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Journal

Energy Technology, 6(1)

ISSN

2194-4288

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Publication Date

2018

DOI

10.1002/ente.201700641

Peer reviewed



Engineering Electronic Band Structure of Indium-doped $\text{Cd}_{1-x}\text{Mg}_x\text{O}$ Alloys for Solar Power Conversion Applications

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CdO-based transparent conducting oxide thin films have great potential applications in many optoelectronic devices because of their high mobility, low resistivity, and high transparency over a wide spectral range. However, because of the low band gap of only 2.2 eV, the transparency of this material is limited in the UV spectral range. Alloying of undoped CdO with a larger band gap material such as MgO increases the band gap but tends to degrade electrical conductivity. Recently, it has been demonstrated that In doping of CdO greatly improves the electrical characteristic of this material

by increasing both the carrier density and the mobility. In this work, we present a comprehensive study on CdMgO alloys doped with up to 4% In. We show that the doping with In extends the composition range of conducting films with a composition of up to 40% of Mg and a band gap of 3.5 eV. Our results could open up a new pathway to transparent conductive oxides that could be used as low-resistivity contacts and UV-transparent electron emitter windows in thin-film photovoltaic technologies.

Introduction

The last decades have witnessed an impressive growth in applications of conductive transparent materials (TCMs).^[1] Such materials are frequently a necessary component of electronic or optoelectronic devices and widely used as electrodes for liquid-crystal displays, thin-film transistor screens,^[1–3] and a variety of different thin-film solar cell technologies.^[3–6] Transparent conductive oxides (TCOs) are the most extensively studied TCMs. Thus, F-doped tin oxide (FTO), Sn-doped In oxide (ITO),^[1–3] or Al-doped ZnO (AZO)^[7] are well-established and commercially used TCOs. All these materials can be efficiently n-doped despite their relatively large band gap. The propensity of simple metal oxides for the n-type conductivity can be attributed to a very low location of the conduction band edge (CBE) relative to the vacuum level.^[1,8] In a stark contrast, despite years of intense studies there exists no well-known p-type TCMs with conductivity and transparency comparable to their n-type counterparts.^[9,10] Again, this can be understood by the fact that all the wide-gap semiconductors have a low location of the valence band edges (VBE) and cannot be efficiently p-doped.^[11,12]


CdO with a rock-salt crystal structure is one of the oldest TCOs. Recently it has received growing attention as it has been shown that it can be doped with In to achieve electron concentrations higher than 10^{21} cm^{-3} with mobilities exceeding $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[13–17] The high electron mobility of CdO is a direct consequence of a very large dielectric constant ($\epsilon_0 = 22$) and an efficient screening of ionized impurity potentials and reduced electron scattering in CdO.^[16] The less-efficient electron scattering is also responsible for reduced free-carrier absorption, making CdO a unique material with very good transparency in the infrared spectral region. The excellent IR

transparency offers a potential of using CdO-based TCOs for solar-cell technologies that rely on the infrared part of the solar spectrum. This includes high-efficiency multi-junction and Si photovoltaics (PVs) that currently use metal grids for transparent contacts.

One of the major disadvantages of CdO is its relatively small intrinsic direct band gap of only 2.2 eV. Even though the Burstein–Moss effect caused by free carriers in the conduction band can shift the absorption edge to about 3 eV in most heavily doped CdO, this is still not sufficient for the PV applications that utilize the UV part of the solar spectrum.^[16] Herein, we explore methods for improving short-wavelength transparency of CdO-based TCOs by alloying this material with MgO, a larger band gap metal oxide with the same (rock salt) crystal structure. We have synthesized In-doped CdMgO ($\text{Cd}_{1-x}\text{Mg}_x\text{O}:\text{In}$ or $\text{CdMgO}:\text{In}$) alloys in the whole composition range and show that conducting materials can be obtained with band gaps as high as 3.5 eV. We show that CdMgO:In could be used for transparent windows and electron emitters in thin-film PV technologies.

