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Phys. Rev. Materials **7**, 074602 — Published 13 July 2023

DOI: [10.1103/PhysRevMaterials.7.074602](https://doi.org/10.1103/PhysRevMaterials.7.074602)

# Transition metal elements as donor dopants in CdO

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## ABSTRACT

CdO has been shown to achieve a high electron concentration  $N$  ( $>10^{21}\text{cm}^{-3}$ ) doped and at the same time a high mobility  $\mu$  ( $>100\text{cm}^2/\text{Vs}$ ) when doped with conventional shallow dopants (In or Ga), and consequently making it a transparent conducting oxide with very low resistivity  $\rho < 10^{-4}\ \Omega\text{-cm}$ . In this work, properties of CdO thin films doped with a series of transition metal elements (CdO:TM) with partially filled 3d and 4d shells, including Sc, Ti, V, Cr, Fe, Y, Mo and W were investigated. We find that doping with these TM elements can effectively increase the  $N$  in CdO to a maximum  $N(N_{max})$  of  $\sim 7\text{-}12 \times 10^{20}\text{cm}^{-3}$  with a dopant concentration  $x_{max}$  of 4-7%. However, unlike CdO:In, the  $\mu$  of CdO:TM films drops rapidly from  $>100$  to  $<10\ \text{cm}^2/\text{Vs}$  as the dopant concentration  $x$  increases, so that they can only achieve a minimum  $\rho$  of  $\sim 1\text{-}2 \times 10^{-4}\ \Omega\text{-cm}$ ,  $\sim$ a factor of 2-3 higher than that in CdO:In. As a result, free carrier absorption and plasma reflection effects limit their optical transparency to  $<1200\ \text{nm}$ . For most 3d TM dopants, qualitatively a higher d-donor level  $E_{d,donor}$  gives rise to higher  $E_{F,max}$  or a higher  $N_{max}$ . Although at low  $x$ , the optical bandgap  $E_{opt}$  of CdO:TM follows the calculated values due to free carrier effects, as  $x$  increases,  $E_{opt}$  values are significantly higher than the calculated values. This is believed to be the effects of the anticrossing interaction of the localized d-levels and the extended CdO conduction band (CB) states, giving rise to a lower occupied  $E_-$  and an upper unoccupied  $E_+$  sub-bands. The restructured CBs have much flatter dispersion, which also results in a much higher effective mass  $m_e^*$ , and hence can also explain the much lower  $\mu$  of CdO:TM films with high  $N$ .

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## INTRODUCTION

Transparent conducting oxides (TCOs) are wide gap oxide semiconductors with a high conductivity ( $\sim 10^3$ - $10^4$  S/cm) and optical transparency which have been widely used in recent years for various applications, [1,2,3,4,5,6] such as photovoltaic solar cells, flat-panel displays, light emitting diodes and optoelectronic devices [7,8,9,10,11,12,13]. Up to now, Sn doped  $\text{In}_2\text{O}_3$  (ITO), F doped  $\text{SnO}_2$  (FTO) and Al doped ZnO (AZO) are the most extensively used TCOs [1,5,13,14,15,16,17]. Although these conventional TCOs have high conductivity and good transparency over the visible and ultraviolet parts of the solar spectrum, due to their high electron concentration and low mobility, which gives rise to strong free carrier absorption and plasma reflection at the  $\lambda > 1000$  nm, their transparency for the long wavelength photons is limited. This drawback limits their application in devices which utilize near infra-red photons, such as Si PVs and high efficiency multi-junction solar cells. In order to extend the applications of these TCOs, their mobility has to be improved so that a high conductivity can be attained with only moderate electron density. Recent reports demonstrated that instead of Sn doping,  $\text{In}_2\text{O}_3$  can achieve much higher mobility when doped with transition metal (TM) dopants (such as Mo, W, Ti and Zr) [18,19,20,21,22,23,24] and H [25,26,27]. Similar mobility enhancement was also reported for  $\text{SnO}_2$  doped with TM dopant Ta [28]. In particular, Swallow et al. reported Mo doped  $\text{In}_2\text{O}_3$  thin films with a resistivity of  $< 10^{-4}$   $\Omega$ -cm and a mobility as high as  $150 \text{ cm}^2/\text{V-s}$  grown by chemical vapor deposition [20]. This enhanced mobility in  $\text{In}_2\text{O}_3$  was explained by the Mo 4d donor states being resonant in the conduction band of  $\text{In}_2\text{O}_3$ , and hence do not modify the conduction band dispersion.

Recently, CdO has received considerable attention because of its high mobility and electron concentration [29,30]. It has been shown that appropriately doped CdO can have electron concentration exceeding  $10^{21} \text{ cm}^{-3}$  and still has a mobility higher than any of the previously studied TCOs [30,31,32]. Electrical and optical properties of the CdO doped with various common group III donor species, including In, Ga, Al, have been extensively studied [31,33,34,35], and these common donors were demonstrated to be effective to increase the electron concentration to  $> 10^{21} \text{ cm}^{-3}$  and still maintaining a high mobility of  $> 100 \text{ cm}^2/\text{V-s}$ . Hence, highly conducting CdO thin films with a resistivity  $< 10^{-4}$   $\Omega$ -cm and a high transparency  $> 85\%$  over a wide spectral window of  $400 < \lambda < 2000$  nm have been achieved. However, only a few works on the doping of CdO with transition TM dopants have been reported [31,36,37,38,39].

