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Dopant-induced band filling and bandgap renormalization in CdO:In films

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Abstract

The effect of carrier concentration on the Fermi level and bandgap renormalization in over 30 indium-doped cadmium oxide (CdO:In) films with carrier concentrations ranging from 1 to $15 \times 10^{20} \text{ cm}^{-3}$ was studied by using the two band **k·p** model with electron-electron and electron-ion interactions. It is shown that the Tauc relation, which is based on parabolic valence and conduction bands, overestimates the optical bandgap in CdO films. Theoretical calculations of the optical bandgap give good agreement with experiments by taking into account the Burstein-Moss effect for a nonparabolic conduction band and bandgap renormalization effects. The band filling and bandgap renormalization in these CdO:In films are about 0.5~1.2 eV and 0.1~0.3 eV, respectively.

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Introduction

Transparent conductive oxides (TCOs) have attracted much interest due to their tremendous importance in applications such as displays, photovoltaic cells, optical communications, gas sensors, and thin-film resistors [1-3]. Cadmium oxide (CdO) exhibiting high electrical conductivity and optical transparency is a promising TCO material. Due to their outstanding properties, undoped CdO films or those doped with trivalent elements have been fabricated by various techniques [4-8]. However, there is still controversy regarding the optical bandgap of CdO [6]. Table 1 shows a large dispersion of the optical bandgap as a function of carrier concentration as taken from recent literature. All the reported optical bandgaps in table 1 were obtained from Tauc plots [9] of α^2 [or $(ahv)^2$] versus hv as derived from transmittance measurements (with some groups also accounting for reflectance). Under most circumstances, it has been ignored that the Tauc relation is based on parabolic valence and conduction bands. As such, the Tauc relation is extensively misused to determine the optical bandgap in doped CdO since the conduction band exhibits clear nonparabolicity [4, 5, 10]. Thus, optical bandgaps obtained from Tauc plots may add controversy when studying the bandgap shift. This is especially true if the object is to determine the carrier-concentration-dependent effective mass due to the conduction-band nonparabolicity.

For heavily doped TCOs, the bandgap shift is the result of two competing effects: bandgap widening via the Burstein-Moss effect, and renormalization due to many-body interactions [11, 12]. In this study, the optical bandgap of many indium-doped cadmium oxide (CdO:In) thin films were investigated using the two band **k·p** model [13] which proved successful for InN [14], $\text{Ga}_x\text{In}_{1-x}\text{N}$ [15], ZnO [16], and CdS [16]. Though Kane's two band **k·p** model was derived from InSb which shows a different valence band dispersion shape at the Gamma point compared to CdO, this model has been previously used to predict the Fermi level in CdO films and good agreement with the experimental data was obtained [5, 17]. Despite the upward valence band at the Gamma point [18], the two band **k·p** model is generally valid for predicting the bandgap shift in CdO. In any case, renormalization due to electron-electron and electron-ion interactions must be accounted for to accurately describe the measured data.

1. Experiment

Pulsed filtered cathodic arc deposition (PFCAD) was utilized to grow the CdO:In films. Separate cadmium and indium rods were used as two source cathodes and were alternately pulsed in order to control the doping level between 0 and 9%. Borosilicate glass microscope slides and c-axis sapphire were used as the substrates. The CdO:In films were grown in oxygen pressures of 3~7 mTorr and at substrate temperatures ranging from room temperature to 425 °C. Optimized electrical properties were typically achieved in 7 mTorr oxygen with a substrate temperature of about 230 °C. Material of similar quality was deposited on the glass and sapphire substrates. Most of the samples were about 230 nm thick. Some thicker films of around 460 nm were also deposited. Details of the growth process have been described elsewhere [8].

Extensive descriptions of the properties of these arc-grown CdO films can be found in our previous work [8], and they are summarized here. X-ray diffraction showed that the as-deposited CdO:In films are polycrystalline with some preferred orientation along the (200) direction. The transmittance of glass substrate with about 230 nm thick CdO:In films is over 80% in the 500~1300 nm wavelength range as measured by a Perkin Elmer Lambda 950 dual beam photo-spectrometer. The carrier concentration was measured in the Van der Pauw geometry using an Ecopia HMS-3000 system with a 0.6 T magnetic field. It ranges from about $1 \times 10^{20} \text{ cm}^{-3}$ in the undoped films to as high as $1.5 \times 10^{21} \text{ cm}^{-3}$ in the heavily doped CdO films. These high quality arc-grown CdO and CdO:In films show a Hall mobility of 70~150 cm^2/Vs .

