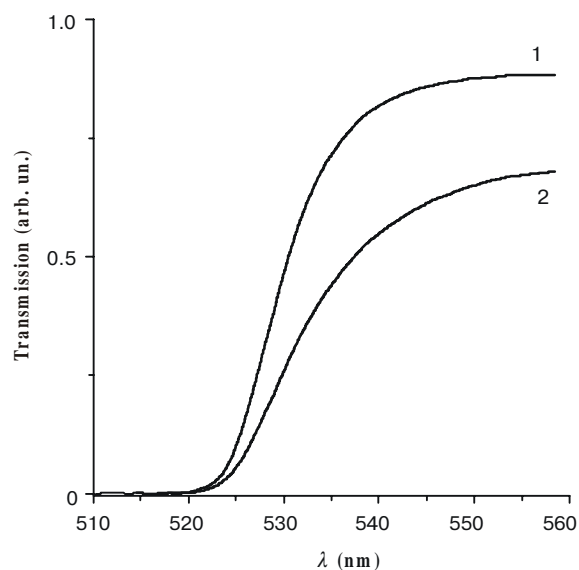


Fig. 2. Transmission spectra of CdS crystal before (1) and after (2) Ag incorporation and after next Ag extraction (1).

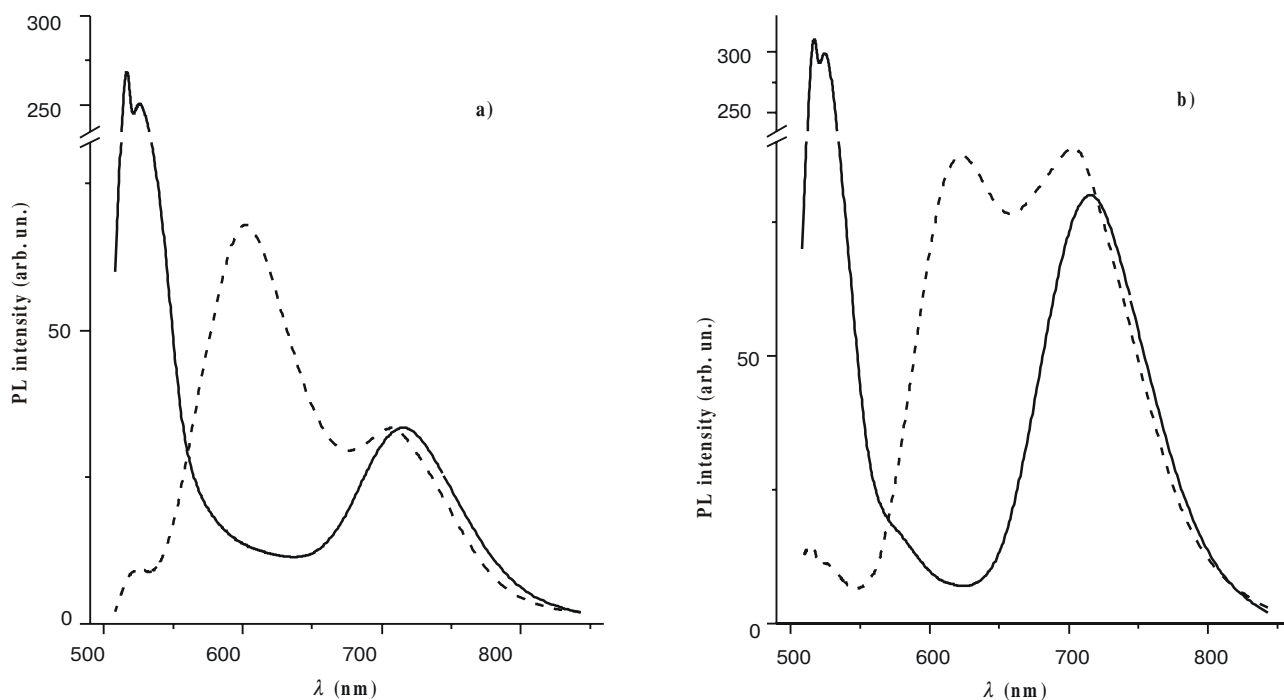


Fig. 3. Photoluminescence spectra of CdS crystals after Ag incorporation (dashed line) and Ag extraction (solid line): (a) – nominally undoped crystal; (b) – crystal doped with Ag during growth.

ange» region (Fig. 4). In order to elucidate whether photo-enhanced defect reactions took place in investigated crystals PC spectra of undoped, then doped and next purified sample region were measured at 300K after cooling from 450 to 300K first in dark and next under visible light illumination [5]. In undoped sample a slight photosensitizing reaction was observed (Fig. 4, curves 1,2). Such reaction often takes place in nominally undoped CdS and has been shown to be due to rearrangement of native defects [5]. After Ag incorporation considerable photosensitivity degradation was observed as a result of illumination in 450–30 K temperature range (Fig4, curves 3,4). Similar reaction had been earlier investigated in CdS:Cu crystals [5]. In CdS doped with Ag degradation reaction was observed for the first time and was found to occur at higher temperatures then in CdS:Cu. When Ag was extracted from the sample, degradation reaction disappeared and photosensitizing reaction restored.