It has been shown that a TM element with  $4s^2 3d^n$  electronic configuration (e.g. Sc, Ti, V, Fe, Cr) can act as a donor when substituting cation atoms in II-VI compounds by changing its d-level configuration from  $3d^n$  to  $3d^{n-1}$ . Because of the highly localized nature of d states the energies of the donor levels remain constant relative to the vacuum level ( $E_{vac}$ ) [40]. The energies of the donor-levels vary from  $\sim -4.8$  eV for Ti to  $\sim -5.8$  eV for Cr. Since the CdO conduction band minimum (CBM) is located at  $-5.9$  eV, these TM dopant donor levels typically lie above the CdO CBM and can dope CdO by dropping an electron from the d-level to the conduction band. Yang et al. compared properties of In doped CdO with  $3d$  TM dopants (Y and Sc). [31] They found that while both Y and Sc increase the electron concentration in CdO up

to  $\sim 7 \times 10^{20} \text{ cm}^{-3}$  the electron mobility dropped to  $< 10 \text{ cm}^2/\text{Vs}$  with increasing dopant concentration. This is in contrast to In doped CdO which showed a high mobility of  $\sim 70 \text{ cm}^2/\text{Vs}$  for In concentration  $> 8\%$ . They attributed this to the presence of d-states in Y and Sc which affect the CB dispersion of CdO.

In this work, we studied the doping of CdO with different transition metal (TM) elements with partially filled  $3d$  or  $4d$  orbitals, namely, Sc, Ti, V, Cr, Fe and Y. The doped CdO thin films were grown by radio-frequency (RF) magnetic sputtering (Ti, V, Y) and pulsed filtered cathodic arc deposition (PFCAD) (Sc, Ti, Cr, Fe). We show that TM dopants act as donor dopants in CdO and when the dopant concentration is high enough the d-states can modify the electronic band structures of CdO. Such modification affects both the electrical and optical properties of CdO. The maximum electron concentration achieved through TM doping is related with the position of the localized donor d-levels of different transition metal elements.

## EXPERIMENTAL

The TM doped CdO thin films were synthesized by two different methods, radio frequency magnetron sputtering and pulsed filtered cathodic arc deposition (PFCAD) [41]. The Ti, Fe, Cr, and Sc doped CdO were deposited by dual cathode PFCAD. Films were deposited on soda lime microscope glass slides at  $250^\circ\text{C}$  with pure oxygen ( $\text{O}_2$ ) background pressure of about 5 mTorr. The ratio of transition metal elements and Cd can be controlled by the pulsing sequence of the respective metallic cathodes. The pulse duration is 1 ms with a current amplitude of 600 A. The rate of pulse is 1 pulse per second. A total of 1200~1800 pulses were used for each sample. Ti, V and Y doped CdO were deposited by RF magnetron sputtering. A  $\text{TiO}_2$ , a  $\text{V}_2\text{O}_3$  and a  $\text{Y}_2\text{O}_3$  ceramic targets were co-sputtered with a CdO target for Ti, V and Y doping, respectively. The composition of the dopants was controlled by varying the power of the dopant targets. The films were also deposited on soda lime microscope glass slides at either room temperature or  $270^\circ\text{C}$  with pure argon (Ar) pressure of about 5 mTorr. The deposition time was varied from 15 to 20 min to achieve a film thickness of  $\sim 100\text{-}200 \text{ nm}$ .

The composition and thickness of the samples were measured by Rutherford backscattering spectrometry (RBS) using a 3.04 MeV  $\text{He}^{++}$  ion beam at a backscattering angle of  $165^\circ$ . The thickness of the films ranged from 100 to 200 nm. A typical RBS spectrum from a 157 nm CdO doped with  $\sim 3.2\%$  V is shown in Fig. S1 in the Supplementary Materials [42]. The RBS spectra were analyzed using the software package SIMNRA [43]. The crystal structure of the films was determined by x-ray diffraction (XRD). Fig. S2 in [42] shows an XRD pattern from the same sample as in Fig. S1. Diffraction peaks from the (111) and (200) planes of rocksalt CdO can be clearly observed. The relatively sharp peaks with high intensity suggest that the samples are polycrystalline with an average grain size of  $\sim 20 \text{ nm}$  as estimated from the peak width using Scherrer's equation. Electrical properties were determined by Hall Effect measurements in the van der Pauw geometry using an Ecopia HMS3000 system with a 0.55 T magnet at room temperature. Room temperature optical properties of the films were determined from optical transmission and reflectance spectra measured with a Perkin-Elmer Lambda 950 spectrophotometer.

