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Deep Levels on Zinc Cadmium Selenide Alloys

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Abstract. Deep level defects in $Zn_x Cd_{1-x} Se$ mixed crystals (with x = 0.93, 0.90, 0.86), grown from the vapor phase, were investigated by steady state photocapacitance and infra-red quenching photocapacitance techniques. A total of five deep levels have been obtained, one with an activation energy at about 0.75 – 0.94 eV below the conduction band and four with activation energy of about 0.22, 0.45, 0.70 and 0.85 eV above the top of the valence band. Also some parameters calculated from the capacitance-voltage data at room temperature, the values of the maximum electric field at the interface of the metal and semi conductor (E_{max}) and the lowering of the potential barrier are determined in this study.

Introduction

The diversity of energy band gap and lattice parameters available with the ternary II-VI compounds offers unique opportunities for tailoring materials to suit specific applications [1]. The full range of the ternary compound Cd Zn Se material was demonstrated as early as 1951 [2], and since then there has been a small number of isolated studies concerned primarily with the preparation and use of Zn Cd Se as a phosphor [1-6].

Bulk crystal growth from the vapor phase was reported in 1969 [7] and more recently by Burger and Roth [8] and by Al-Bassam *et al.* [9]. The structure of Zn_xCd_{1-x} Se undergoes a transition from the wurtzie to the sphalerite structure at $x = 0.5$ [3;9] being hexagonal when $x < 0.5$ and cubic when $x > 0.5$. The lattice parameters vary linearly with composition. This range of composition provides an extensive choice of band gap energies. The energy band gap is known to vary smoothly, though not linerarly [3;6], with composition from 1.74 eV (CdSe) to 2.67 eV (ZnSe). Since this encompasses most of the visible and part of the near infra-red spectrum, $Zn_xCd_{1-x}Se$ may become an important material in optoelectronic applications [1].

Burger and Roth suggested the use of ZnCdSe as a possible replacement for CdSe in the fabrication of nuclear detectors. The increased band gap of the ternary alloy causes a reduction in the thermal generation of carriers leading to less leakage and an improved noise performance [10].

This paper is primarily concerned with the detailed study of deep levels present in $Zn_xCd_{1-x}Se$ single crystals (with x = 0.86, 0.90, 0.93) grown from the vapor phase. The work was carried out using a variety of space-charge region capacitance and photo capacitance (PHCAP) techniques including infra-red quenching of photocapacitance.

Experimental

The single crystal materials used in this study were grown from the vapor phase, using the closed space procedure described by Clark and Woods [11] and the Piper – Polich [12] techniques. Samples ($4\times4\times3$ mm^3) were cut from the boules and mechanically polished down to a grit size of 1 um with alumina powder. After cleaning and a final etch in 2% bromine in methanol solution for about 2 minutes, and then for a further 2 minutes in concentrated HCl, the sample were loaded into a vacuum coating system and a 1 mm diameter gold dot was evaporated into one of the large area faces to form the rectifying contact. (This completes the fabrication of the Schottky barrier diodes). Indium was deposited on the reverse face for use as an injecting contact. The spectral dependence of the steady-state photocapacitance was measured using a Barr and Stroud type VL2 prism (Silica) monochromator with a tungsten light source and Boonton 72B differential capacitance meter. Infra-red quenching of the photocapacitance was obtained using the same system modified by the inclusion of an additional source of sub-band gap primary illumination, provided by a second tungsten light with a combination of interference filters to give the desired radiation profile.

All the measurements presented in this paper were obtained on materials with the compositions x = 0.86, 0.90, 0.93.

Results and Discussion

Generally the $Au\text{-}Zn_xCd_{1-x}Se$ diodes (with x = 0.93, 90, 86) gave good rectifying characteristics with little reverse bias leakage. Figure 1 shows the forward I-V characteristics for these compositions.