In Fig.5 TSC spectra of CdS:Ag crystal before and after Ag extraction were shown. It is seen that none TSC peak disappeared when Ag was extracted. The decrease of current level in whole temperature range after sample purification is obviously due to the decrease of photosensitivity (Fig. 4). In TSC spectra of the most initially undoped crystals only peak at $T_m = 95$ K was present and any new peak did not appear after Ag incorporation.

2.2. Diffusion characteristics

Diffusion of Ag under electric field was carried out both parallel and perpendicular to the c-axis. Corresponding

diffusion coefficients $D_{||}$ and D_{\perp} were calculated from Einstein's relation $D = \mu k T_d / e$, where $\mu = l_d / E_d \Delta t_d$ – impurity ion mobility, l_d – length of doped (or purified) region, k – Boltzmann constant, e – electron charge. Activation energies of diffusion $E_{d||}$ parallel and $E_{d\perp}$ per-

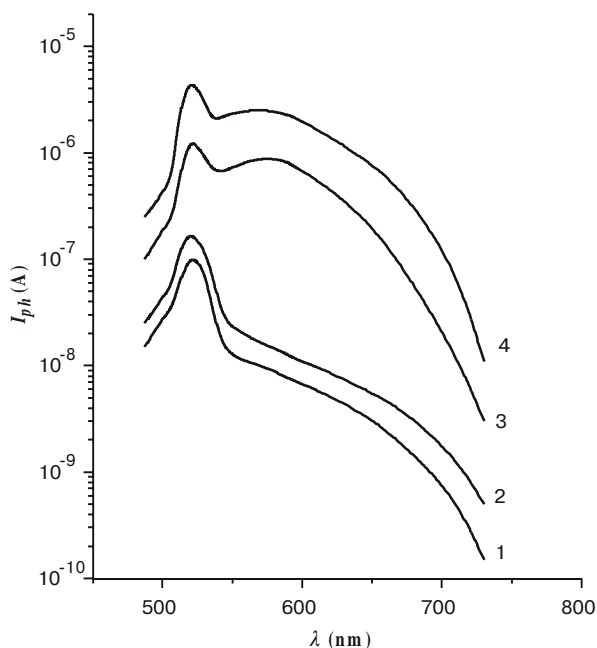


Fig. 4. Photocurrent spectra of CdS crystal before (1,2) and after (3,4) Ag incorporation after cooling from 420 K to 300 K in dark (1,4) and under intrinsic light illumination (2,3).

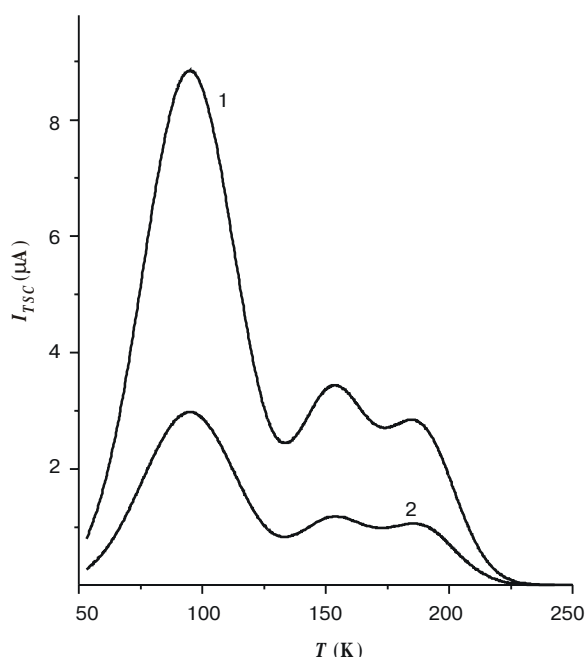


Fig. 5. TSC spectra of CdS:Ag crystal before (1) and after (2) Ag extraction.

pendicular to the c -axis were determined from $D_{||}$ and D_{\perp} temperature dependencies (Fig. 6). Diffusion parameters obtained from the velocities of both Ag incorporation and extraction processes were proved to coincide. As it is seen from fig.6, considerable diffusion anisotropy takes place, diffusion being some times faster parallel to the c -axis. The values of $E_{d||}$ and E_{\perp} are different and equal to 1.1 ± 0.05 and 1.35 ± 0.05 eV correspondingly.