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Results and Discussion

Figure 1 shows the grazing incident X-ray diffraction (GIXRD) patterns of $\text{Cd}_{1-x}\text{Mg}_x\text{O}:\text{In}$ alloy thin films over the entire composition range. Patterns from CdO-rich alloys consist of four diffraction peaks corresponding to the (111),

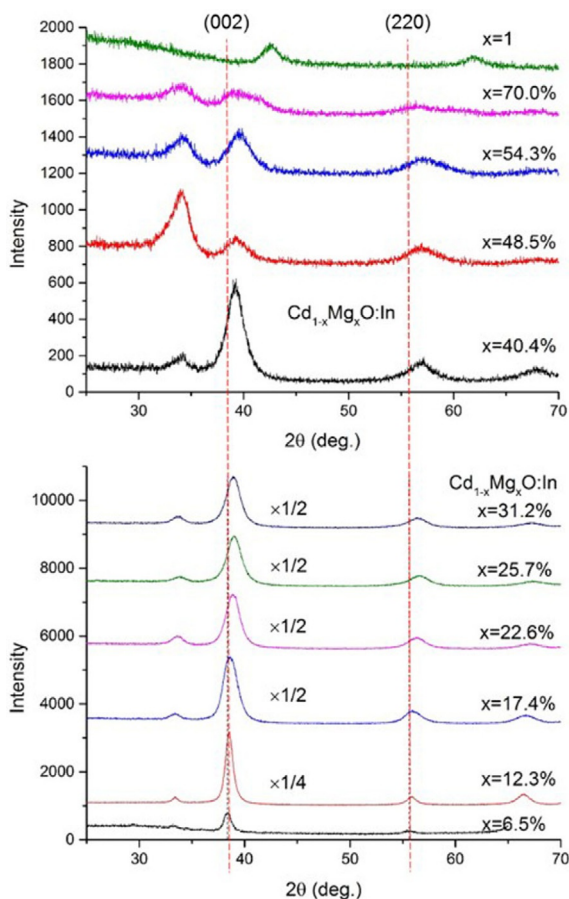


Figure 1. GIXRD patterns of $\text{Cd}_{1-x}\text{Mg}_x\text{O}:\text{In}$ alloys films with x in the range of 0.065 to 1.

(002), (220), and (113) planes at $\approx 33^\circ$, 38° , 55° , and 66° , respectively. As both CdO and MgO have a rock-salt structure with lattice parameters of 4.6958 and 4.212 Å, respectively, the positions of all peaks shift to higher diffraction angles with increasing Mg content in the alloy film. The Mg content in the alloy can be estimated from the lattice parameter calculated from the diffraction peaks according to Vegard's law. A comparison of the Mg content x in $\text{Cd}_{1-x}\text{Mg}_x\text{O}:\text{In}$ measured by GIXRD and Rutherford backscattering (RBS) is shown in Figure 2. It reveals that for $x > 0.3$ the Mg content measured by GIXRD becomes significantly lower than that determined from RBS. Note that RBS measures the total Mg content in the alloy irrespective of the site occupancy, whereas, in principle, GIXRD measures Mg atoms substituting Cd sites. However, it should be noted that the shift in diffraction angles in GIXRD can also arise from lattice distortion due to strain and defects such as interstitials and vacancies. In

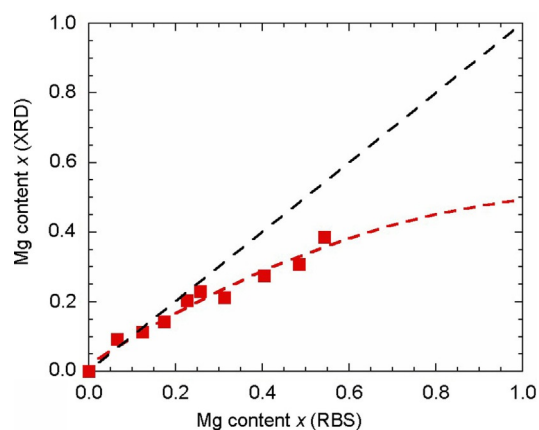


Figure 2. Comparison of Mg content x in $\text{Cd}_{1-x}\text{Mg}_x\text{O}:\text{In}$ measured by XRD and RBS.

the following discussion we use GIXRD results as a measure of the Mg content. From the width of the diffraction peaks, we also estimate that the average grain size decreases from ≈ 10 to 3 nm with increasing Mg content.

