Optical properties of copper indium diselenide near the fundamental absorption edge

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In this work we report on an optical absorption study near the band gap of n-type $CuInSe_2$ at 7 K. From the analysis of the results the energy gap is found to be 1.02 ± 0.01 eV. The binding energy of the exciton and the ionization energy of acceptors and donors are determined to be 18, 54, and 26 (±5) meV, respectively. It is suggested that In_{Cu} antisite donors and V_{Cu} acceptors are the predominant active intrinsic defects in "In-rich" $CuInSe_2$.

I. INTRODUCTION

The chalcopyrite compound semiconductor copper indium diselenide ($CuInSe_2$) which appears to be a promising candidate for solar-cells applications,[1] has recently received considerable attention. Electrical and optical measurements made on nonintentionally doped samples show the simultaneous existence of several donor and acceptor levels originating from intrinsic defects.[2] These act as trapping centers for minority charge carriers which minimize the efficiency of the devices. In fact, the highest efficiency reported for any thin-film $CuInSe_2$-based solar cell is only around 11%.[3] This is significantly lower than the value required to make this device economical.[1] For this reason a detailed knowledge of the defect chemistry of this compound is necessary before $CuInSe_2$ can be efficiently used as a solar-cell component.

Since electrical measurements can determine only the most active shallow-defect state parameters, the information about the defect levels in $CuInSe_2$ has been obtained mainly from photoluminescence measurements.[4–8] However, in such measurements it is not easy to identify the different transitions, and for this reason discrepancies exist in the literature about the nature and origin of these levels.

In the present work we report on the optical absorption study near the band gap of n-type $CuInSe_2$ at 7 K. From the analysis of the results, by using a model which allows us to identify the acceptor and donor states, the ionization energy of these states has been determined and their possible origin has been suggested.

II. EXPERIMENTAL DETAILS

Single crystals of nominal $CuInSe_2$ were grown from the melt by a directional solidification technique which is described elsewhere.[9] An as-grown n-type sample with an electron concentration of about 4×10^{16} cm^{-3} at room temperature, as measured by the van der Pauw technique, was used for the measurements. The absorption spectrum was obtained at 7 K using an Air Products cryostat cooled by helium gas. A tungsten-filament lamp was used as a light source. The transmitted radiation was analyzed by means of an Hilger Watts D330 monochromator with a 600-lines/mm grating and detected by a Rofin germanium photodiode connected to a Princeton Applied Research model No. 124A lock-in amplifier. A variable-frequency chopper provided the reference signal.

III. RESULTS AND DISCUSSION

A. Optical measurements

Figure 1 shows the absorption coefficient α, as a function of energy, of n-type $CuInSe_2$ at 7 K. A strong increase of α around 1.0 eV, a sharp line at about 0.99 eV, a broad band between 0.96–0.99 eV, and a small peak at 0.93 eV, are observed on the curve. The first feature

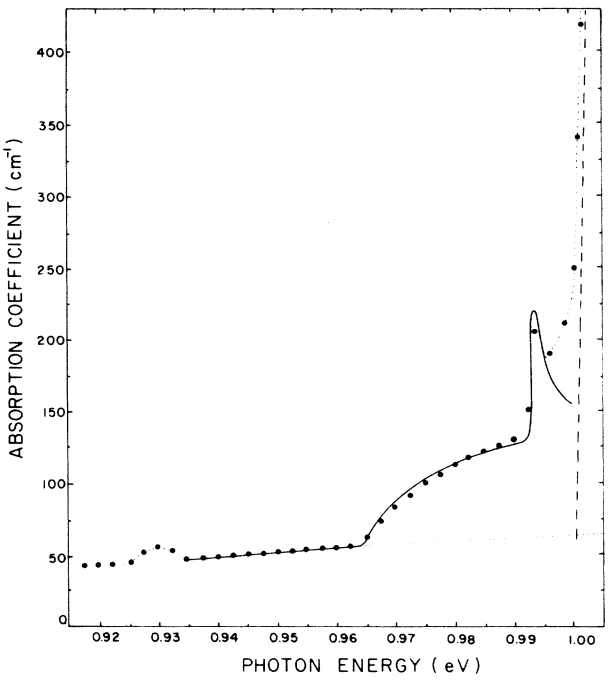

FIG. 1. Absorption coefficient spectrum of n-type $CuInSe_2$ at 7 K. The continuous line represents the theoretical fit of the residual absorption. The free-exciton energy is indicated by the dashed line.

