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About the nature of diffusion anisotropy in CdS crystals

L.V.Borkovskaya, B.R.Dzhumaev*, L.Yu. Khomenkova, N.E.Korsunskaya, I.V.Markevich and M.K. Sheinkman

Institute of Semiconductor Physics, NAS Ukraine, 45 prospect Nauki, Kyiv, 03028, Ukraine,
Tel: (044) 265-72-34, Fax: (044) 265-83-44, E-mail: kors@lumin.semicond.kiev.ua
**Turkmen Polytechnic Institute, Khalmamedov Str., 1, Ashgabat, 744025, Turkmenistan*

Abstract. Electrodiffusion of copper into nominally undoped high-resistivity CdS crystals at 250-400°C has been investigated. A strong diffusion anisotropy has been observed, copper diffusion in perpendicular to the c-axis direction being more than one order faster as compared with its diffusion in parallel to the c-axis direction. The effect has been shown to be not due to greater density of perpendicular to the c-axis dislocations than that of parallel to the c-axis ones, as it was thought earlier. Electrically active dislocations lying in the basal plane are supposed to be channels of fast diffusion owing to their intensive decoration with intrinsic defects and residual impurities.

Keywords: diffusion, dislocations.

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1. Introduction

Processes of point defect diffusion in crystal lattice arose consistent interest of investigators due to wide application of doped materials in microelectronics. On the other hand, investigation of these processes allows to understand the mechanisms of lattice – defect interaction which is an important problem of solid state physics. One of the most interesting diffusion phenomena is diffusion anisotropy which was observed in some metals and semiconductors with cubic (Mo [1], Si [2]) and hexagonal (Zn [3], CdS [4]) lattices. To explain this effect a number of hypotheses were proposed, such as anisotropic defect distribution due to electrostatic interaction between impurity atoms and intrinsic defects [3], existence of elastic long-range forces between impurity atoms [5], influence of dislocations on diffusion [2, 4]. Other explanations of the effect are also possible. To elucidate the real mechanism of diffusion anisotropy detail study is necessary in every case.

Strong anisotropy of impurity diffusion in hexagonal II-VI crystals was for the first time reported in [4]. Under doping of high-purity low-resistivity ($\rho = 0.1 \div 10$ Ohm·cm) CdS crystals with copper author [4] found that the impurity diffusion coefficient in perpendicular to the c-axis direction $D_{Cu\perp}$ was by one or two orders greater, than in parallel to the c-axis direction $D_{Cu||}$. The same magnitude of Cu diffusion anisotropy has been obtained in this work for high-resistivity CdS crystals. Impurity diffusion anisotropy in CdS with $D_{\perp} = 3D_{||}$ was also observed for In [6] and Ga [7]. At the same time some authors who studied Cu [8-10] and Ag [9,11] incorporation in both low-resistivity and high-resistivity CdS crystals obtained practically equal values for $D_{Cu\perp}$ and $D_{Cu||}$. Besides, it is necessary to note the wide range of diffusion coefficient values reported by various investigators (Table 1). Owing to present data one has to think that impurity atom diffusivity in CdS crystals, as well as degree of diffusion anisotropy are influenced by certain defects which density can be different in various crystals. According to [4], these defects are dislocations. In order to explain obtained ratio $D_{Cu\perp} > 10\, D_{Cu||}$ author [4] supposed that density of dislocations perpendicular to the c-axis $N_{d\perp}$ was much more than that of dislocations parallel to the c-axis $N_{d||}$. Analysis of data available in the literature [12-14], however, allows to conclude that in as-grown CdS crystals, as a rule, the ratio $N_{d\perp} \leq N_{d||}$ takes place. So, the nature of the observed diffusion anisotropy effect remained unclear. To obtain more information on impurity diffusion anisotropy in CdS crystals and on dependence of this effect on dislocation density the present work has been undertaken.

