Impact of degenerate *n*-doping on the optical absorption edge in transparent conducting cadmium oxide

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ABSTRACT

In order to facilitate the development of next-generation display devices or modern solar cells, material performance is critically important. A combination of high transparency in the optical spectral range and high electrical conductivity under ambient conditions is attractive, if not crucial, for many applications. While the doping-induced presence of free electrons in the conduction bands of CdO can increase the conductivity up to values desired for technological applications, it is, however, expected to impact the optical properties at the same time. More specifically, variations of the band gap, effective electron mass, and optical-absorption onset have been reported. In this work recent results from modern theoretical-spectroscopy techniques are compared to experimental values for the optical band gap in order to discuss the different effects that are relevant for an accurate understanding of the absorption edge in the presence of free electrons with different concentrations.

Keywords: cadmium oxide, parameter-free calculations, electronic structure, effective mass, Burstein-Moss shift, band-gap renormalization, optical absorption

1. INTRODUCTION

Transparent conducting oxides (TCOs) are currently attracting enormous interest because they combine many different promising material properties. Most importantly, they feature large fundamental band gaps, leading to transparency across parts of or the entire visible spectral range. While this would cause *ideal* bulk metal oxides to be insulating, it turns out that free carriers play an important role and many TCOs are either inherently highly *n*-type or can be heavily doped.

Transparent conductive cadmium oxide (CdO) thin films, for instance, have been known at least since 1907 and, in that sense, CdO can be seen as a pioneering TCO.[1] Pure bulk CdO has a band gap of about $2.1 - 2.3$ eV,[2] but even undoped samples of this material can show high unintentional electron concentrations as large as 10^{20} cm^{-3} [Ref. 3]. In addition, also intentional doping has been achieved, leading to free-electron concentrations up to 2×10^{21} cm^{-3} [Refs. 4,5]. Material properties like these enable applications of TCOs e.g. in the context of transparent electronics,[6] photovoltaics,[7] and, more recently, they are also discussed as potential candidates for low-loss plasmonics.[8]

While the presence of free electrons is essential for many of these technological applications of TCOs, the impact of the free carriers on the electronic (e.g. fundamental band gaps, effective electron masses) and the optical-absorption properties is still the subject of recent debate.[2,9,10,11] Specifically, as elucidated for zinc oxide in Refs. 11,12,13, the free electrons in the lowest conduction band cause a strong contribution to the dielectric screening of the electron-electron interaction (EEI). While (for typical doping concentrations) this can be described by an additional Thomas-Fermi like contribution,[11,12,13] it does lead to a reduction of the quasiparticle band gap[14,15] and also of the exciton binding energy.[11,12,13] In addition,

ionized-impurity scattering (IIS) reduces the quasiparticle band gap;[15] the sum of the EEI and the IIS contributions is called band-gap renormalization (BGR) in the following. The free electrons also occupy the lowest conduction-band states in the doped system which is why transitions from the valence bands into those states no longer contribute to the optical-absorption spectrum. As a consequence of this so-called Pauli blocking, an increase of the apparent optical band gap emerges and is known as Burstein-Moss shift (BMS) in the literature.[16,17] In Ref. 18 it was shown for zinc oxide that modeling BMS using a parabolic two-band model is not sufficient.

In the present work modern parameter-free electronic-structure methods based on many-body perturbation theory and optical-absorption experiments are used to explore different effects of free electrons on the electronic structure and the optical absorption of n-type CdO. In Section 2 the theoretical and the experimental approaches are briefly outlined. Results for CdO are presented and discussed in Section 3. Section 4 summarizes and concludes this paper.

2. COMPUTATIONAL AND EXPERIMENTAL DETAILS

The calculations in the present work are carried out using the theoretical lattice parameters derived in an earlier work,[19] based on density functional theory using a (semilocal) generalized-gradient approximation to describe the exchange-correlation functional. However, it is well known that Kohn-Sham eigenvalues from density functional theory (along with a local or semilocal approximation to exchange and correlation) cannot be interpreted as single-particle excitation energies. Quasiparticle effects have to be taken into account, as has been shown for CdO and various other TCOs e.g. in Refs. 20, 21, 22, 23 (and references therein). Unfortunately, the corresponding parameter-free electronic-structure approaches, for instance the HSE+G_0W_0 scheme,[24,25,26] are computationally very demanding. This constitutes a severe limitation for calculations like the ones in the present work, where a very dense sampling of $\mathbf{k}$ space is necessary to resolve free-electron densities on the order of 10^{18} cm^{-3}.