2. Results and discussions

3.1 Theoretical bandgap calculation

CdO with high carrier concentration shows a nonparabolic conduction band. This nonparabolicity results from the $\mathbf{k} \cdot \mathbf{p}$ interaction across the direct gap between the conduction and valence bands in heavily doped semiconductors [13, 14]. Neglecting perturbations from remote bands, an analytical form of the conduction band dispersion obtained by solving Kane's two band $\mathbf{k} \cdot \mathbf{p}$ model is given by [13, 14]:

$$E_c(k) = E_G + \frac{\hbar^2 k^2}{2m_0} + \frac{1}{2} \left(\sqrt{E_G^2 + 4E_p \frac{\hbar^2 k^2}{2m_0}} - E_G \right) \quad (1)$$

where E_G is the direct bandgap energy of undoped CdO, k is the wave vector, m_0 is the (bare) electron mass, and E_p is an energy parameter related to the momentum matrix element. Due to the nonparabolicity of the conduction band, the effective electron mass is k -dependent [19]:

$$m^*(k) = \frac{\hbar^2 k}{dE_c(k)/dk} \quad (2)$$

At the Fermi level, the effective mass is evaluated from the Fermi wave vector $k_F = (3\pi^2 n)^{1/3}$. Using $E_G = 2.16 \text{ eV}$ [4], the effective mass calculated as a function of electron concentration for different E_p values is shown in figure 1. For the measured data shown in figure 1, the electron effective mass (m^*) of each CdO:In film was calculated from

the (angular) Drude plasma frequency (ω_p) using:

$$m^* = \frac{ne^2}{\varepsilon_0 \omega_p^2} \quad (3)$$

where n is the electron concentration, e is the elementary charge, and ε_0 is the permittivity of free space. For these CdO and CdO:In samples, ω_p was obtained by simultaneously fitting the NIR transmittance and reflectance of each film, and n was taken from Hall measurements [10]. Using Pisarkiewicz's model [20], it has been observed that the nonparabolicity factor and the band edge effective mass of arc-grown CdO:In films are about $0.5 \pm 0.2 \text{ eV}^{-1}$ and $0.16 \pm 0.05 m_0$, respectively [10]. The obtained values are in line with the results using the alpha approximation which was derived from Kane's two band $\mathbf{k}\cdot\mathbf{p}$ model [21].

Figure 1 shows that m^* calculated from the $\mathbf{k}\cdot\mathbf{p}$ conduction band dispersion is strongly dependent on n . Using $E_p=6.5 \text{ eV}$ gives reasonably good agreement with the measured m^* values from the NIR data when taking into account the measurement uncertainties. This result is a bit lower than $E_p=7.5 \text{ eV}$ obtained by Segura *et al.* [6] but it is still in agreement within the error range. However, in their calculation, E_p , m^* , and E_G were simultaneously fit from the optical bandgap and they did not account for bandgap renormalization. For comparison, ZnO has $E_p=13.4 \text{ eV}$ and CdS shows about 14 eV [14, 16]. A large spread was found for GaN and InN. For GaN, E_p ranges from about 7.7 eV [22] to a maximum value of 18.6 eV [16], and InN shows E_p about $9.5 \text{ eV} \sim 18 \text{ eV}$ [14, 23]. Taking $E_p=6.5 \text{ eV}$ into equation (1), the conduction band dispersion energy of CdO can be obtained. To study the effect of E_p carefully, the upper and lower bounds for E_p fitting results showing about 8.5 eV and 4.5 eV are also used for conduction band dispersion calculation.