might be associated with the free-exciton absorption (the so-called A transition). The residual absorption structures are probably related to the transitions due to the acceptor and donor defect levels. The fact that these transitions are observed near the band gap of $CuInSe_2$, which is around 1.0 eV at room temperature, suggest that they occur from the valence band to the donor levels or from the acceptor levels to the conduction band.[10,11] A quantum-mechanical calculation for such transitions has been made.[12] In this calculation for parabolic bands, it has been assumed that the material has a direct gap and the defect states are shallow, discrete, and nonoverlapping. It can be seen that these conditions are very nearly fulfilled in the present case of $CuInSe_2$.

According to this model for the valence-band-to-donor-state transition we have

$$\alpha_1=\frac{A(h\nu+E_D-E_G)^{1/2}}{h\nu}\times\sum_{=\mathrm{lh,hh}}\frac{(m_i/m)^{3/2}}{[1+m_i(h\nu+E_D-E_G)/m_eE_D]^4}\ , \tag{1}$$

where the sum is taken over the light (lh) and heavy (hh) holes and A is a constant nearly independent of the photon energy $h\nu$. For the acceptor-state-to-conduction-band transition one obtains

$$\alpha_2=\frac{B(h\nu+E_A-E_G)^{1/2}(m_e/m)^{3/2}}{h\nu[1+m_e(h\nu+E_A-E_G)/m_hE_A]^4}\ , \tag{2}$$

where m_e is the electron effective mass, m_h is the density-of-states effective mass of the holes, and B is a constant, again nearly independent of $h\nu$.

The analysis of the experimental points show that, in addition to a slowly increasing background absorption which varies from 55 to 65 cm^{-1} in the range of interest, the shoulder and the broad-band absorption follow an energy dependence which is in agreement with Eqs. (1) and (2), respectively. Thus, adjusting the residual absorption points of Fig. 1 to these equations with E_G, E_A, E_D, A, and B as variable parameters, and using $m_{\mathrm{lh}}=0.092m$, $m_{\mathrm{hh}}=0.71m$, $m_h=0.73m$, and $m_e=0.09m$ for $CuInSe_2$ (Ref. 13), a good fit, as shown in the Fig. 1 by the continuous line, was obtained with the values $E_G=1.020$ eV, $E_A=54$ meV, $E_D=27$ meV, $A=11544$ $cm^{-1}eV^{1/2}$, and $B=17490$ $cm^{-1}eV^{1/2}$.

On the other hand, the small peak at 0.930 eV is probably due to the other donor level whose ionization energy is $E_D=90$ meV. The binding energy of the free exciton E_x can then be calculated by taking into consideration that in a direct-gap semiconductor the free exciton occurs when the photon energy is $h\nu=E_G-E_x$.[14] In the present case the value $h\nu\simeq1.001$ eV can be estimated from Fig. 1. We then obtain $E_x\simeq19$ meV.

The donor and acceptor concentrations of the sample can also be estimated from the values of the constants A and B according to the relations[12]

$$A=\frac{256\pi e^2\hbar\langle P\rangle^2(N_D-n_D)}{n_0cm^2(m_eE_D/m)^{3/2}} \tag{3}$$

and

$$B=\frac{512\pi e^2\hbar\langle P\rangle^2(N_A-p_A)}{n_0cm^2(m_hE_A/m)^{3/2}}\ , \tag{4}$$

where n_0 is the refractive index, c is the vacuum velocity of light, and N_D-n_D and N_A-p_A is the number of unfilled donors and acceptors, respectively. $\langle P\rangle$ is the average interband matrix element of the momentum operator which can be obtained by the "f sum rule" for the electron effective mass as[12]

$$(m/m_e)-1=(4/m)\langle P\rangle^2[(2/E_G)+(1/E_G+\Delta E)]\ . \tag{5}$$

Here ΔE is the spin-orbit splitting of the valence bands at $\mathbf{K}=0$. For $CuInSe_2$ with $\Delta E=0.233$ eV (Ref. 12), we obtain $\langle P\rangle^2=0.92$ meV.