Results of Hall-effect measurements are shown in Figure 3 as a function of the Mg content. The results in Figure 3 indicate that both, electron concentration (n) and electron mobi-

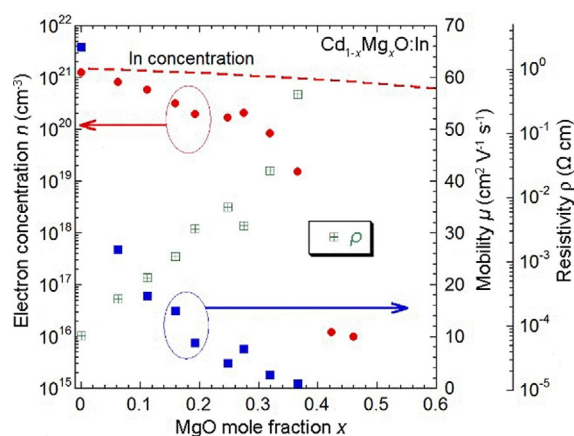


Figure 3. Composition dependence of the electrical properties (electron concentration n , mobility μ , and resistivity ρ) of $\text{Cd}_{1-x}\text{Mg}_x\text{O}:\text{In}$ alloys. The dashed line represents the concentration of In doping in the alloy.

lity (μ) drop rapidly from $\approx 1.3 \times 10^{21}$ to $< 10^{19} \text{ cm}^{-3}$ and ≈ 70 to $< 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively with increasing x . This is in agreement with results reported earlier by Chen et al. where a reduction of the electron concentration with increasing Mg content was observed in undoped $\text{Cd}_{1-x}\text{Mg}_x\text{O}$ alloys.^[18] The reduction of n and μ in undoped samples was explained by a rapid upward shift of the CBE with increasing Mg concentration.^[18] We note that, because of the use of a single In-doped target ($\text{CdO}:\text{In}$), the In concentration linearly depends on the alloy composition as shown by the dashed line in Figure 3. However, the results in Figure 3 indicate that the electron concentration is lower and decreases faster with the composition than the In doping level.

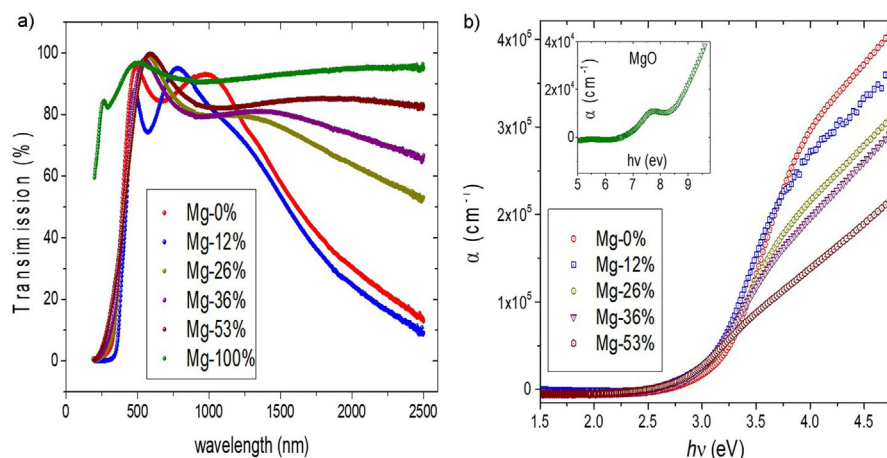


Figure 4. Composition dependence of a) Transmittance and b) absorption coefficient (α) of $\text{Cd}_{1-x}\text{Mg}_x\text{O}:\text{In}$. The inset in (b) shows the absorption coefficient of pure MgO (no alloy).