The value of the ideality factor, n, of a particular diode can be calculated from the equation [13]

$$n = \frac{q}{KT} (d \ln J / dV)^{-1} \qquad (1)$$

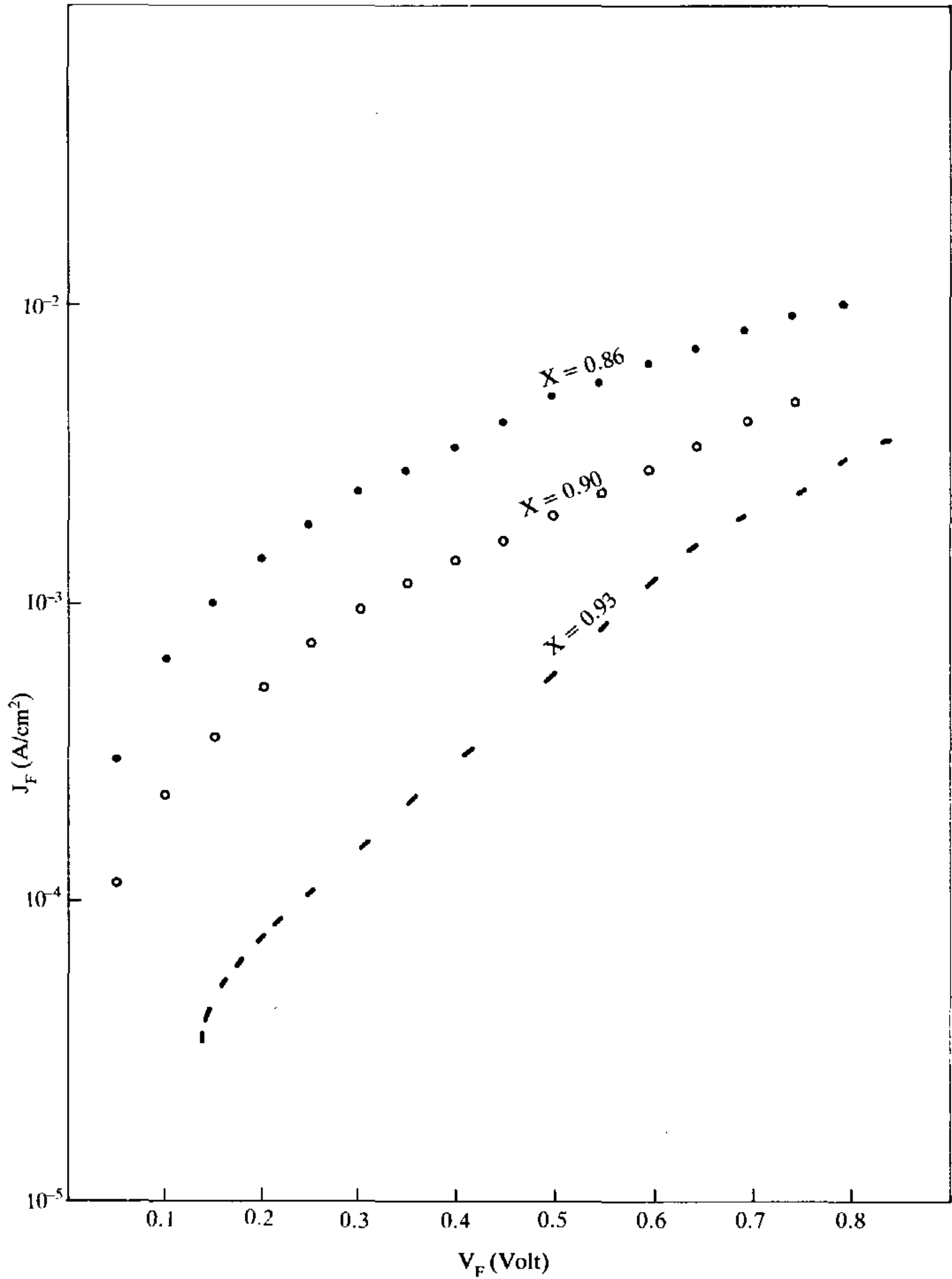

Fig. 1. Forward current density versus applied voltage of $Zn_x Cd_{1-x} Se$ diodes.

where

KT/q is the thermal voltage at 300 K and equal to 0.0259 eV,
J is the saturation current
q is the elementary charge
K is Boltzmann constant

n have been found to vary between 1.7 to 2.5 with practical Schottky diodes. Values of n between 1 and 2 are commonly encountered [13]. According to Card and Rhoderick [13], the ideality factor increases with an increase in the insulating layer thickness which was present after the etching process prior to the deposition of the gold.