Evaluating the expressions (4) and (5) with $n_0\simeq3$ (Ref. 15), and considering that at 7 K $N_A-p_A\simeq N_A$ and $N_D-n_D\simeq N_D$ we obtain $N_A\simeq7\times10^{16}$ cm^{-3} and $N_D\simeq4\times10^{16}$ cm^{-3}. These values are of the same order of magnitude as the electron concentration of the sample determined at room temperature. This result that $N_A>N_D$ is physically not acceptable for an n-type semiconductor if N_A and N_D are the total acceptor and donor concentrations, respectively. However, it should be pointed out that in the present theoretical fit to the absorption data near the fundamental absorption edge, N_D represents only a fraction of the total donor concentration since we only take into account the contribution to the donor concentration originating from the most shallow level. It is well known that n-type $CuInSe_2$ has at least one more donor level, not so shallow, which also contributes to the total donor concentration. On the other hand, in the model proposed by Dumke, $\langle P\rangle^2$ is assumed to be the same for the light and heavy holes and for the split of the valence bands and an average value $\langle P\rangle^2$ is taken in the

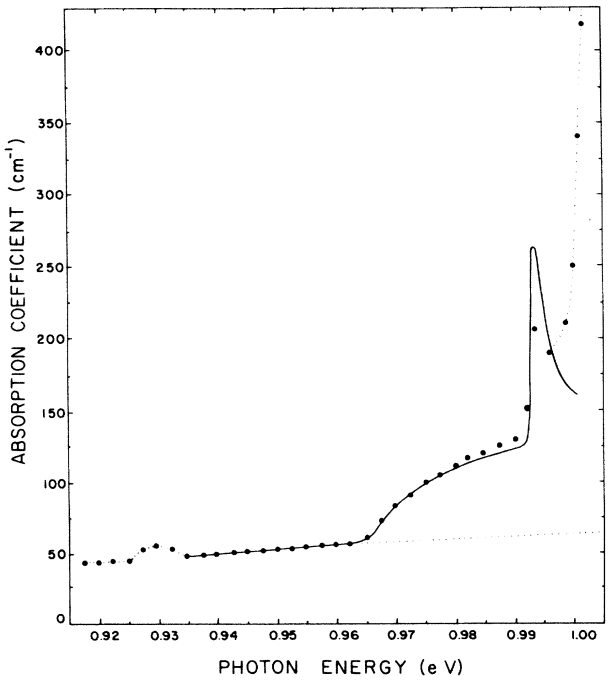

FIG. 2. Theoretical fit of the residual absorption under the condition $N_A/N_D\simeq1$.

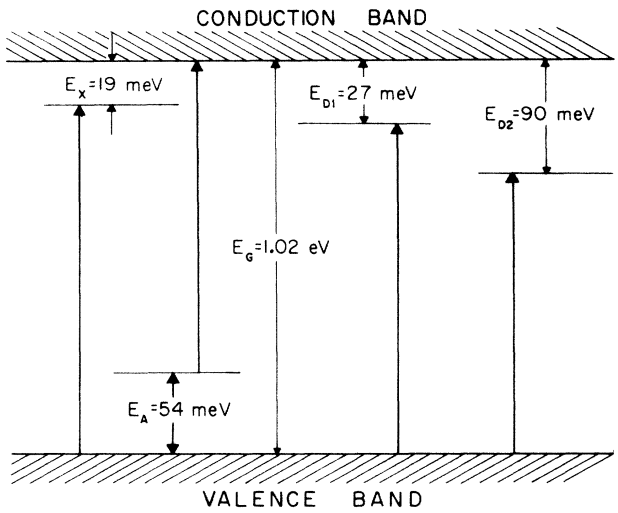

FIG. 3. Energy-level diagram of In-rich n-$CuInSe_2$ indicating the acceptor and donor levels, the position of the free exciton level, and the band gap. The transitions observed in the present study are indicated by arrows.

calculation. This assumption, perhaps not valid for $CuInSe_2$, may also lead to some uncertainty in the values of N_D and N_A determined here. Since $CuInSe_2$ has been reported to be a highly compensated semiconductor with $N_A/N_D \simeq 0.95$ (Refs. 16 and 17), an attempt was also made to adjust the curve with values of A and B that would give $N_A/N_D = 1$. The best fit, as shown in Fig. 2, was obtained with $A = 19163$ cm^{-1} eV$^{1/2}$, $B = 16616$ cm^{-1} eV$^{1/2}$ which gave $N_A = N_D = 6.7 \times 10^{16}$ cm^{-3}.