Besides the Burstein-Moss band filling, bandgap renormalization effects in CdO:In films must also be taken into account. Bandgap renormalization results from the electron-electron and electron-ionized impurity interactions. According to the random perturbation theory by Berggren and Sernelius (BS model) [11], the down-shift of the conduction band due to the electron-electron interaction is (SI units):

$$\Delta E_{e-e} = \frac{e^2 k_F}{2\pi^2 \varepsilon_0 \varepsilon_s} + \frac{e^2 \lambda}{8\pi \varepsilon_0 \varepsilon_s} \left[1 - \frac{4}{\pi} \tan^{-1} \left(\frac{k_F}{\lambda} \right) \right] \quad (4)$$

where $\lambda = 2/\sqrt{\pi} (k_F/a_B)^{1/2}$ is the Thomas-Fermi screening wave vector, $\varepsilon_s=21.9$ is the static dielectric constant of CdO [24], and $a_B = 4\pi \varepsilon_0 \varepsilon_s \hbar^2 / (m^* e^2)$ is the effective Bohr radius. The contribution of the electron-ionized impurity interactions to the conduction band edge shift is [11]:

$$\Delta E_{e-i} = \frac{e^2 n}{\varepsilon_0 \varepsilon_s a_B \lambda^3} \quad (5)$$

It should be mentioned that another useful expression called the Jain model could also be utilized to estimate the bandgap renormalization in CdO films [25]. In fact, the Jain model, which has been demonstrated to be valid for AZO, ITO and other IV, III-V, and II-VI semiconductors [26-28], has a similar physical meaning as the BS model but it is less rigorous

due to its simplified derivation. In this study, compared with the BS model, the Jain model gives a 0.04~0.06 eV larger result depending on the carrier concentration but exhibits a very similar trend.

Taking the conduction-band nonparabolicity and the many-body interaction effects into account, the theoretical bandgap for CdO films can be calculated as a function of carrier concentration.

3.2 Experimentally measured bandgap

Optical bandgaps of thin films can be evaluated from the absorption curves. Using the transmittance and reflectance, the absorption coefficient (α) is calculated by [29].

$$T(h\nu) = \frac{(1 - R)^2 \exp\{-\alpha(h\nu)d\}}{1 - R^2 \exp\{-2\alpha(h\nu)d\}} \quad (6)$$

where d , T , and R are film thickness, transmittance, and reflectance, respectively. In figure 2, it is observed that the absorption edge blueshifts with increasing carrier concentration. Importantly, a lower energy absorption edge is calculated if the reflectance is neglected, as shown in figure 2, resulting in a measured optical bandgap which is reduced by 0.02~0.05 eV. In order to avoid using the parabolic Tauc relation in this inherently nonparabolic system, the bandgap of CdO:In films is calculated using the first derivative of the transmittance spectra from a pseudo-Voigt fit [30]. As shown in figure 3, the transmittance-derived bandgap is typically about 0.1~0.3 eV lower than that obtained from a Tauc analysis of the same spectra [8]. In any case, a clear Burstein-Moss shift of the optical bandgap is observed with increasing carrier concentration.

When comparing the theoretical bandgaps calculated by accounting for nonparabolicity and renormalization, good agreement with the transmittance-derived bandgaps is observed in figure 3. The upper and lower bounds of theoretically calculated bandgaps are also shown in figure 3. All the parameters used in the calculations of the bandgap (E_G , E_P , ϵ_s) have been determined from independent measurements and no parameter has been adjusted further to achieve the good agreement in figure 3. Thus, the data show that the Burstein-Moss shift and bandgap renormalization in these CdO:In films are about 0.5~1.2 eV and 0.1~0.3 eV, respectively. For comparison, the optical bandgaps taken from the literature and listed in table 1 are also shown in figure 3. Importantly, it can be seen that the Tauc relation overestimates the optical bandgap in these CdO:In films and the transmittance-derived values are in better agreement with theory. In contrast, Segura *et al.* reported an underestimation of the optical bandgap in CdO when using the Tauc relation [6]. Their underestimation was concluded by comparing the optical bandgaps of different CdO samples as a function of carrier concentration and not accounting for the non-negligible bandgap renormalization in CdO samples showing high carrier concentration. In this work, the overestimation of optical bandgap is directly deduced from separately obtained theoretical and experimental results using the same spectra from the same samples.