Similarly, the capacitance-voltage characteristics usually produce straight lines. The uncompensated donor density N_d was calculated from the slope of the C^{-2} versus V plot. The N_d of these samples with different compositions was found to lie between 10^{16}–10^{17} cm^{-3}. Also the carrier density decreases as the Zinc content increases. Kwok and Chan [14] and Chow *et al.* [15] showed that the carrier density increased initially with increasing Zinc. Chynoweth and Bube [16] found that the carrier density decreases as the Zinc content of $Zn_xCd_{1-x}S$ increases. The depletion width (W) is calculated from

$$W = \varepsilon_s A/C \quad (2)$$

where is the relative permittivity and was obtained by linear interpolation between the relative permittivity values of CdSe (9.4) and ZnSe (8.1) [17]. A is the area of the diode and C is the capacitance at zero bias. The values of W for these compositions have been calculated and are shown in Table 1.

The maximum electric field E_{max} at the interface of the metal and semiconductor under zero bias is given by

$$E_{max}^2 = \frac{2qN_d}{\varepsilon_s}\left(V_{dif} - \frac{KT}{q}\right)$$

where

N_d	is the donor density
V_{dif}	is the diffusion potential
KT/q	is thermal voltage at 300K
ε_s	is the relative permittivity of the sample.

The lowering of the potential barrier by (also called the Schottky effect) as a result of combining the effect of the image force potential and electric field, is according to Sze [16]:

$$\Delta \phi_{bn} = (q E_{max} / 4 \pi \varepsilon_0)^{0.5} \quad (4)$$

The values of E_{max} and $\Delta \phi_{bn}$ are also shown in Table 1.

Table 1. Parameters calculated from capacitance – Voltage data at room temperature

x	E_{max}	$\Delta\phi_{bn}$ (eV)	W (μm)
0.93	4.46×10^4	0.151	0.90
0.90	5.15×10^4	0.143	0.70
0.86	5.38×10^4	0.139	0.68

In general, the parameters calculated here were very much dependent on the resistivity of the samples. Corresponding steady state photocapacitance curves for mixed crystals (x=0.86, 0.90, 93) are shown in Figs. 2 and 3 at room and liquid nitrogen temperatures respectively. With x = 0.86, at room temperature (Figure 2), the first threshold leading to an increased PHCAP was observed at a photon energy of about 0.94 eV, indicating that there is a process whereby excitation of the electron from a level 0.94 eV below the conduction band to 1.5 eV above the valence band (Eg = 2.44 eV) occurs.

As the photon energy was increased, a second threshold was observed at hv = 2.16 eV corresponding to the emptying of an acceptor at about 0.28 eV above the valence band.

Measurements were also carried out on these samples using steady state infrared quenching. Quenching spectra measured at 300 K and 90 K for diodes on samples with x=86 are illustrated in Figure 4. They show clearly the presence of thresholds at 1.0 eV,m 1.2 eV and 1.9 eV at room temperature. At liquid nitrogen temperature, three thresholds were also observed for the diodes. A summary of thresholds obtained is contained in Table 2.

The present work has revealed that a deep level is situated at about 0.75 – 0.94 eV below the conduction band for these compositions. The activation energy observed from PHCAP and IRQ PHCAP spectra are summarized in Table 3,

The level observed in infra-red quenching at about 0.54 eV above the valence band was probably the same as that observed in the PHCAP at 0.56 eV.