Measurements of the optical properties of $\text{Cd}_{1-x}\text{Mg}_x\text{O}:\text{In}$ films are illustrated in Figure 4. The transmittance results in Figure 4a indicate a very good IR transparency even for the samples with very large electron concentration. The absorption coefficients (α) of films with different Mg concentrations were obtained using the Beer–Lambert law with transmittance and reflectance data and are shown in Figure 4b. Interestingly, for all compositions with up to 36% Mg the absorption curves overlap at low α with a common absorption onset at about 3 eV. This is a reflection of the Burstein–Moss shift of the absorption edge caused by electron occupation of the conduction band states. To determine the intrinsic band gap we applied a procedure that accounts for the Burstein–Moss shift as well as corrections to the band gap originating from electron–electron and electron–ion interactions.^[19] As is seen in Figure 5, the overall correction to the band gap can be as large 0.8 eV for CdO with $1.2 \times 10^{21} \text{ cm}^{-3}$ electrons in the conduction band. Results in Figure 5 show that alloying CdO with MgO results in a clear blue-shift of the intrinsic

band gap from 2.2 eV in CdO to about 7.8 eV in MgO. The dependence can be described by a standard formula for the composition dependence of the band gap of semiconductor alloys with a bowing parameter $b = 3.1 \text{ eV}$ (Figure 5, inset).

To determine the composition dependence of the band offsets we use previously determined locations of the CBEs of 5.9 eV for CdO and 0.9 eV for MgO relative to the vacuum level.^[20,21] The composition dependencies of the band edges are shown in Figure 6. It is seen that the increase of the band gap is mostly associated with a rapid upward movement of CBE. This result has important implications for understanding the electrical properties of the alloy. Figure 6 shows the composition dependence of the Fermi energy relative to the vacuum level calculated from the measured electron concentration. Interestingly, the Fermi energy shifts down from -4.2 eV in CdO to saturate at -4.9 eV for $x > 0.2$. The saturation energy level perfectly coincides with the location of the Fermi level stabilization energy (E_{FS}), which is a universal energy reference defined by the location of the Fermi energy in the presence of a large concentration of native de-

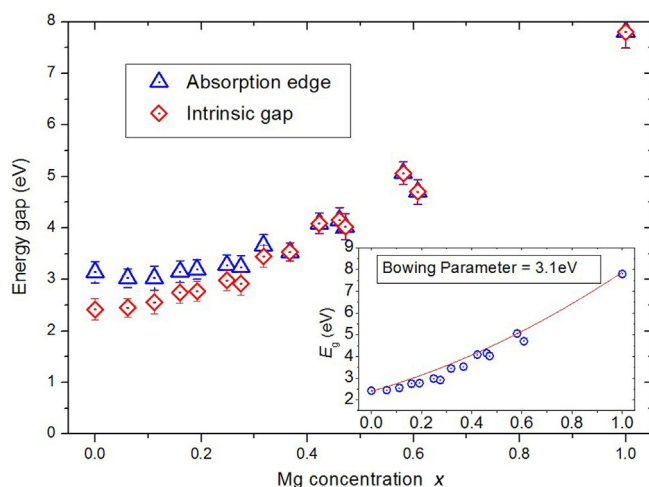


Figure 5. Optical absorption edge (E_{opt}) and intrinsic band gap (E_g) of $\text{Cd}_{1-x}\text{Mg}_x\text{O}:\text{In}$ films as a function of Mg composition x . The inset shows the fit of the intrinsic band gap using a bowing parameter $b = 3.1 \text{ eV}$.

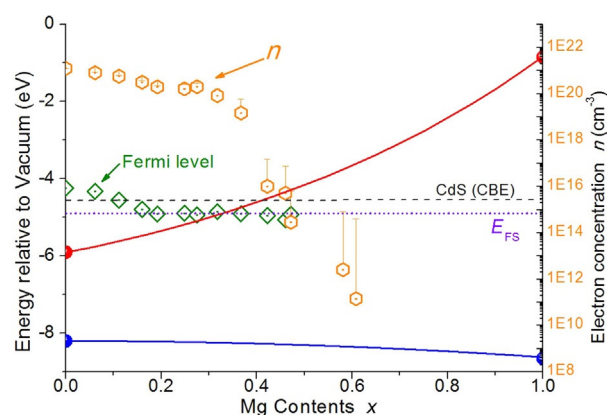


Figure 6. Composition dependence of the conduction and valence band edge energies relative to the vacuum level. Also shown are the Fermi level (green symbols) calculated from the experimental electron concentration (orange symbols). The horizontal lines represent the energy of the CBE of CdS (dashed line) and E_{FS} (dotted line).