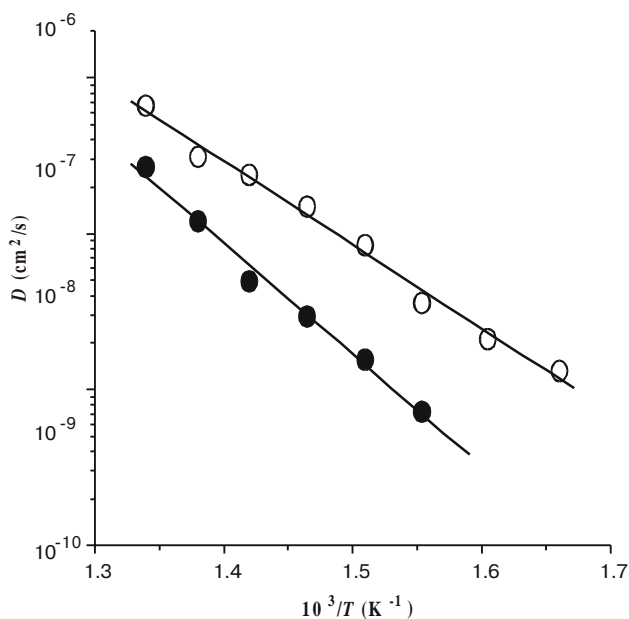


Fig.6. Temperature dependencies of Ag coefficients of diffusion parallel (1) and perpendicular (2) to the c -axis.

3. Discussion

The basic Ag-related defects in CdS are silver in the Cd site Ag_{Cd} and silver interstitial Ag_i . These defects must act as a single charged acceptor and a single charged donor correspondingly [6]. Appearance of PL band at $\lambda_m = 610$ nm after Ag incorporation and its quenching after Ag extraction prove that this band is due to Ag-related defects. It is known that a number of orange emission bands can be observed in CdS PL spectra in 580-640 nm wavelength range. Some of these bands are ascribed to different impurities, others (so-called self-activated) are thought to be related to native defects [6,7]. All orange bands were shown to result from recombination of free electrons on complex centres consisting of deep acceptors and shallow donors [8]. One can conclude, therefore, that acceptor responsible for the band at $\lambda_m = 610$ nm is Ag_{Cd} . At the same time the orange band at $\lambda_m = 590$ nm which is observed in nominally undoped crystals and does not change after action of electric field is obviously due to immobile native acceptor V_{Cd} .

In CdS crystals doped with Ag, as a rule, intensive red emission at $\lambda_m = 710-720$ nm was also observed and usually ascribed to Ag-related centres [7,9,10]. On the other hand, such band is often present in PL spectra of undoped CdS (self-activated red band) [6,7]. An emission band at $\lambda_m = 710$ nm takes place in PL spectra of investigated crystals too. Our data show, however, that Ag incorporation or extraction does not influence on this band intensity in neither initially «pure», nor initially doped crystals. One can think, therefore, that this band is due to native defects. Perhaps, the presence of Ag enables the creation of defects responsible for self-activated red emission. Thus, by means of electric field it is possible to separate emission bands related to immobile native defects and mobile impurities.

The direction of drift in electric field shows that silver incorporates in crystal and diffuses in it as positively charged ions, i.e. interstitials Ag_i^+ , so, these defects are present in the crystal during its doping or purification. Then acceptors Ag_{Cd} create due to reaction



In available literature Ag_i centres were stated to be deep donors [9,11] that in highly compensated material will act as deep electron traps. The analysis of TSC data shows, however, that any new electron traps do not appear after Ag incorporation or disappear after its extraction. The absence of Ag_i centres in noticeable concentrations can be explained by the shift of the equilibrium (1) to the right side.

