

Intermediate Band to Conduction Band Optical Absorption in ZnTeO

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Abstract—ZnTe doped with high concentrations of oxygen has been proposed in previous works as an intermediate band (IB) material for photovoltaic applications. The existence of extra optical transitions related to the presence of an IB has already been demonstrated in this material and it has been possible to measure the absorption coefficient of the transitions from the valence band (VB) to the IB. In this study, we present the first measurement of the absorption coefficient associated with transitions from the IB to the conduction band (CB) in ZnTeO. The samples used are 4- μm -thick ZnTe layers with or without O in a concentration $\sim 10^{19} \text{ cm}^{-3}$, which have been grown on semiinsulating GaAs substrates by molecular beam epitaxy (MBE). The IB–CB absorption coefficient peaks for photon energies $\sim 0.4 \text{ eV}$. It is extracted from reflectance and transmittance spectra measured using Fourier transform infrared (FTIR) spectroscopy. Under typical FTIR measurement conditions (low light intensity, broadband spectrum), the absorption coefficient in IB-to-CB transitions reaches 700 cm^{-1} . This is much weaker than the one observed for VB–IB absorption. This result is consistent with the fact that the IB is expected to be nearly empty of electrons under equilibrium conditions in ZnTe(O).

Index Terms—High-efficiency solar cells, infrared absorption, intermediate band solar cells (IBSC), novel photovoltaic concepts.

I. SUBBANDGAP ABSORPTION IN THE INTERMEDIATE BAND SOLAR CELL

THE intermediate band solar cell (IBSC) [1] is a photovoltaic device designed to achieve high efficiency through

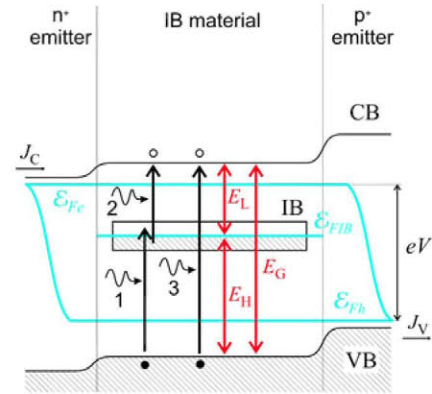


Fig. 1. Simplified band diagram of an IBSC illustrating its operation. The IB divides the semiconductor gap in two subbandgaps (E_L and E_H) and enables the absorption of extra photons (labeled 1 and 2).

the exploitation of subbandgap photons. In this device, low-energy photons are absorbed thanks to the existence of an extra band, the IB, within the semiconductor bandgap of the absorber. As it is shown in Fig. 1 this band enables two different transitions: VB–IB (labeled “1”) and IB–CB (labeled “2”). For the device to achieve high efficiency, it is of utmost importance that both transitions are operative and not just one of them (if we exclude impact ionization processes). In this respect, it is important that the IB is disconnected from the external contacts by the layers called “emitters.” Since only electrons and holes exit the cell, and not IB carriers, it is not possible to extract photocurrent if only one subbandgap transition is used. In practice, it may be possible to extract a current if the lattice thermal energy is used to sustain a carrier escape flux that replaces the failing optical transition. But in that case, the price paid is a reduction of the voltage. By disconnecting the IB from the contacts and exploiting simultaneously the two subbandgap transitions, the IBSC can work at a voltage similar to the one it would have if no IB was present.

In order to generate a significant subbandgap photocurrent, it is important that the IB is partially filled so that both transitions can take place at a high rate [2]. There are two ways of achieving this. The first one is to have the Fermi level located at the IB under equilibrium conditions. It has been predicted that this occurs naturally for some IB materials [3], but in other cases it is also possible to tune the occupancy of the IB through codoping [4]. If the density of states in the IB is sufficiently high, the quasi-Fermi level associated with it will remain at the IB under illumination conditions. This situation of *prefilling* of the IB is generally assumed for efficiency limit calculations.

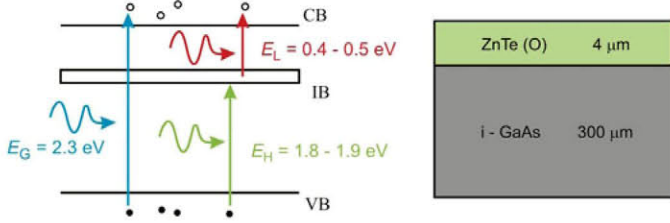


Fig. 2. (Left) Expected band diagram of the ZnTeO bulk IB material. (Right) Structure of the test samples grown for this absorption study.

The second possibility is to rely on *photofilling*, i.e., the optical absorption in one transition provides the carriers to be pumped by the other transition. It has been demonstrated theoretically that the efficiency that can be achieved relying on photofilling only approaches the prefilling efficiency under high illumination. In [5], it is shown that the difference between the two cases becomes small for a concentration of 1000 suns (assuming equal optical cross section in both subbandgap transitions).