## RESULTS AND DISCUSSION

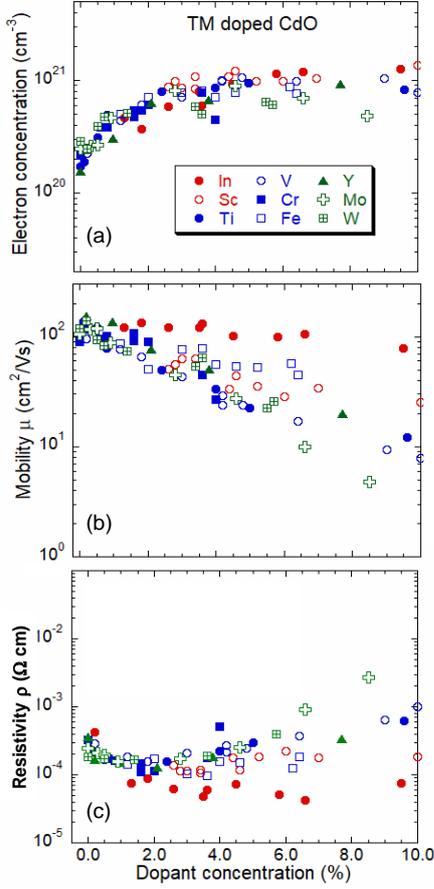


Fig. 1. A comparison of electrical properties: (a) electron concentration  $N$ , (b) mobility  $\mu$ , and (c) resistivity  $\rho$  of CdO thin films doped with In and various TM dopants (Sc, Ti, V, Cr, Fe, Y, Mo and W).

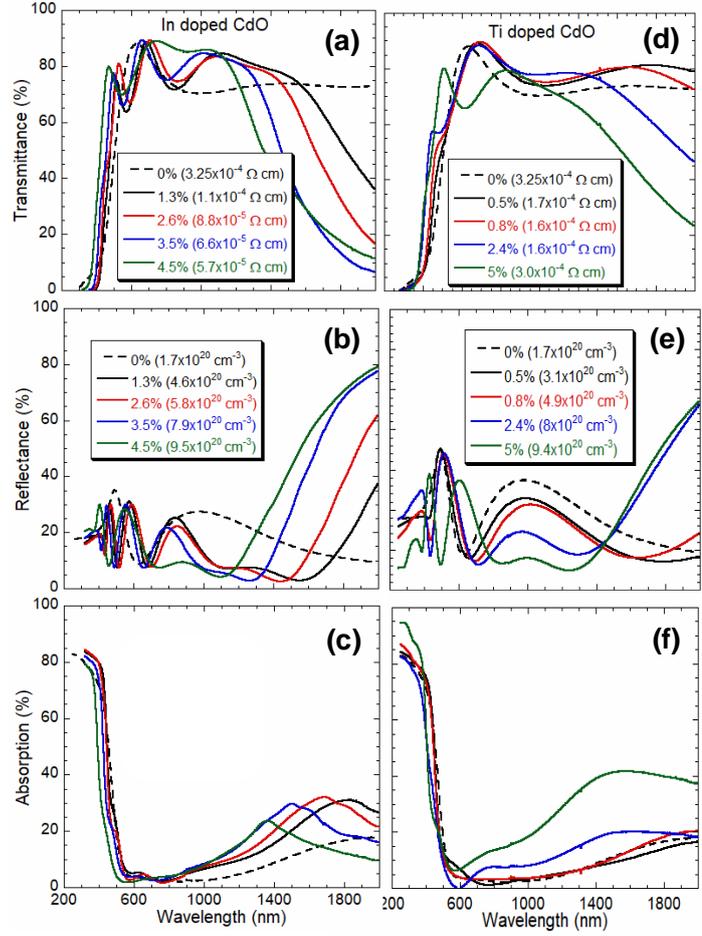


Fig. 2 A comparison of optical properties of In doped ((a) Transmittance, (b) Reflectance, (c) Absorption) and Ti doped ((d) Transmittance, (e) Reflectance, (f) Absorption) CdO thin films. The resistivity  $\rho$  and electron concentration  $N$  of the films is given in parenthesis in the figure legend of (a, d) and (b, e), respectively.

Figure 1 (a) shows the electron concentration  $N$ , (b) the mobility  $\mu$  and (c) the resistivity  $\rho$  of CdO doped with increasing concentration of TM elements  $x$  from 0 to 10 mole %. Effects of TM dopants, including Sc, Ti, V, Cr, Fe, Y, Mo and W are directly compared to In dopants. Note that CdO thin films doped with Mo and W doped were sputter deposited at room temperature followed by rapid thermal annealing at  $300^\circ\text{C}$  for 600 s in  $\text{N}_2$ . In general, similar to In doping, the  $N$  increases with increasing TM dopant concentration and reaches a maximum  $N$  ( $N_{max}$ ) of  $\sim 7\text{-}12 \times 10^{20} \text{ cm}^{-3}$  with a dopant concentration  $x_{max}$  of 4-7%. This confirms that TM elements with partially filled d orbitals ( $3d$  or  $4d$ ) are effective donors in CdO, and possibly also for other wide gap oxides such as  $\text{In}_2\text{O}_3$ ,  $\text{SnO}_2$  and  $\text{ZnO}$ . However, the  $\mu$  of CdO films doped with all TM elements drops sharply to as low as  $<10 \text{ cm}^2/\text{Vs}$  as  $x$  increases. The strong reduction in  $\mu$  with  $x$  was reported previously for Sc, Y, and V doped CdO [31, 38,39]. This is in stark contrast to CdO films doped with In (and also Ga) which maintain a high  $\mu$  of  $\sim 100 \text{ cm}^2/\text{Vs}$  even with  $x \sim 10\%$  [31,34,44]. Hence, the decrease of  $\mu$  with increasing  $x$  in CdO:TM cannot be explained by an