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Table 1. Diffusion characteristics of copper in CdS crystals

Crystal conductivity, $Ohm^{-1}\cdot cm^{-1}$	Diffusion coefficient, D, $cm^2\cdot s^{-1}$ at 400^0C		Diffusion activation energy, E_d, eV		Author
	⊥c-axis	| |c-axis	⊥c-axis	| |c-axis	
0,1÷10	$(0.6\div1.5)\cdot10^{-8}$	$(2\div3)\cdot10^{-10}$	0.98÷1,1	0.96	[4]
	$2.2\cdot10^{-9}$	$2.3\cdot10^{-9}$	0.76	0.77	[8]
$1.5\cdot10^{-4}$	$2.9\cdot10^{-7}$	$2.8\cdot10^{-7}$	-	0.68	[9]
0.5÷0.7	$6.5\cdot10^{-9}$	$5.0\cdot10^{-9}$	-	0.98	[9]
1.0	$1.5\cdot10^{-11}$	$1.6\cdot10^{-11}$	0.95	1.17	[10]
1.0	$4.5\cdot10^{-10}$	-	1.05	-	[11]
0.5÷2.0	$4.0\cdot10^{-9}$	-	-	0.58	[15]
$<10^{-8}$	$(3\div6)\cdot10^{-7}$	$(1\div2)\cdot10^{-8}$	0.95÷1,0	0.95÷1,0	This work

2. Experimental procedure

Low-temperature ($250\div400^0C$) electrodiffusion of copper in nominally undoped high-resistivity ($\rho > 10^8$ Ohm·cm) bulk CdS crystals was investigated. The crystals were grown by sublimation from vapour phase and had bright yellow color. Rectangular parallelepipeds of typical dimensions 10×5×1 mm^3 were cut from larger bouls, the c-axis being parallel to the longest side. Then every parallelepiped was cleaved perpendicularly to the c-axis and on opposite planes of each of obtained crystals – basal for the one of them and prismatic for the other – In electrodes were melted. The distance between electrodes was 3÷5 mm. The crystal was mounted on mica, in one of electrodes a piece of copper wire being incorporated. The sample was fastened horizontally on the heater (Fig. 1) and heated to required temperature T_D in air ambient. Temperature was measured with copper-constantan thermocouple. When T_D was established, electric field $E_D = 5\cdot10^1\div2\cdot10^2$ V/cm was applied to the sample, the electrode with Cu wire being anode [9]. It is necessary to note that used electric field does not change mobility of drifting ions. After certain time interval Δt_D electric field was switched off and the sample was cooled to room temperature.

In a short time after the electric field switching on, creation of a coloured region near the anode was observed. The colour of this region was red or brown-red which is characteristic for CdS crystals doped with Cu [8-12]. Since diffusion coefficient of indium in CdS is some orders smaller than that of copper [6], one can think doping of the sample with In negligible in the used temperature range. In course of time the coloured region spread along the sample up to the cathode. A quite sharp boundary took place between coloured and uncoloured crystal regions, which allowed to measure the length of the coloured region l_D with the precision up to 0.1mm (Fig. 1a, b). The velocity of coloured region spreading increased with T_D and E_D rise. When electrode with copper wire was the cathode, coloured region appeared only near this electrode. In the absence of the electric field coloured region also created and spread over the sample as a result of thermal diffusion, but this process was much more slow, than electrodiffusion one. When after electric field switching off the sample was additionally kept at T_D during the same time Δt_D and then was cooled, the boundary of coloured region did not replace. If copper wire was not incorporated in the In electrode, the coloration of the sample did not occur.