In order to circumvent this bottleneck, electronic structures are computed for the atomic geometries of ideal rocksalt-CdO using the GGA+U+Δ approach, as described in Refs. 12, 13, 27, 28. It has been shown[12,13,28] that this scheme is capable of closely reproducing the parameter-free results of the HSE+G_0W_0 approach, however, at a strongly reduced computational cost. While the U parameter is adopted from Ref. 28, it is noted that in the present work $\Delta = 1.41$ eV is used to compensate for small deviations between the experimental and the theoretical band gaps that were discussed before.[12,13,28] This also accounts (in an approximate way) for differences of the band gap at $T = 0$ K (temperature the theoretical calculations correspond to) and $T = 300$ K (temperature at which the measurements have been carried out), which is justified by experiments[2] indicating that the *variation* of the optical gaps as a function of the free-carrier density are essentially the same for different temperatures.

In addition, a full parameter-free treatment of the BGR is currently numerically unfeasible and in the present work this many-body effect is described by means of the model given by Berggren and Sernelius,[15,29] which leads to the following expression for the BGR:

$$\Delta E_{\mathrm{BGR}}(n) = \{\Delta E_{\mathrm{EEI}}(n)\} + \Delta E_{\mathrm{IIS}}(n) = \left\{ -\frac{e^2 k_{\mathrm{F}}}{2\pi^2 \varepsilon \varepsilon_0} - \frac{e^2 q_{\mathrm{TF}}}{8\pi \varepsilon \varepsilon_0} \left[1 - \frac{4}{\pi} \arctan\left(\frac{k_{\mathrm{F}}}{q_{\mathrm{TF}}}\right)\right] \right\} - \frac{n\, m(n)\, e^4}{4\pi \varepsilon_0^2 \varepsilon^2 \hbar^2 q_{\mathrm{TF}}^3}. \quad (1)$$

The dependence of the effective electron mass on the free-electron concentration $m(n)$ is taken from the parabolic fit described below (black curve in Fig. 2) and the parameter-free results for the electronic band structure are used to compute both the Fermi wave vector k_{F} and the Thomas-Fermi wave vector q_{TF} according to:

$$k_{\mathrm{F}} = \sqrt[3]{3\pi^2 n}, \quad (2)$$

$$q_{\mathrm{TF}} = \sqrt{\frac{e^2}{\varepsilon_0 \varepsilon_{\mathrm{eff}}} \cdot \frac{\partial n}{\partial \varepsilon_{\mathrm{F}}}}. \quad (3)$$