increase in ionized impurity scattering. As a direct consequence, the minimum resistivity  $\rho$  of CdO:TM films is  $\sim 1\text{-}2 \times 10^{-4} \Omega\text{-cm}$ , which is comparable to most conventional TCOs [1,3,2]. In contrast, because of the high  $N_{max}$  and  $\mu$ , CdO:In can achieve a  $\rho$  as low as  $5 \times 10^{-5} \Omega\text{-cm}$ .

The lower  $\mu$  for CdO:TM would also affect their optical properties. As an example, Figure 2 compares optical properties of CdO:In and CdO:Ti films with different  $x$ . Fig. 2 (a)-(c) shows respectively the Transmittance, Reflectance and Absorption for CdO:In films with different  $x$ . The  $\rho$  and  $N$  for the different films are given in parenthesis in the legend of Fig 2 (a) and (b), respectively. Similar plots for CdO:Ti are shown in Figs (d)-(f). Fig. 2 (a) shows that the CdO:In film with  $x=4.5\%$  has a very low  $\rho \sim 5.7 \times 10^{-5} \Omega\text{-cm}$  and a high transmittance  $T$  up to  $\lambda \sim 1200$  nm. The drop in  $T$  at  $\lambda > 1200$  nm is related to the high  $N \sim 9.5 \times 10^{20} \text{cm}^{-3}$  in the sample, which gives rise to a strong free carrier absorption (FCA) (Fig. 2 (c) and plasma reflection (Fig. 2 (b) at high  $\lambda$ ). As a comparison, the CdO:Ti film with  $x=5\%$  has a comparable  $N \sim 9.4 \times 10^{20} \text{cm}^{-3}$  but its  $T$  drops at a much shorter  $\lambda$  of 1000 nm. This is attributed to the much stronger FCA due to its low  $\mu \sim 22 \text{cm}^2/\text{Vs}$ . Using the classical Drude model, the FCA coefficient  $\alpha_{FCA}$  can be expressed as

$$\alpha_{FCA} = \frac{e^3 \lambda^2 N}{4\pi^2 \mu m_e^* n \epsilon_0 c^3} \quad (1)$$

where  $e$  is the electron charge,  $N$  is the carrier concentration,  $\epsilon_0$  is the static dielectric constant,  $n$  is the refractive index,  $m_e^*$  is the electron effective mass and  $c$  is the speed of light. Comparing the absorption at  $\lambda=1200$  nm, the In and Ti doped CdO with  $N \sim 9.4 \times 10^{20} \text{cm}^{-3}$  is 15 and 30%, respectively. Fig. 3 compares the Transmittance spectra of several TM doped CdO with  $x \sim 3\text{-}4\%$  and a similar  $\rho \sim 2 \times 10^{-4} \Omega\text{-cm}$  with an CdO:In film with a much lower  $\rho \sim 8 \times 10^{-5} \Omega\text{-cm}$ . While CdO:TM films are transparent up to

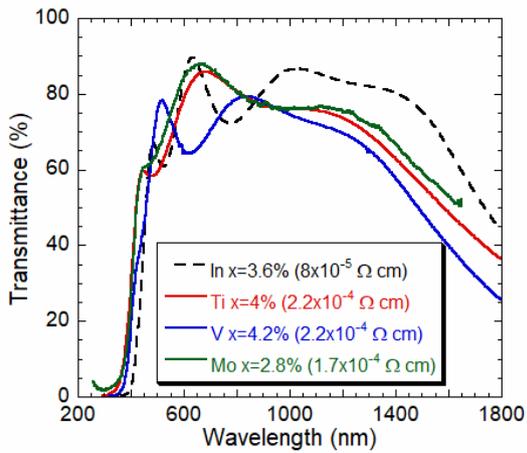


Fig. 3 Transmittance of In doped and TM doped CdO thin films with dopant concentration  $x \sim 3\text{-}4\%$ . The resistivities of the films are given in parenthesis in the figure legend.