Photocurrent (PC) and photoluminescence (PL) spectra were measured both for coloured and uncoloured parts of the sample. To measure PC additional In electrodes were melted. Dislocation densities $N_{d\perp}$ and $N_{d||}$ were calculated from the number of etch pits on prismatic and basal planes correspondingly. Diffusion coefficient was determined from the Einstein relation $D = \mu k T_D/e$, where $\mu = l_D/E_D\Delta t_D$ is a copper ion mobility, k in the Boltzman constant, e is the electron charge. Diffusion activation energy was determined from diffusion coefficient temperature dependence. For this dependence investigation, crystal was cleaved on some parts and then copper electrodiffusion was carried out in obtained samples at different T_D, Δt_D and the same E_D.

3. Results

Typical PC and PL spectra for uncoloured (curves 1) and coloured (curves 2) parts of the sample are shown in Fig. 2a, b. It is seen that coloration results in the rise of photo-sensitivity in both intrinsic and extrinsic spectral range, the increase of extrinsic PC maximum at $\lambda = 0.7$ µm being the largest. Simultaneously in PL spectra $\lambda = 1.0$ µm band intensity increases. It is known that centres Cu_{Cd} are sensitizing recombination centers (r-centres) [16]. Extrinsic PC maximum at $\lambda = 0.7$ µm is due to photoionization of electrons from r-centers to c-band, and PL band at $\lambda = 1.0$ µm is caused by recombination of free electrons with holes at these centres [16]. Thus, crystal coloration under electrodiffusion is really due to copper incorporation. It is ought to note that magnitude of PC

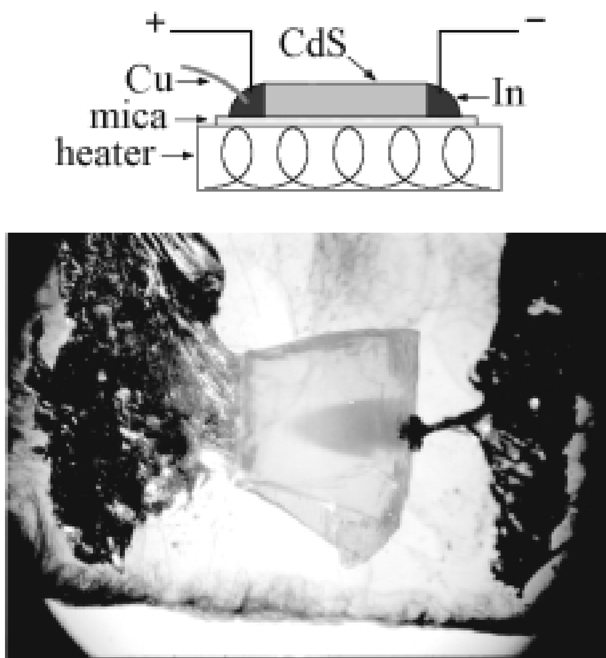

Fig. 1. CdS crystal after Cu electrodiffusion at T_D=350°C in perpendicular to the c-axis direction at E_D = 70 V/cm, Δt_D = 10 min (a) and in parallel to c-axis direction at E_D = 70 V/cm, Δt_D = 45 min (b). Left-side electrode was the anode. Overhead the picture – arrangement of the sample.