Single crystalline CdO(001) films were grown on r-sapphire by metal-organic vapor-phase epitaxy.[30] Samples were annealed at 400°C for between 2 and 24 h to obtain samples with a range of carrier concentrations. Hall effect measurements were performed in the Van der Pauw configuration. Mid-infrared and visible reflectance and transmittance measurements at an incident angle of 11° relative to the surface normal were performed using a Bruker Vertex 70v Fourier-transform infrared (FTIR) spectrometer.
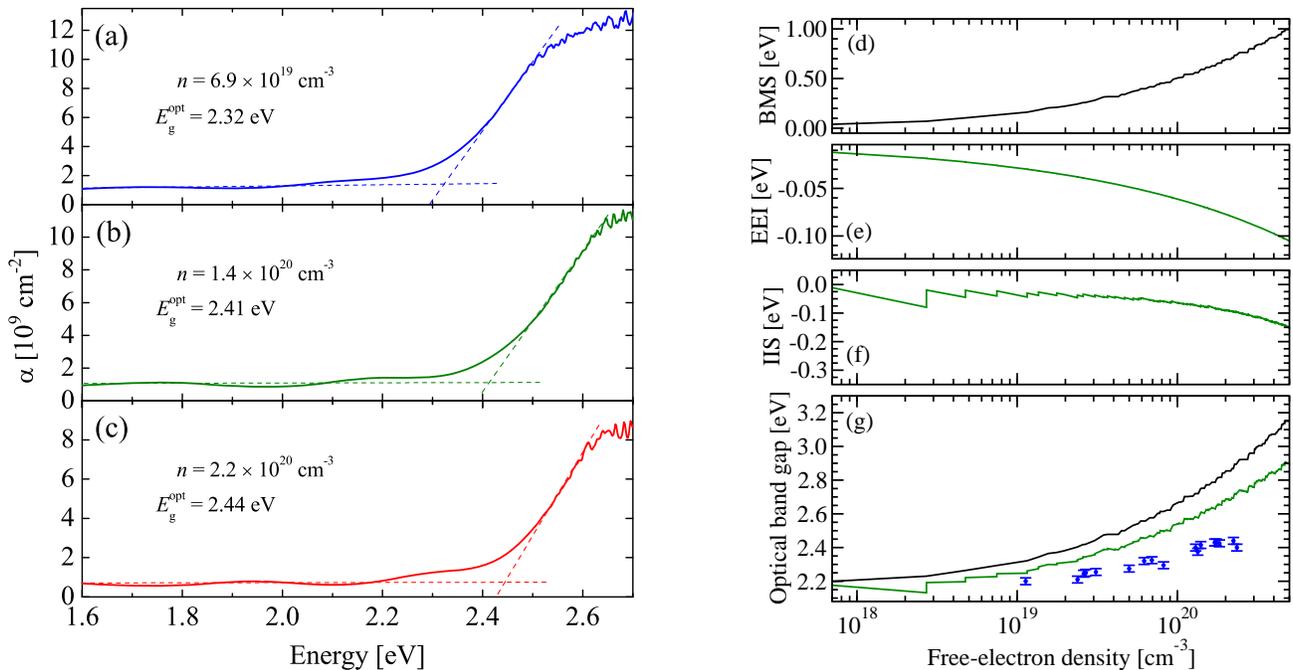
Figure 1. (Color online) Left panel: Square of optical absorption coefficient (in cm^{-2}) measured as a function of photon energy in the visible/ultraviolet region for free-electron concentrations of 6.9×10^{19} cm^{-3} (a), 1.4×10^{20} cm^{-3} (b), and 2.2×10^{20} cm^{-3} (c). The absorption edge is determined through the extrapolation of the sharp onset and baseline of the spectra. Right panel: Dependence of Burstein-Moss shift (in eV) (d), and band-gap reduction [caused by an impact of the free electrons on the electron-electron interaction (e) as well as the ionized-impurity scattering (f)] (in eV) on the free-electron density. In (g) the resulting optical band gap is shown and blue circles with error bars represent experimental results for as-grown and post-growth annealed CdO films. Black curves in (d) and (g) neglect BGR, green curves take BGR [as computed using Eq. (1) along with an effective dielectric constant of 18] into account.

3. OPTICAL ABSORPTION ONSET AND EFFECTIVE ELECTRON MASSES

In Fig. 1(a)–(c) the square of the optical absorption coefficient is shown for three different samples with different free-electron concentrations. For each case, also the optical band gap is indicated. From the figure it is already clear that this gap increases with increasing free-carrier concentrations, i.e., in CdO the BMS is larger than the corresponding BGR for these free-electron densities. Indeed, previous results in Ref. 2 indicate that the increase of the optical gap due to BMS is equal to the decrease resulting from BGR for a free-electron concentration of $\sim 10^{19}$ cm^{-3}.

In order to study this trend in more detail, Fig. 1(d)–(g) shows the separate contributions as derived from parameter-free calculations. A fit to this data shows that the BMS is approximately proportional to $n^{1/2}$ across the range of free-electron densities shown in Fig. 1(d). A static dielectric constant of 18 is used[2] in this work to evaluate Eq. (1) and this effectively takes several aspects of the screening into account in an approximate way: In addition to ionic contributions, the purely electronic screening in the doped system is expected to be reduced with respect to the ideal bulk material because of the band-gap increase caused by the BMS. Test calculations showed a reduction of the high-frequency dielectric constant of about 0.4 when going from ideal bulk to a free-electron concentration of about 1.7×10^{20} cm^{-3}. We note that a full parameter-free calculation of the dielectric screening as well as the BGR would be desirable.