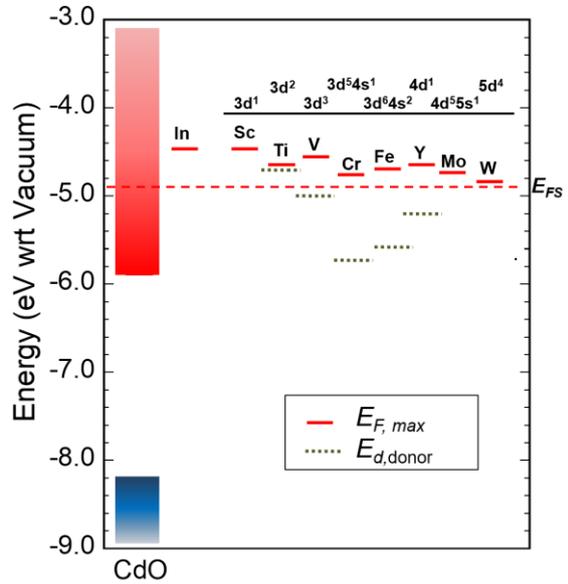


Fig. 4 A schematic diagram showing the Fermi level positions  $E_{F,max}$  (red lines) for In and TM doped CdO with  $N_{max}$ . Energy positions of the corresponding  $d$  donor levels  $E_{d,donor}$  (green dotted lines) and the Fermi level stabilization energy  $E_{FS}$  (red dashed line) are also shown.

$\lambda \sim 1200$  nm, the CdO:In film with a factor of  $\sim 3$  lower  $\rho$  has a transparency window extending to  $\lambda > 1400$  nm. Hence, although TM elements are effective donors in CdO, because of their lower  $\mu$ , their optical properties are not as desirable.

When the electron concentration is high ( $N > 10^{19} \text{cm}^{-3}$ ) in a semiconductor, carrier filling of the conduction band results in a blue shift (or Burstein-Moss shift ( $\Delta E_{BM}$ )) in the absorption edge. At the same time, electron-electron interaction ( $\Delta E_{e-e}$ ) and ion-electron interaction ( $\Delta E_{i-e}$ ) [45,46] give rise to a red shift (band renormalization,  $\Delta E_{BR}$ ) with significantly smaller in magnitude than the  $\Delta E_{BM}$ . Therefore, the measured optical absorption edge ( $E_{opt}$ ) is related to the intrinsic bandgap  $E_G$

$$E_{opt} = E_G + \Delta E_{BM} - (\Delta E_{e-e} + \Delta E_{i-e}). \quad (2)$$

The  $\Delta E_{BM}$  which is the energy separation between the CBM and the Fermi level  $E_F$  or ( $E_F - E_C$ ) can be calculated using the nonparabolic conduction-band model [47,48], while the band renormalization is evaluated by Jain's model [49]. Table 1 compares the electrical properties of the In and Ga doped with TM doped CdO films at their respective maximum  $N$  ( $N_{max}$ ). The position of the  $E_F$  ( $E_{F,max}$ ) with respect to  $E_C$  as well as  $E_{vac}$  are also tabulated. Notice that compared to Ga and In doped CdO, TM doped films with  $x_{max}$  have significantly higher  $\rho$  due to their low  $\mu$ .

Table 1 A summary of the mobility  $\mu$ , resistivity  $\rho$ , dopant concentration  $x_{max}$ , the  $E_{F,max}$  and  $\Delta E_{BR}$  for CdO films doped with TM as well as In and Ga with maximum  $N$  ( $N_{max}$ ). The last column lists the position of the  $E_{F,max}$  with respect to the vacuum level ( $E_{vac}$ ) by assuming that the  $E_{vac} - E_C$  (or the electron affinity) of CdO is 5.9 eV.

Dopant	$N_{max}$ ( $\times 10^{20} \text{cm}^{-3}$ )	$\mu$ ( $\text{cm}^2/\text{Vs}$ )	$\rho$ ( $\times 10^{-4} \Omega\text{-cm}$ )	$x_{max}$ (%)	$E_{F,max} - E_c$ (eV)	$\Delta E_{BR}$ (eV)	$E_{F,max} - E_{vac}$ (eV)
Ga	9.3	90	0.748	4.4	1.26	0.405	-4.64
In	11.9	106	0.495	6.6	1.41	0.43	-4.49
Sc	12	44	1.18	4.6	1.41	0.43	-4.49
Ti	9.4	22.4	2.97	4	1.27	0.41	-4.63
V	10.8	23.8	2.43	4.8	1.34	0.42	-4.56
Fe	8.78	56.8	1.25	6.2	1.21	0.4	-4.69
Cr	7.76	44.9	1.79	3.6	1.13	0.4	-4.77
Y	9.3	20	3.36	7.7	1.25	0.405	-4.65
Mo	8.98	27.6	2.52	4.6	1.24	0.4	-4.66
W	6.43	22.5	4.32	5.5	1.05	0.38	-4.85