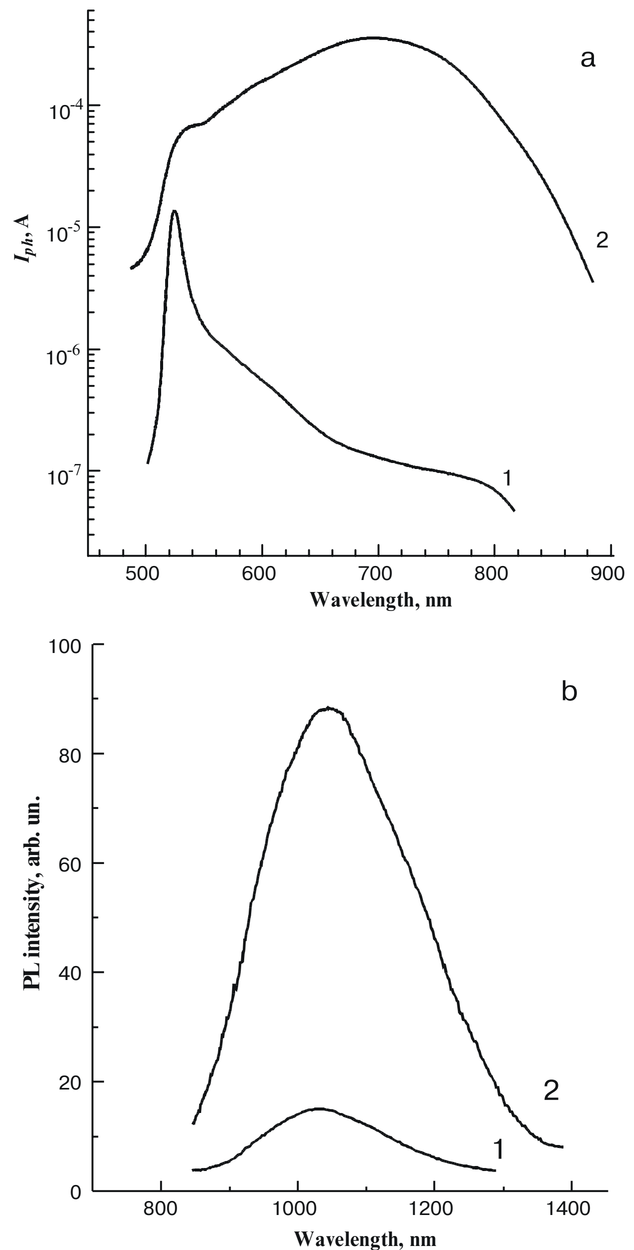

Fig. 2. Photocurrent (a) and photoluminescence (b) spectra of uncoloured (1) and coloured (2) crystal region.

and PL change after electrodiffusion correlates with crystal colour. The strongest increase of PC and PL maxima connected with r-centres was observed in red crystals. The more brown the crystal the less the effect.

Diffusion coefficient values of samples cleaved from various boules were somewhat different (Table1), in brown crystals Cu diffusivity being, as a rule, less than in red ones. In all samples strong diffusion anisotropy $D_{Cu\perp} > 10D_{Cu||}$ was observed. For all measured crystals diffusion activation energy ε_{Cu} was found to be the same in both crystallographic directions and to lie in 0.95÷1.0 eV range (Fig. 3).

Spreading of crystal coloration under electrodiffusion from anode to cathode means that copper ions diffuse through interstitials as donors Cu_i. Thus, creation of acceptors Cu_{Cd} is a secondary process. Since the additional annealing of the sample at T_D after electric field switching off does not result in coloured region boundary replacement, one can conclude that Cu_{Cd} centre creation process «keeps» track of Cu_i diffusion, i.e. the former is more fast than latter in the used temperature range.

Etch pits on basal plane (0001) that correspond to parallel to c-axis dislocations had usual for this plane hexagonal shape [12,14] (Fig. 4a). For all investigated

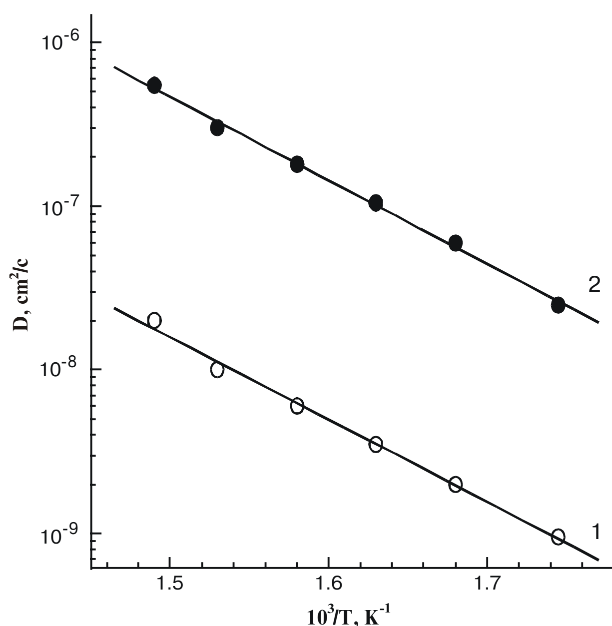

Fig. 3. Temperature dependence of coefficient of copper diffusion in CdS crystal in parallel to c-axis direction (1) and in perpendicular to the c-axis direction (2).