Adding BMS and BGR to the band gap of 2.16 eV leads to the behavior shown in Fig. 1(g). As expected, this plot shows that the theoretical curve that entirely neglects BGR does not agree well with the experimental results; taking BGR into account improves the agreement.

In addition, the theoretical results also yield a highly accurate description of the position of the Fermi level in the conduction band [cf. Fig. 2(a)] as a function of the free-electron concentration. In the following we use these results along with the dispersion relation of a parabolic band and Eq. (2) to compute the dependence of the electron mass on the
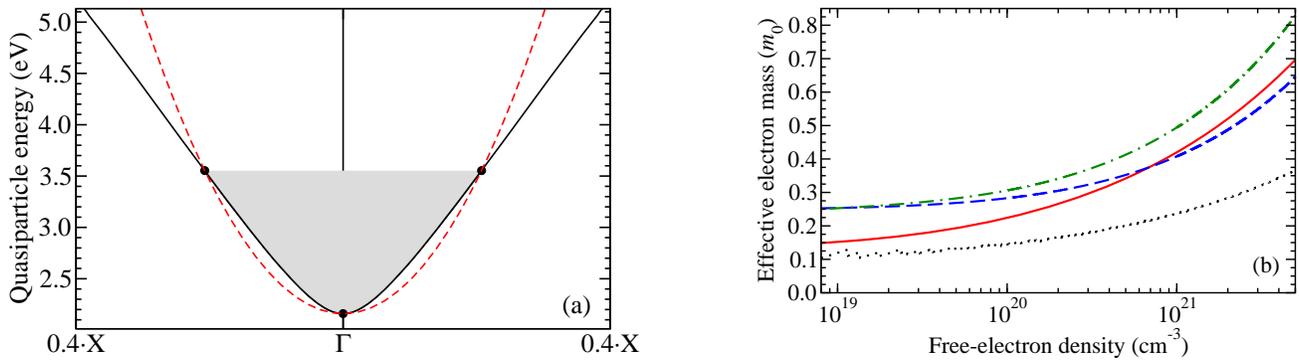
Figure 2. (Color online) Black curve in (a) shows the theoretical result for the lowest conduction band in the vicinity of the Γ point of the Brillouin zone. Grey shaded area indicates a conduction-band filling of about 8×10^{20} cm^{-3}, corresponding to a Fermi level about 1.4 eV above the conduction-band minimum. Red dashed represents a parabolic fit to the band structure. In (b) the dependence of the effective electron mass on the free-electron concentration is shown: Black (dotted) curve is computed from the theoretical band structure using Eq. (4), red solid line takes the non-parabolicity into account (see Ref. 31). The green (dash-dotted) and blue (dashed) curves represent, respectively, the effective electron mass at the Fermi level and the density-of-states-averaged effective electron mass calculated within the two-band $\mathbf{k} \cdot \mathbf{p}$ approximation of the band structure in the vicinity of the Γ point with parameters derived from modeling of previous experimental results presented in Refs. 2, 32.

free-electron concentration according to

$$\frac{m(n)}{m_0} = \frac{n^{2/3}}{E_\mathrm{F}} \cdot \frac{\hbar^2 \left(3\pi^2\right)^{2/3}}{2m_0}. \tag{4}$$

These results are shown in Fig. 2(b) over a large range of free-carrier concentration and we note that this procedure effectively averages over all directions in $\mathbf{k}$ space. In Fig. 2(b) we compare to the effective mass at the Fermi energy, taking the non-parabolicity into account [cf. Eq. (6) in Ref. 31]. We note that the results in this work are obtained for "rigid" electronic structure, i.e., any *deformation* of the lowest conduction band due to the free electrons is neglected.

The remarkable increase of the effective electron mass observed in this figure clearly arises due to the non-parabolicity of the lowest conduction band of CdO. This is shown in Fig. 2(a) along with a parabolic fit directly to the theoretical band structure. From this plot, it is immediately clear that the effective mass obtained from either of these approaches will be smaller the closer the fitting is restricted to the Γ point. In addition, Fig. 2(b) also shows that a parabolic approximation is fairly well justified for a $\mathbf{k}$-space region around the Γ point that corresponds to free-carrier densities of about 10^{20} cm^{-3}. We confirmed that the effective mass extracted from the parabolic fit approaches the mass parameter of a non-parabolic model[31] to fit the band structure when the fit is restricted to the close vicinity of the Γ point. From these results we conclude that the effective electron mass in CdO should be about $0.12m_0$ in the immediate vicinity of the Γ point.