Fig. 4 is a schematic diagram showing the Fermi level positions  $E_{F,max}$  (red lines) for In and TM doped CdO with  $N_{max}$ . Energy positions of the corresponding  $d$  donor levels  $E_{d,donor}$  (green dotted lines) and the Fermi level stabilization energy  $E_{FS}$  (red dashed line) are also shown. The Fermi level stabilization energy is the Fermi level at which the formation energies of donor and acceptor type native defects in a semiconductor are equal and is located at  $\sim 4.9$  eV below  $E_{vac}$ . [50,51,52,53] Consequently, when a semiconductor is doped n- (p-) type with the  $E_F$  above (below)  $E_{FS}$ , the formation of compensating native acceptors (donors) become favorable, and hence limiting the maximum doping of a semiconductor. Typically, a semiconductor can be doped n- (p-) type with  $E_F$  within  $\sim 1$  eV above (below)  $E_{FS}$  [54,55]. Langer et al. [56] showed that  $d$  shell derived states are localized states which remain relatively constant with respect to  $E_{vac}$  and compiled energy levels of several d-donor ( $E_{d,donor}$ ) and d-acceptor ( $E_{d,acceptor}$ ) states in II-VI compounds. The  $E_{d,donor}$  levels for several TM elements are also shown in Fig. 4 as green dotted lines. Note that  $E_{F,max}$  of all the TM dopants lie higher than  $E_{FS}$  so that a significant amount of compensating native acceptors are present in the films with  $N_{max}$ . This may contribute to the lower  $\mu$  found in these films. Moreover, for most  $3d$  TM dopants, higher  $E_{d,donor}$  gives rise to higher  $E_{F,max}$ . Fig. 5 shows a schematic energy diagram showing the formation energies of various substitutional dopants in CdO as estimated from their  $E_{F,max}$ , where  $D_f^-$  and  $D_f^+$  are the singly charged native acceptor and donor, respectively. In CdO,  $D_f^-$  and  $D_f^+$  are most likely Cd vacancy ( $V_{Cd}$ ) and O interstitial  $O_i$  [30]. Note that the formation energies of the substitutional dopants are significantly lower than that of the native donors even at  $E_{FS}$ .

The optical gap  $E_{opt}$  of the CdO films were obtained by extrapolating the  $\alpha^2$  versus photon energy plots to the energy intercept. Fig. 6 shows the  $N$  and  $E_{opt}$  of CdO:TM (Ti, V, Mo) compared to CdO:In as a function of  $x$ . For CdO:In, both  $N$  and  $E_{opt}$  increases with  $x$ , consistent with the BM effect. However, for films doped with TM elements, at high  $x$ , the  $N$  decreases while  $E_{opt}$  either saturates (Mo) or continues to increase (Ti, and V). This suggests that the TM dopants modify the electronic band structure so that the  $E_{opt}$  in these samples is no longer entirely determined by free carriers at high  $x$ . Garcia-Hemme *et al.* studied V doping in ZnO and showed that localized V  $d$ -levels modifies the CB of ZnO [57] through the anticrossing interaction between the V  $d$ -levels and CB extended states of the ZnO. Such

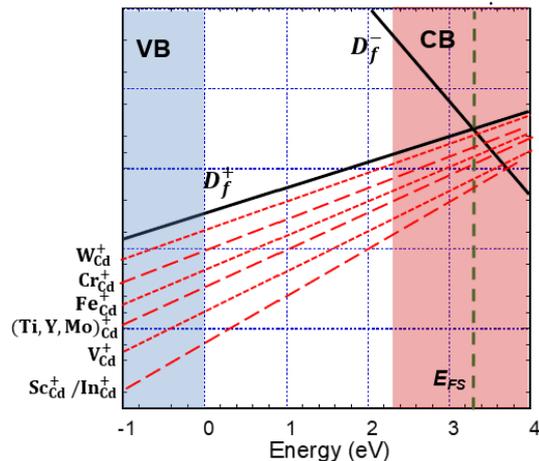


Fig. 5 A schematic energy diagram showing the formation energies of various substitutional dopants in CdO as estimated from their  $E_{F,max}$ .

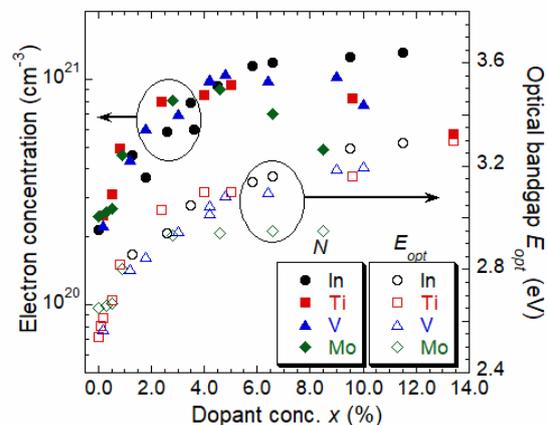


Fig. 6 The electron concentration  $N$  and optical gap  $E_{opt}$  of TM (Ti, V, Mo) compared to In doped CdO as a function of dopant concentration  $x$ .

interaction results in the splitting of the CB into a mostly unoccupied upper CB ( $E_+$  sub-band) and a lower broadened occupied narrow band ( $E_-$  sub-band). This Band Anticrossing (BAC) model was developed to describe the modification of the CB and VB of Highly Mismatched Alloys (HMAs) (e.g. dilute  $\text{GaN}_x\text{As}_{1-x}$ ) in which metallic anions (e.g. As in GaAs) in a compound semiconductor are partially replaced with more electronegative atoms (e.g. N) [58,59,60]. The increasing  $E_{opt}$  with  $x$  for TM dopants shown in Fig. 6 even at high  $x$  when  $N$  drops cannot be explained by BM effect, but is consistent with the BAC model where localized  $d$ -states of TM dopants interact with extended CB states of CdO.  $E_{opt}$  in these CdO:TM films at high  $x$  correspond to transitions from the VB to the unoccupied  $E_+$ .