Based on this information the proposed energy-level diagram and the different transitions observed in $CuInSe_2$ are shown in Fig. 3.

B. Defect chemistry considerations

According to the model proposed by Groenick and Janse[18] the defect chemistry of a ternary compound is dominated by an acceptor-donor majority defect pair. The conditions for the existence of such a pair are determined by the deviations from the molecularity and the valence stoichiometry, Δx and Δy, respectively.

These parameters are defined as

$$\Delta x = \frac{[\mathrm{Cu}]}{[\mathrm{In}]} - 1 \; ; \quad \Delta y = \frac{2[\mathrm{Se}]}{[\mathrm{Cu}] + 3[\mathrm{In}]} - 1 \; , \tag{6}$$

where [Cu], [In], and [Se] represent the total concentration of Cu, In, and Se atoms in the crystal. In the present case, from differential thermal analysis and the phase diagram of $CuInSe_2$ reported elsewhere,[9] we determine that our sample is "In-rich" and thus $\Delta x < 0$. This gives us, according to Ref. 18, five possible majority defect pairs which could be present in the material. These are shown in Table I. However, according to the defect formation energies in $CuInSe_2$,[19] given in Table II, the last two possibilities can be discarded because selenium interstitials and indium on selenium sites are energetically highly unfavorable. Similar considerations apparently indicate that In_{Cu} and V_{Cu} are the predominant active intrinsic defects in In-rich $CuInSe_2$. Hence, we suggest that the donor and acceptor levels at 27 and 54 meV, which need smaller energies of formation, can be attributed to this defect pair. Our interpretation is in agreement with those of Abou-Elfotouh *et al.*[6] who propose that In_{Cu} and V_{Cu} are the dominant defects in In-rich $CuInSe_2$. Neumann *et al.*[16] have also interpreted that the shallow donor level which has always been found in n-type $CuInSe_2$ is due to the In_{Cu} antisite defect. The assignment of the acceptor level to V_{Cu} is in agreement with the results of Migliorato *et al.*[4] and Masse and Redjar,[7] who report an acceptor level at around 40 meV as due to this defect. However, Bardeleben[20] considers that this acceptor is due to the Cu_{In} antisite defect. Such a possibility has been discarded in the present case because Cu_{In} is less probable in In-rich $CuInSe_2$ samples.

The nature of the level at about 90 meV is not completely clear. However, a similar transition observed in photoluminescence studies,[4,7] which disappears when the sample is annealed in Se vapor, has been attributed as due to V_{Se}. Hence, we believe that the transition at 90 meV, observed in the present case, is also due to V_{Se} which has a smaller formation energy than that of the other donor states such as Cu_i, In_i, and In_{Se}.

TABLE I. Majority defect pairs in $CuInSe_2$ under the condition $\Delta x < 0$.

Majority defect pair		Deviation from stoichiometry
Acceptor	Donor	(Δy)
V_{Cu}	In_{Cu}	<0
V_{Cu}	V_{Se}	<0
V_{Cu}	In_i	>0
Se_i	In_{Se}	>0
Se_i	In_i	>0

TABLE II. Formation energies of intrinsic defects in $CuInSe_2$ [after Neumann (Ref. 19)].

Defect type		Formation energy (eV)
Vacancies	V_{Se}	2.4
	V_{Cu}	2.6
	V_{In}	2.8
Interstitials	Cu_i	4.4
	In_i	9.1
	Se_i	22.4
Antisites	In_{Cu}	1.4
	Cu_{In}	1.5
	In_{Se}	5.0
	Se_{In}	5.5
	Se_{Cu}	7.5
	Cu_{Se}	7.5

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