The results are in good agreement with results which have been reported for a $Zn_{0.3}Cd_{0.7}Se$ crystal by Lewis *et al.* [1] and Burger and Roth [8] for $Zn_{0.25}Cd_{0.75}Se$

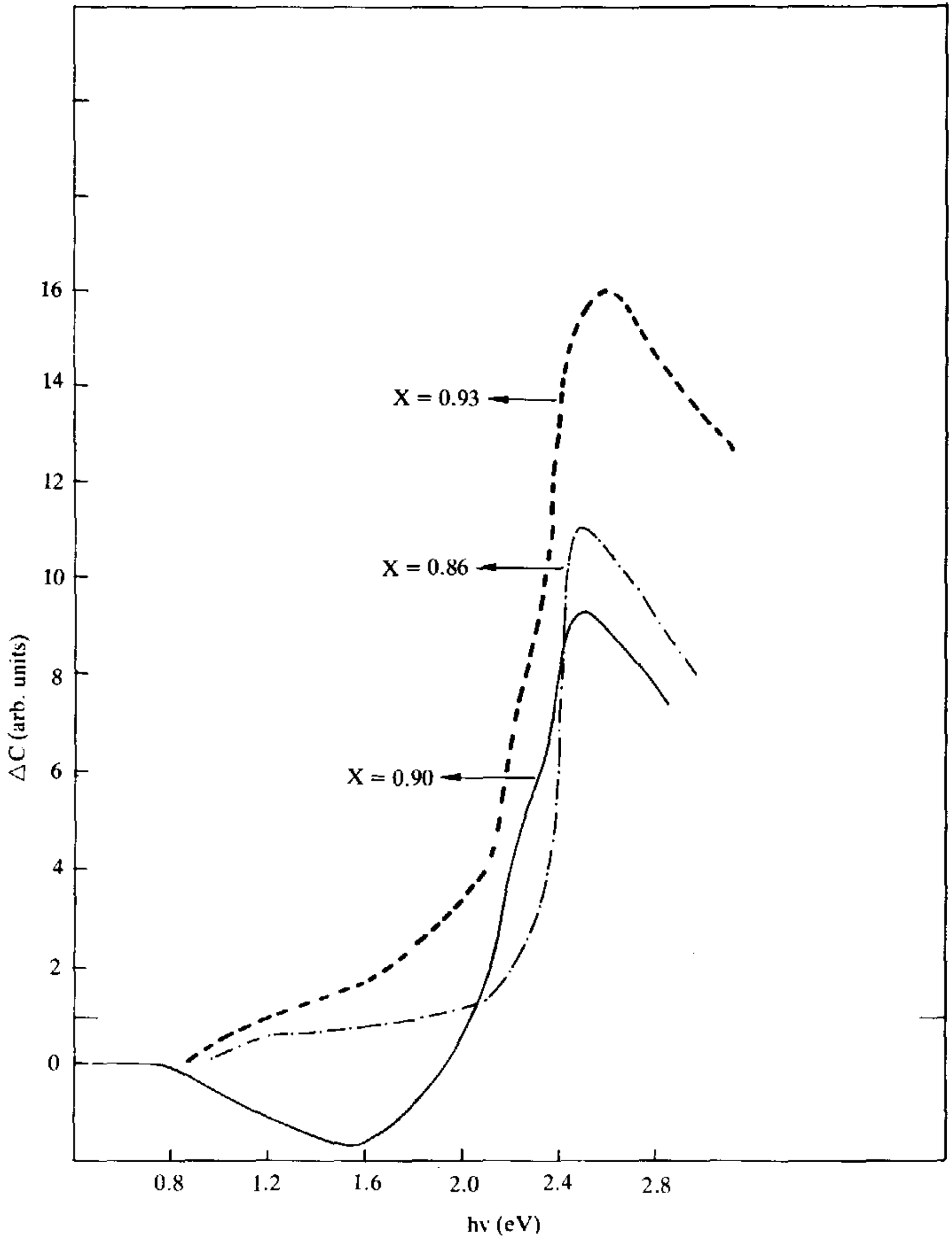

Fig. 2. Photocapacitance spectra of $Zn_x Cd_{1-x} Se$ at 300k.