Fig. 7 shows  $E_{opt}$  with increasing  $N$  for CdO thin films undoped and doped with In, Ga and the various TM elements. The dashed line shows the calculated  $E_{opt}$  with free carrier effects (namely BM shift and band renormalization) [47,49,53,61,] taken into account by assuming an intrinsic gap of 2.3 eV for CdO. Note that for the Ga and In doped CdO, the experimental  $E_{opt}$  follow the calculated values closely, which confirms that the increased  $E_{opt}$  in these samples with  $N$  can be fully explained by free carrier effects. However, for CdO:TM, although at low  $x$ ,  $E_{opt}$  follows the calculated values, as  $x$  increases, the CB of CdO is modified by the anticrossing interaction, and hence  $E_{opt}$  values are significantly higher than the calculated values.

As a consequence of the anticrossing interactions of the localized  $d$ -states and the extended CB states, the dispersion of both the  $E_+$  and  $E_-$  sub-bands are significantly flattened. The dispersion shown in the inset of Fig. 8 illustrates the band restructuring due to the anticrossing interaction. Since the electron effective mass  $m_e^*$  is related to the reciprocal of the derivative of the CB dispersion,  $m_e^*$  for the CdO:TM films is also significantly larger because of the flatter band dispersion. Figure 8 shows the effective mass for the CdO films doped with In, Ga, V and Ti as a function of  $N$  extracted from spectroscopic ellipsometry (SE) measurements [35]. For the CdO films doped with In and Ga, the dependence of the  $m_e^*$  on the electron concentration  $N$  follows the nonparabolic conduction band model [47,48]

$$m_e^* = m_o^* \sqrt{1 + 2C \frac{\hbar^2}{m_o^*} (3\pi^2 N)^{\frac{2}{3}}}. \quad (3)$$

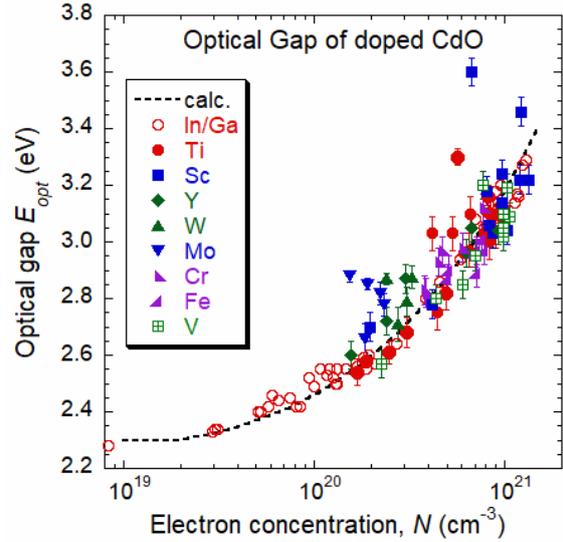


Fig. 7 The  $E_{opt}$  of CdO thin films undoped and doped with TM elements as compared to those doped with In and Ga. The calculated  $E_{opt}$  taken into account BM shift and band renormalization effects is shown as the dashed line curve.

where  $m_o^*$  is the effective mass at the bottom of the conduction band and  $C$  is a nonparabolicity parameter. A best fit of the data from CdO samples doped with In and Ga (dashed line in Fig. 8) using Eq. (3) shows a  $m_o^* = 0.13m_o$  and  $C=0.49$  eV<sup>-1</sup> with  $m_o$  being the free electron mass. However, at high  $N$ , values of  $m_e^*$  for V and Ti doped CdO deviate significantly from the fit and cannot be described by Eq. (3). The much higher  $m_e^*$  for the Ti and V doped films are consistent with the much flatter restructured CdO CB as shown in the inset of Fig. 8, and can explain the much lower  $\mu$  of these samples at high  $N$  shown in Fig. 1.

In contrast to previous reports on the mobility enhancement of In<sub>2</sub>O<sub>3</sub> doped with transition metal species, such desirable effect in CdO:TM studied in this work is rather subtle, if not totally absent. Note that mobility is related to the mean free time of carrier scattering  $\tau$  and electron effective mass  $m_e^*$  ( $\mu=e\tau/m_e^*$ ). Since the  $m_e^*$  of CdO is only slightly smaller than that of In<sub>2</sub>O<sub>3</sub>, the inherently high  $\mu$  of CdO originates primarily from the reduced scattering (increase in  $\tau$ ) due to its high static dielectric constant ( $\epsilon_o \sim 22$  for CdO as compared to 8.9 for In<sub>2</sub>O<sub>3</sub>) which effectively screens ionized impurity centers. Swallow *et al.* [20] suggested that the much higher  $\mu$  of Mo doped In<sub>2</sub>O<sub>3</sub> compared to ITO arises from its smaller  $m_e^*$  due to resonant Mo 4*d* states which do not perturb the host CBM. In CdO, this effect, if present become relatively insignificant when compared to the effect due to carrier scattering since the electron scattering cross section  $\sigma \propto 1/\epsilon_o^2$ . Nevertheless, in several cases, e.g. Ti, Mo and W doping of CdO, a slight increase in the  $\mu$  is still visible when the dopant concentration is <1%. Only when the dopant concentration is >2%, the mobility drops significantly, which we attribute to the flattening of the CB due to the anticrossing interaction of dopant *d* states and CB extended states. In fact, despite the increase in  $\mu$  for In<sub>2</sub>O<sub>3</sub> with moderate TM dopant concentration, it was also reported that a reduction in  $\mu$  is observed at high dopant concentration [18,22,24,62,63,64]. The difference in the exact dopant concentration where the reduction of  $\mu$  occurs may depend on the TM dopant species and/or film deposition methods and conditions. For CdO, TM donors such as Sc, Y, Lu and La with  $nd^1$  outer electron after using the  $2(n-1)s^2$  electrons for bonding would be good potential donors. However, the exact orbital energy levels of these dopants are not accurately known, and therefore theoretical calculations are required to fully understand these experimental results and give a more complete picture on the TM doping in CdO.