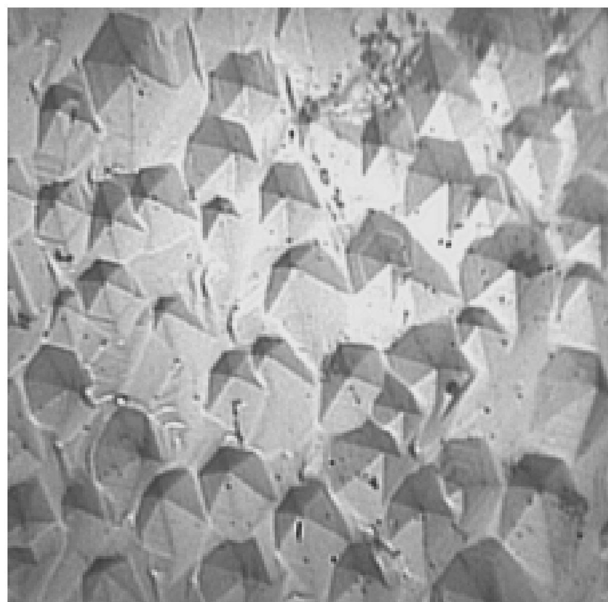

Fig. 4. Etch pits on basal (a) (×125) and prismatic (b) (×600) CdS crystal planes after Cu electrodiffusion.

crystals their density lay within $(8\div10)\cdot10^4$ cm^{-2} (which was standard value for bulk CdS crystals grown by sublimation) and did not change after copper electrodiffusion. Etch pits on prismatic planes that correspond to perpendicular to the c-axis dislocations appeared only after coloration and had characteristic shape of «seeds» [12-14] (Fig. 4b). Their density reached only 10^4 cm^{-2}. These results agree with available literature data [12-14]. Inside the «seeds» unshapely hollows of about 2-3 μm linear size were often observed. In all probability, these hollows correspond to etched precipitates.

Results qualitatively similar to described above, particularly, a strong diffusion anisotropy we found also for Ag.

4. Discussion

Dislocations are known to influence considerably on point defect diffusion [see, for instance, [17]. In principle, they can both accelerate and decelerate this process [2]. In CdS:Cu crystals intensive decoration of dislocations with Cu takes place, which is usually accounted for prevailing Cu motion along dislocations [18]. In [4] the increase of density of dislocations parallel to the c axis resulted in the rise of Cu diffusivity in this direction. Thus, one can conclude that dislocations really accelerate Cu diffusion in CdS. On the other hand, results obtained in this work show that Cu diffusivity in certain crystallographic direction does not correlate with dislocation density in the corresponding crystal plane. Moreover, the relation of densities of dislocations parallel and perpendicular to *c*-axis ($N_{d||}>N_{d\perp}$) was found to be reversal to the relation of coefficients of diffusion in corresponding directions ($D_{Cu||} < D_{Cu\perp}$). To explain this paradox, one has to suppose that the velocity of diffusion along dislocation strongly depends on dislocation properties, such as the presence or absence of electric charge, type of broken bonds, extent of decoration, *etc*. Really, in wurtzite structure crystal dislocations perpendicular to the c-axis have broken bonds of one kind atoms along dislocation line, either metal (α-dislocations) or non-metal (β-dislocations), so such dislocations are electrically active [19]. Dislocations parallel to the c-axis have broken bonds of