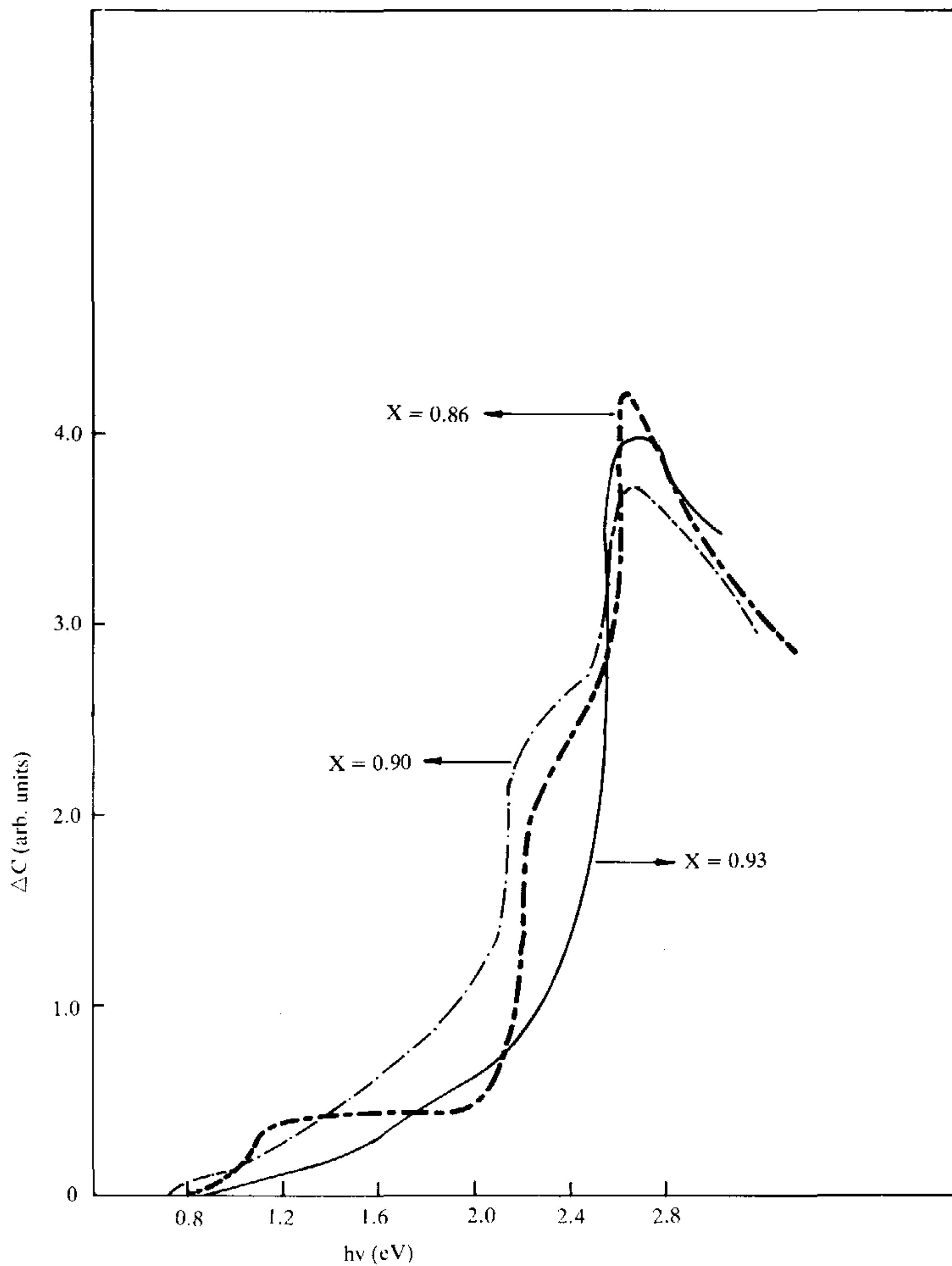

Fig. 3. Photocapacitance spectra of Zn_x d_{1-x} Se at 90 k

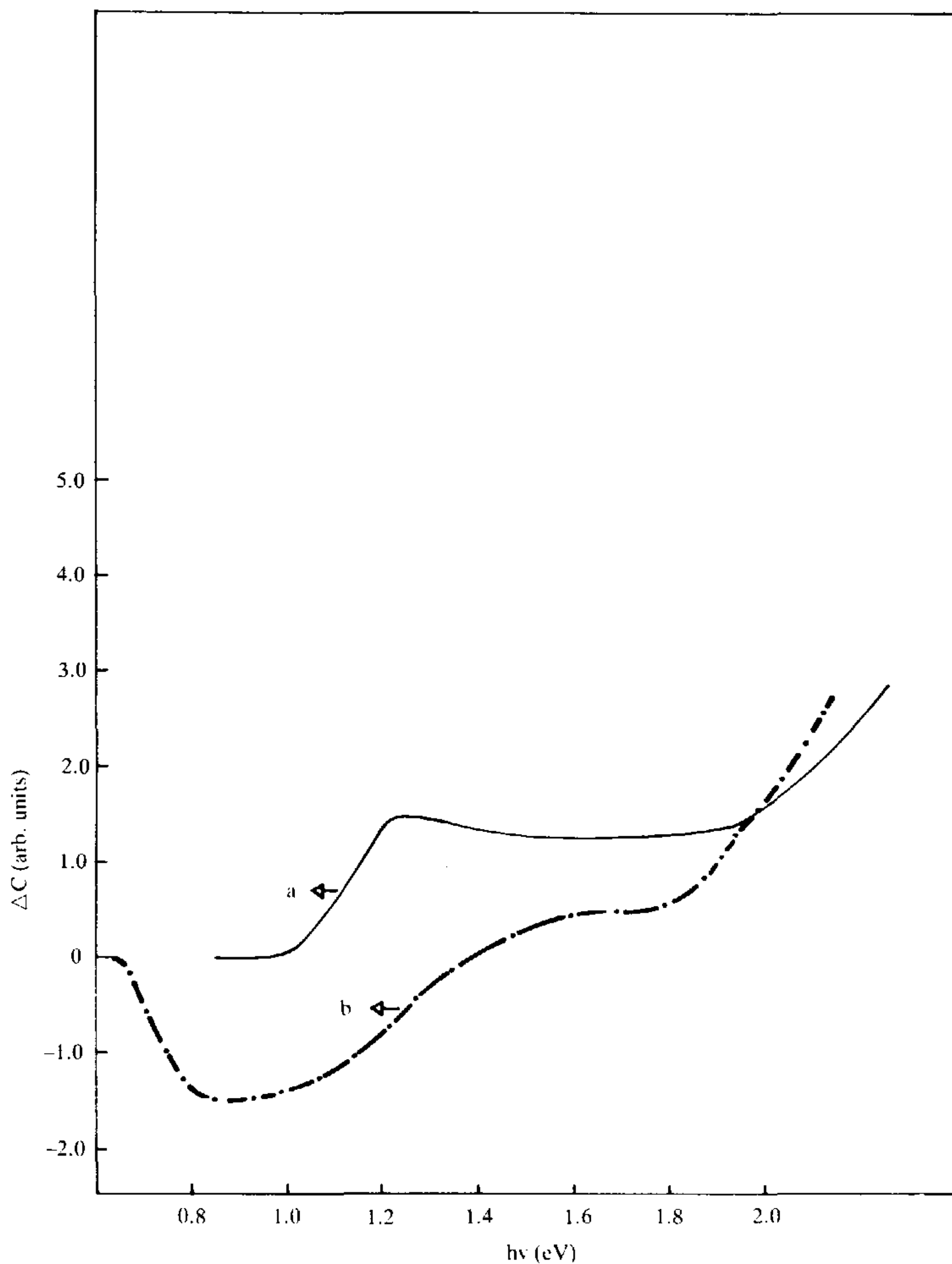

Fig. 4. Infra - red quenching of Photocapacitance spectra of $Zn_{0.86}Cd_{0.14}Se$ at a) 300 k b) 90 k.