## CONCLUSION

In this work, we explore a series of transition metal (TM) elements with partially filled 3*d*

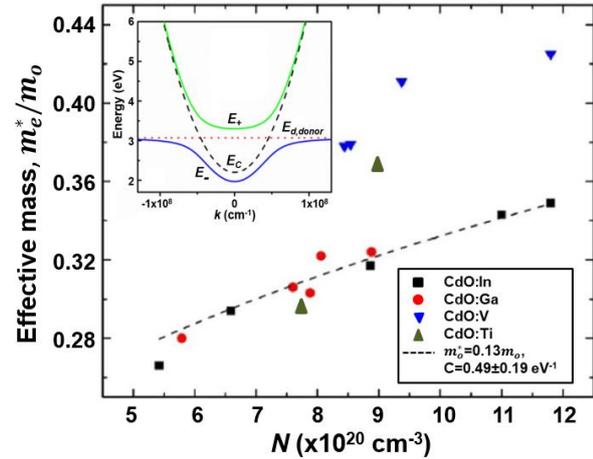


Fig. 8 Electron effective mass  $m_e^*$  for CdO derived from spectroscopic ellipsometry measurements for CdO with different dopants. The black dashed line is the best fit for the In and Ga doped samples according to Eq (3). The inset shows the dispersion of the restructured conduction band due to band anticrossing between the TM *d*-states ( $E_{d,donor}$ ) and CdO CB ( $E_C$ ).

and 4d shells, including Sc, Ti, V, Cr, Fe, Y, Mo and W as possible donors in CdO (CdO:TM). We find that these TM elements can act as effective donors in CdO with the electron concentration  $N$  increases to a maximum  $N$  ( $N_{max}$ ) of  $\sim 7-12 \times 10^{20} \text{cm}^{-3}$  with a dopant concentration  $x_{max}$  of 4-7%, comparable to CdO doped with In. Because of the high  $N_{max}$ , the corresponding Fermi levels  $E_{F,max}$  lie higher than the CdO conduction band minimum (CBM) ( $>1$  eV). In general, we also find that TM dopant with a higher d-donor level  $E_{d,donor}$  gives rise to a higher  $N_{max}$ , and thus also a higher  $E_{F,max}$ . However, in contrast to CdO:In which has a high mobility  $\mu$  of  $>100 \text{cm}^2/\text{Vs}$  even with  $N > 10^{21} \text{cm}^{-3}$ , the  $\mu$  in CdO:TM films drops rapidly to  $<20 \text{cm}^2/\text{Vs}$  as the dopant concentration  $x$  increases to  $>4\%$ . As a result, CdO:TM films have a minimum  $\rho$  of  $1-2 \times 10^{-4} \Omega\text{-cm}$ , a factor of  $\sim 2-3$  higher than that of CdO:In. The low  $\mu$  of CdO:TM increases the free carrier absorption at high  $N$ , and hence limits the optical transparency to  $<1200$  nm. Finally, unlike undoped and In doped CdO where the optical bandgap  $E_{opt}$  is determined by free carrier effects, namely BM shift and band renormalization, in TM doped CdO, as  $x$  increases,  $E_{opt}$  values are significantly higher than the calculated values. This is believed to be the effects of the anticrossing interaction of the localized d-levels and the extended CdO CB states, giving rise to a lower occupied  $E_-$  and an upper unoccupied  $E_+$  subbands. The observed  $E_{opt}$  in CdO:TM arises from electrons transitioning from the VB to the unoccupied  $E_+$  subband. The restructured CBs have much flatter dispersion, which also results in a much higher effective mass  $m_e^*$ , which also explain the much lower  $\mu$  observed in CdO:TM films with high  $N$ .

## ACKNOWLEDGMENTS

The work performed at LBNL 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. KMY was supported by CityU SGP project No. 9380076. YJL was supported by the China Scholarship Council, National Natural Science Foundation of China (No. 51602121) and PhD Start-up Program of Huizhou University (No.2016JB006). GC acknowledges support from National Natural Science Foundation of China (No. 11174101), and C. P. Liu acknowledges the support from Department of Science and Technology of Guangdong Province under Project No. 2021A0505030081.

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