The results of investigation of Ag diffusion dependence on crystallographic direction turned out quite interesting. The available information about impurity diffusion anisotropy in II-VI compounds is rather scanty. For the first time this effect in CdS was reported for Cu, ratio $D_{Cu\perp}/D_{Cu||} > 10$ being found [12]. Then In [13] and Ga [14] diffusion anisotropy in CdS with $D_{\perp} = 3D_{||}$ was ob-

served. Later we investigated Cu diffusion in CdS under electric field both perpendicular and parallel to the c -axis [15] and obtained data coincided with [12]. Dependence of Ag diffusion on crystallographic direction was not reported thus far. The fact that the direction of Ag diffusion anisotropy ($D_{||} > D_{\perp}$) is opposite to the direction of Cu diffusion anisotropy ($D_{||} < D_{\perp}$) is surprising. In general, different directions of diffusion anisotropy for different impurities were earlier found in hexagonal Zn crystals [16]. This effect was accounted for different interaction of impurity-related defects with Zn vacancies due to different charges of these defects in Zn crystal lattice [16]. However, both Cu and Ag diffuse in CdS interstitially as single charged ions Cu_i^+ and Ag_i^+ , so the same diffusion mechanism could be expected for these impurities. At the same time, opposite directions of diffusion anisotropy indicate that mechanisms of copper and silver diffusion in CdS are different. To elucidate the nature of this phenomenon more detailed investigations are planned.

Conclusions

Diffusion of Ag in high-resistivity CdS crystals parallel and perpendicular to the c -axis was carried out. The impurity was introduced in the sample and extracted from it under electric field $E_d = 50\text{--}300$ V/cm at $T_d = 300\text{--}450$ K. It was shown that Ag incorporation (extraction) resulted in:

- decrease (increase) of crystal transparency and shift of absorption edge to the long (short) wavelength side;
- appearance (disappearance) of orange emission band at $\lambda_m = 610$ nm;
- rise (vanishing) of photo-enhanced defect reaction resulting in photosensitivity degradation;

Any influence of electric field on the intensities of self-activated emission bands at $\lambda_m = 514$ nm, $\lambda_m = 590$ nm and $\lambda_m = 715$ nm was not observed.

Diffusion coefficients and activation energies of Ag diffusion parallel and perpendicular to the c -axis were determined. Diffusion anisotropy was found, diffusion being some times faster parallel to the c -axis.

References

1. F.A. Kröger, *The chemistry of imperfect crystals*, 654 p., Eds. North-Holland publishing company, Amsterdam (1964).
2. B.J. Boltaks, *Diffuziya v poluprovodniakh*, 462 p., Eds. Fizmatgiz (1961).
3. B.L. Timan, Yu.A. Zagoruiko // *Fiz. Tverd. Tela*, **21** (9), pp. 2849-2851 (1979).
4. L.V. Borkovskaya, B.R. Dzhumaev, L.Yu. Khomenkova, N.E. Korsunskaya, I.V. Markevich // *Proceedings of the 3^d Int. Conf. ASDAM-2000, Smolenice Castle, Slovakia, October 16-18, 2000*, p. 187-190.
5. *Fizika soedinenii A₂B₆* edited by A.N. Georgobiani and M.K. Sheinkman, 320p., chap.4., Eds. Nauka, Moskva (1986).
6. *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J.S. Prener, 624 p., Eds. North-Holland publishing company, Amsterdam (1967).
7. I.B. Ermolovich, G.I. Matvievskaia, G.S. Pekar, M.K. Sheinkman // *Ukr. Phys. Zhurn*, **18** (5), pp. 729-737 (1973).
8. I.B. Ermolovich, G.I. Matvievskaia, M.K. Sheinkman // *Fiz. Tech. Poluprov.*, **9** (8), pp. 1620-1623 (1975).
9. H.H. Woodbury // *J. Appl. Phys.*, **36** (7), pp. 2287-2293 (1965).
10. T. Lukaszewicz // *Phys. Stat. Sol. (a)*, **73** (2), pp. 611-616 (1982).
11. E.M. Zobov, G.G. Garyagduev, M.A. Rizahanov // *Fiz. Tech. Poluprov.*, **21** (9), pp. 1637-1641 (1987).
12. G.A. Sullivan // *Phys. Rev.* **184**(3), pp. 796-805 (1969).
13. E.D. Jones, H. Mykura // *J. Phys. Chem. Sol.*, **39** (1), pp. 11-18 (1978).
14. E.D. Jones, H. Mykura // *J. Phys. Chem. Sol.*, **41** (11), pp. 1261-1265 (1980).
15. L.V. Borkovskaya, B.R. Dzhumaev, L.Yu. Khomenkova, N.E. Korsunskaya, I.V. Markevich, M.K. Sheinkman // *Semicond. Phys., Quant. Electron and Optoelectr.*, **3** (3), pp. 282-286 (2000).
16. A.P. Batra, H.B. Huntington // *Phys. Rev.*, **145** (2), pp. 542-546 (1966).