The Fermi level of the CdO:In films is calculated by using Kane's two band $\mathbf{k}\cdot\mathbf{p}$ model and is shown in figure 4. The experimental data in the figure is obtained from the measured optical bandgap by removing the renormalization effects due to the electron-electron and electron-ion interactions. It can be seen that Kane's two band $\mathbf{k}\cdot\mathbf{p}$ theory shows good

agreement with the experimental data. For comparison, the Fermi energy based on a parabolic conduction band is calculated by using the parabolic Burstein-Moss equation.

$$E_F = \frac{\hbar^2}{2m^*} (3\pi^2 n)^{2/3} \quad (7)$$

Using constant effective masses of $0.17 m_0$ [10] and $0.27 m_0$ [17], it is shown that the simple parabolic conduction band model calculating the bandgap shift overestimates the Fermi energy in CdO:In films with high carrier concentration.

3. Conclusions

We have shown the dopant-induced Burstein-Moss band filling and bandgap renormalization in undoped CdO and CdO:In films. By combining the nonparabolic dispersion of the conduction band and the bandgap renormalization effects, it is found that the Tauc relation overestimates the optical bandgap in CdO:In films. Bandgap widening in these films, as evaluated from the derivative of the measured transmittance spectra, can be well described by the **k.p** interaction model when the electron-electron and electron-ion interactions are properly accounted for. Compared with the **k.p** interaction model, the simple parabolic conduction band model overestimates the Burstein-Moss effect in the heavily doped CdO films.

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Table 1 Recently reported optical bandgaps (E_g) of CdO films with various carrier concentrations.

Films	d (nm)	$n (\times 10^{20} \text{ cm}^{-3})$	E_g (eV)	Reference
CdO	114	0.17	2.4	[31]
CdO	576	0.21	2.31	[32]
CdO	160	0.44	2.42	[33]
CdO	330	0.66	2.41	[34]
CdO	500	0.92	2.4	[2]
CdO	659	1.5	2.58	[32]
CdO	100	1.5	2.4	[35]
CdO	480	1.7	2.4	[4]
CdO	450	2.2	2.52	[36]
CdO	320	2.3	2.6	[37]
CdO	300	2.6	2.8	[38]
CdO	152	2.7	3.08	[31]
CdO	530	2.9	2.84	[39]
CdO	500	10.5	2.27	[40]
CdO	1630	12.4	3.05	[39]
CdO:In	450	3.7	2.72	[41]
CdO:In	200	9.3	3.18	[42]
CdO:In	250	10.9	2.97	[34]
CdO:In	150	15.1	3.1	[7]

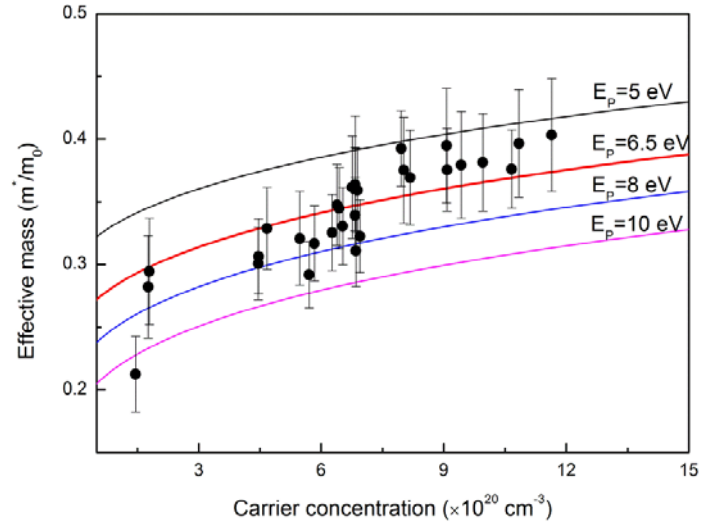


Figure 1 Effective mass of CdO:In films as a function of carrier concentration. The curves are calculated using equation (2) with different E_p values.