This contrasts with the value of $\sim 0.24m_0$ derived from previous modeling of IR reflectivity, Hall effect and optical absorption results which used a two-band $\mathbf{k} \cdot \mathbf{p}$ approximation of the band structure in the vicinity of the Γ point.[2,32] The electron effective mass at the Fermi level and the density of states averaged electron effective mass as a function of free-electron density are also shown in Fig. 2(b).

Consequently, we observe that different approaches to deriving electron effective mass in the immediate vicinity of the Γ point of CdO give different results. Comparing the conduction band edge effective mass values reported or quoted in the literature, they appear to fall, more or less, into two groups corresponding to close to our value of $0.12m_0$ derived from density functional theory and near to our experimental value of $0.24m_0$. The first of these groups includes values of about $0.13m_0$ [Ref. 10], $0.14m_0$ [Refs. 33, 34], and $0.1m_0$ [Ref. 35]. And in the second group, references report larger numbers of about $0.21m_0$ [Ref. 3], $0.24m_0$ [Ref. 32], $0.23m_0$ [Ref. 36], and also other theoretical results indicate effective electron masses larger than $0.12m_0$ [Refs. 28, 37]. While some of these different literature values have been noted before in Ref. 38, their origin is not entirely clear at present, except that the various reports define in different ways the carrier density dependence of the effective electron mass in the presence of a non-parabolic conduction band.

Returning to the comparison between the calculated and experimental optical gap presented in Fig. 1(g), there are at least three possible ways to improve the agreement. First, the calculations only consider the optical gap at Γ. In contrast to

most semiconductors, CdO exhibits upward valence band dispersion at Γ, because the p-d repulsion is symmetry-forbidden at the center of the Brillouin zone, but not outside of it.[12, 13, 19] In optical absorption experiments on degenerately doped samples, vertical transitions occur at wave vectors significantly away from Γ. In CdO, the upward valence band dispersion contributes a decrease in the optical gap as the free-electron density is increased. Second, the higher electron effective mass value obtained from our experiments would increase the IIS contribution to BGR, bringing the calculated curve closer to the experimental points. Third, the experimental optical gap values have so far been obtained from the absorption spectra by performing linear extrapolations of α^2 versus $h\nu$ plots, a procedure that is only strictly valid for parabolic bands. Comparison of the experimental absorption curves with spectra calculated from the computed band structure may yield a more accurate determination of the experimental optical gaps.

4. SUMMARY AND OUTLOOK

In this work we combined theoretical and experimental results to investigate the influence of free electrons on the optical absorption edge in n-doped CdO. We disentangled the contributions of Burstein-Moss shift and band-gap renormalization. We found good agreement with optical band gaps measured for CdO samples with different free-electron concentrations. In addition, we studied different approaches to derive the dependence of the effective electron mass on the free-electron concentration and found that our results as well as values reported in the literature seem to fall into two groups.

Overall, from the present work it is clear that there is room for improvement and that this topic deserves further attention. For ZnO, the explicit influence of free electrons on the electron-hole interaction and bound excitonic states has been discussed, see e.g. Refs. 11, 12, 13, and it has been shown that the shape of the optical-absorption spectra is strongly influenced, in particular, in the vicinity of the absorption edge. Even though the influence of excitonic effects on the line shape of the absorption spectrum is smaller for CdO (due to the larger dielectric screening), such a study would be insightful and, in particular, would allow for the direct comparison with experimental results, ruling out any potential artifacts arising from the fitting procedure used to derive the band gap from the absorption spectrum. Moreover, a fully parameter-free description of the quasiparticle energies in the presence of free electrons in general and the band-gap renormalization in particular would be desirable. Other possible extensions of the present work are related, for instance, to free-carrier absorption[39, 40] and inter-conduction-band absorption.[11, 12, 13, 41]

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