fects.^[22] This provides a straightforward explanation for the composition dependence of the Fermi energy and thus also electron concentration. Thus, at small Mg content ($x < 0.2$) the electron concentration is determined by the large concentration of In donors and the Fermi level is located above E_{FS} . The observed reduction of the electron concentration with increasing Mg content is associated with the reduced concentration of In donors and an increased compensation by native acceptor-like defects. Eventually, as is seen in Figure 6, the native defects dominate the electrical properties and pin the Fermi energy at E_{FS} for $x > 0.2$. The electron concentration drops exponentially for $x > 0.3$ when the E_{FS} and thus also the Fermi energy fall below the CBE.

Previously, in the work of Chen et al. for undoped $Cd_{1-x}Mg_xO$ films, as the CBE of the alloy moved above E_{FS} for $x > 0.28$, the material became insulating ($n < 10^{14} \text{ cm}^{-3}$).^[18] Herein, we show that In doping extends the range of conducting alloy composition to $x \approx 0.38$, where the CBE is already above E_{FS} but the alloy is still conducting with $n \approx 2 \times 10^{19} \text{ cm}^{-3}$ and $\rho \approx 0.03 \text{ } \Omega \text{ cm}^{-1}$. Note that at this composition the intrinsic energy gap $E_g \approx 3.5 \text{ eV}$ and the CBE is located at about 4.5 eV below the vacuum level, indicating that, as is illustrated in Figure 6, n-type CdMgO could replace CdS as an electron-emitter window in CdTe PV technology. The important advantage of the CdMgO over CdS is its much larger band gap and hence very little absorption of the solar light.

Conclusions

We performed an extensive study of In-doped CdMgO alloys synthesized by radio frequency magnetron sputtering. It is shown that alloying allows engineering of the band gap and the location of the conduction-band-edge energy whereas intentional In doping extends the range of the alloy compositions exhibiting n-type conductivity. CdMgO:In alloys with about 40% Mg have a band gap of 3.5 eV and a reasonable n-type conductivity. With the location of the conduction band edge at about 4.5 eV below the vacuum level the alloys offer a potential as a replacement for CdS as UV-transparent electron emitter for thin-film photovoltaics technologies.

Experimental Section

CdMgO:In thin film samples were deposited using a dual-gun radio frequency (RF) magnetron sputtering system. An In-doped CdO (4 at%) and a MgO targets were used to grow the alloy of CdMgO:In. The composition of the alloys was controlled by varying the power of the two guns. As only the CdO target was doped with In, the doping level decreased with increasing Mg composition. Prior to deposition, the chamber was pumped down to $\approx 1 \times 10^{-6}$ Torr (1 Torr = 133 Pa), and the background pressure was maintained at 5 mTorr by flowing pure Ar into the chamber during deposition. All depositions were carried out at a substrate temperature of 200°C on soda-lime glass and sapphire substrates.

The crystalline structure of the CdMgO:In films was determined by GIXRD. Film composition and thickness were measured by RBS using a 3.04 MeV He^{++} beam in a 165° backscattering ge-

ometry. Film thickness was further confirmed by X-ray reflectivity (XRR) measurements. Carrier concentration and mobility of the films were obtained from Hall-effect measurements in the van der Pauw configuration. Optical properties were studied by transmission and reflection measurements using a PerkinElmer Lambda 950 spectrophotometer in the spectral range of 200 to 2500 nm. All measurements were carried out at room temperature (300 K).

Acknowledgements

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 and by Singapore National Research Foundation through the Singapore-Berkeley Research Initiative for Sustainable Energy (SinBeRISE) CREATE Program. The characterization work performed at CityU HK was supported by the General Research Fund of the Research Grants Council of Hong Kong SAR, China, under Project No. CityU 11267516.

Keywords: band-structure engineering • cadmium magnesium oxide • photovoltaics • thin films • transparent conductors

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Manuscript received: September 5, 2017
Revised manuscript received: October 25, 2017
Accepted manuscript online: October 26, 2017
Version of record online: November 20, 2017