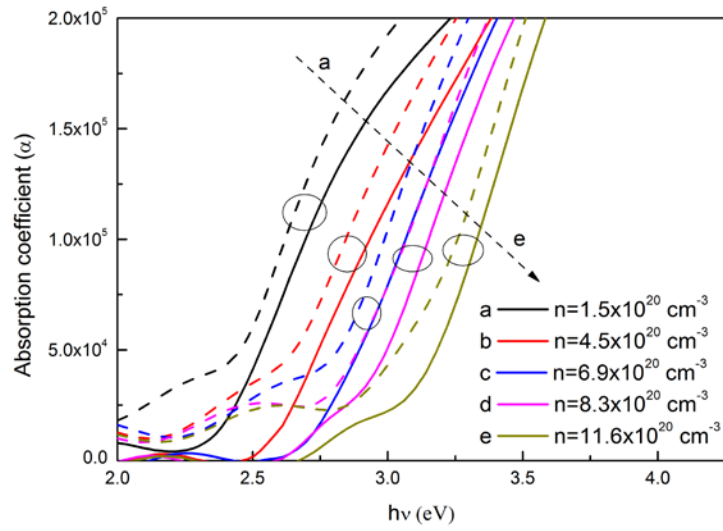


Figure 2 Absorption coefficient of CdO:In films with different carrier concentrations. The solid lines are calculated with the reflectance considered, and the dash lines are the same calculation but without including the reflectance.

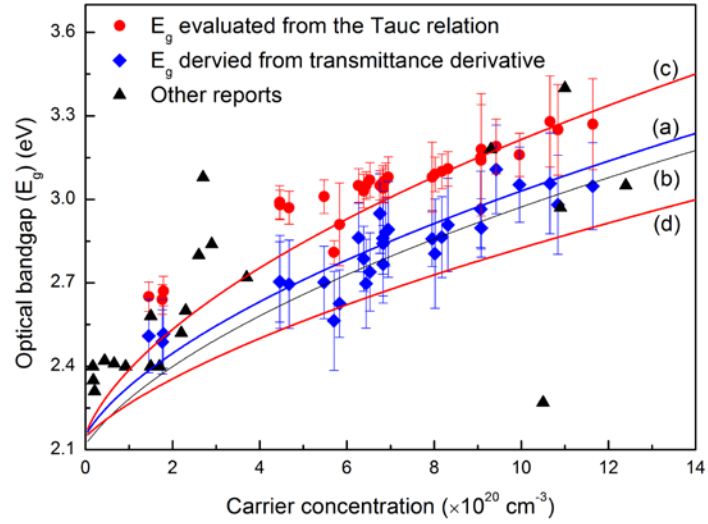


Figure 3 Optical bandgap of pure CdO and CdO:In films as a function of carrier concentration. The curves (a) and (b) are theoretically calculated bandgaps based on the BS model and the Jain model, respectively. The curves (c) and (d) are the upper and lower bounds of theoretically calculated bandgaps based on the BS model using $E_p=8.5$ eV and 4.5 eV, respectively.

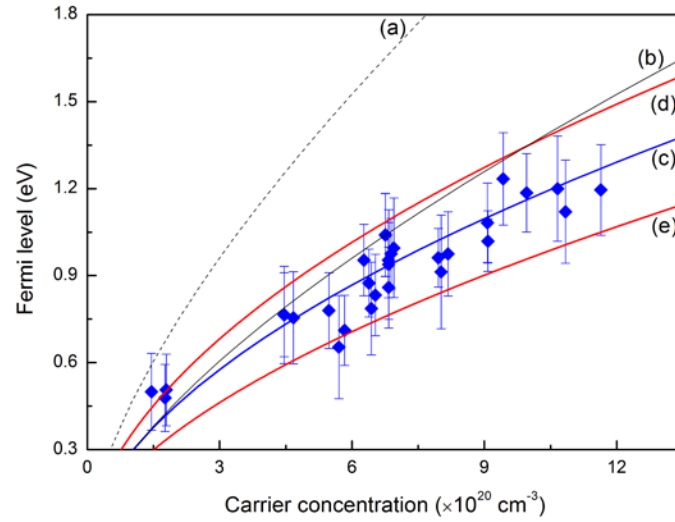


Figure 4 Fermi level of the CdO:In films with the conduction band edge taken as 0. The measured values come from optical bandgap measurements after bandgap renormalization has been accounted for. The fundamental bandgap of CdO is set to be 2.16 eV [4]. (a) and (b) a parabolic conduction band using a constant effective mass of $0.17 m_0$ [10] and $0.27 m_0$ [17], respectively, (c) $\mathbf{k}\cdot\mathbf{p}$ model, (d) and (e) the upper and lower bonds of $\mathbf{k}\cdot\mathbf{p}$ model using $E_p=8.5$ eV and 4.5 eV, respectively.