Table 2. Thresholds obtained from PHCAP and IRQPhCAP measurements

x	Measurements	Thresholds (eV)
0.93	PHCAP (300 K)	+ 0.86, + 1.7, + 2.10
	PHCAP (90 K)	+ 0.78, + 1.94, + 2.2
0.90	PHCAP (300 K)	−0.76, + 1.58 + 2.2 + 2.36
	PHCAP (90 K)	+ 0.75, + 2.12, + 2.44
0.86	PHCAP (300 K)	+ 0.94, + 1.7, + 2.16
	PHCAP (90 K)	+0.86, + 1.92, + 2.2, + 2.52
	IRQPHCAP (300 K)	+ 1.0, −1.2, + 1.9
	IRQPHCAP (90 K)	−0.65, + 0.97, + 1.77

Table 3. Summary of the levels obtained from PHCAP and IRQPHCAP measurements (CB) indicates the energy as obtained from conduction band and (VB) from valence band

x	Energy (eV)		
0.93	0.86 (CB)	0.77 (CB)	0.45 (VB)
	0.85 (VB)	0.21 (VB)	0.5 (VB)
0.90	0.75 (CB)	0.92 (VB)	0.3 (VB)
		0.54 (VB)	0.22 (VB)
0.86	0.94 (CB)	0.68 (VB)	0.28 (VB)
	0.86 (CB)	0.74 (VB)	0.4 (VB)

who identified a level located at 0.49 eV below the conduction band. They attributed this center to Cd vacancy – Cu – intestitial pairs. Lewis *et al.* [1] reported that five deep levels have been observed, two with activation energies of 0.54 and 1.04 eV with respect to the conduction band and three with activation energies of 0.2, 0.55 and 0.85 eV relative to the valence band. They suggested that the activation energy of this level is close to that widely reported at about 0.62 eV above the valence band edge in CdSe [18;19] which has been associate with double ionised Cd vacancies [20;21].

Conclusion

Mixed crystals of $Zn_x Cd_{1-x}Se$ with (x= 0.93, 0.90, 0.86) have been grown from the vapor phase and used to fabricate M-S diodes for an investigation of deep levels by steady state photocapacitance and infra-red quenching of photocapacitance techniques. The work has revealed that a deep level is situated at about 0.75 – 0.94 eV below the conduction band for the composition (x = 0.93, 0.90, 0.86). Also there are other levels at 0.22, 0.45, 0.7 and 0.85 eV above the valence band.

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مستويات العمق في الزنك كادميوم سيلفايد

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(سُلِّمَ في ١١ رمضان ١٤١٢هـ، وقُبل للنشر في ١٦ رجب ١٤١٣هـ).

ملخص البحث. دُرست عيوب مستوى العمق في خليط الزنك كادميوم سيلفايد البلوريّة مع (x = 0.93, 0.90, 0.86) والتي نمت من طور البخار.

ودرست السعة الضوئية للحالة المستقرة كما استخدمت طريقة الكبت بالأشعة فوق الحمراء.

وقد تم الحصول على خمسة مستويات عميقة أحدها له طاقة تنشيط ما بين (0.75 – 0.94eV) بالنسبة لشريط التوصيل، في حين كان للمستويات الأربعة الأخرى طاقة تنشيط عند حوالي (0.22, 0.45, 0.70, 0.85eV) بالنسبة لشريط التكافؤ، وكذلك تم حساب بعض المتغيرات من العلاقة ما بين السعة ـ الجهد عند درجة حرارة الغرفة، وأيضًا حساب قيم التغير العظمى للحقل الكهربائي (Emax) في المنطقة الفاصلة ما بين الفلز ـ شبه الموصل وأخيرًا تم تعيين قيمة الانخفاض في حاجز الجهد لهذه الدراسة.