Another important requirement for optimum performance of the IBSC is the selectivity of absorption coefficients. The efficiency of the device would decrease if part of the energy of the photons is lost because they are absorbed in a transition of energy lower than possible. For instance, if we consider an IB material as depicted in Fig. 1 where the IB is closer to the CB, then it would be a loss that photons with energy enough to be absorbed in a VB–IB transition are absorbed in an IB–CB transition. Ideally, the way to avoid this is that the absorption coefficients α_{VC} , α_{VI} , and α_{IC} , associated respectively with the VB–CB, VB–IB, and IB–CB transitions are selective. This implies that α_{IC} should be zero in the range where α_{VI} is nonzero (photon energies $\geq E_H$) and α_{VI} should behave analogously with respect to α_{VC} .

II. ZnTeO AS AN INTERMEDIATE BAND MATERIAL

One way that is currently being investigated to engineer an IB material is the doping of a semiconductor with an impurity species that introduces levels within the gap. It has been proposed that, if the impurity concentration is very high, the levels become delocalized, which suppresses the nonradiative recombination processes that usually accompany the presence of levels in the gap [6]. Among the possible candidates, ZnTe doped with oxygen has been one of the most studied materials [7]–[11] (in some cases adding a small amount of Mn to enlarge the total bandgap). Fabrication of IBSC prototypes has been reported [8], [10] and subbandgap transitions have been identified in ZnTeO by modulated photoreflectance techniques [7], [10]. Also, it has been possible to measure the absorption coefficient of the VB–IB transitions, which has been reported to be high ($\sim 10^4 \text{ cm}^{-1}$) [10], [11].

III. EXPERIMENTAL DESCRIPTION

In this study, we have grown by MBE relatively thick samples ($4 \mu\text{m}$) of ZnTe(O) on GaAs (001) substrates (see Fig. 2, right) and have used them to measure the absorption coefficient associated with IB–CB transitions. The MBE system includes solid

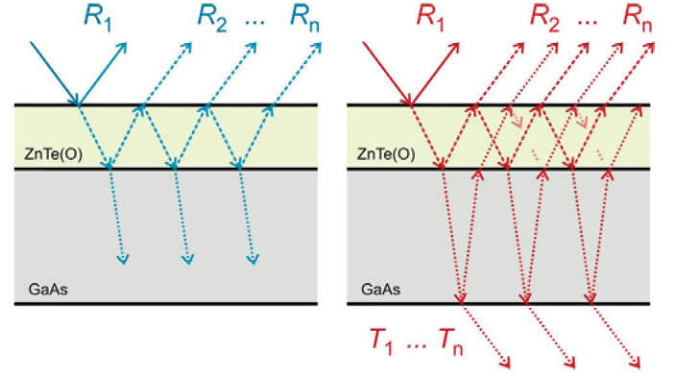


Fig. 3. Light beam components present in the reflectance and transmittance experiments. On the left, photons have energy larger than the gap of GaAs. On the right, photon energy is below the gap of GaAs.

source effusion cells for Zn and Te, and an RF plasma source for oxygen incorporation (and nitrogen when required as *p* dopant). An oxygen flow rate of 1 sccm was applied (1 cubic centimeter per minute at standard pressure and temperature), which results in an oxygen partial pressure during growth in the order of 10^5 Torr. Under these conditions, the O content is estimated to be in the order of 10^{19} cm^{-3} , assuming similar incorporation rates to N. SIMS measurements on samples grown under identical conditions have confirmed an O content of $1 \times 10^{19} \text{ cm}^{-3}$, while the characterization by nuclear reaction analysis gives an higher estimation of $1 \times 10^{20} \text{ cm}^{-3}$. The difference between these estimations lies within the uncertainty range of the measurements. The band diagram of the material depends on the amount of O that is introduced [7], [12], [13]. In our case, based on previous PL studies [8], we expect a band diagram as depicted in Fig. 2, left. As a reference, a similar ZnTe sample with no oxygen has also been grown. The GaAs substrates used in all cases are semi-insulating to avoid free carrier absorption in the IR.

The objectives of this study are: 1) to demonstrate that both subbandgap absorptions take place in ZnTeO and 2) to initiate the empirical study of the aspects discussed in the introduction on a fabricated IB material (impact of the IB occupancy on the absorption and selectivity of the absorption coefficients). It is known that ZnTe is naturally *p*-doped due to the presence of Zn vacancies. Since O is an isovalent impurity, there is no reason for the O doping to change the *p*-character of ZnTe if the O is Te-substitutional. Prior capacitance–voltage measurements based on materials grown under similar conditions have indicated a background *p*-type carrier concentration $< 10^{16} \text{ cm}^{-3}$ for ZnTeO. Therefore, the IB is most likely to be almost empty under equilibrium.

To measure the absorption of the VB–IB transition, a setup has been used including a monochromator covering the visible range, Si detector, and lock-in amplifier. For those energies, the GaAs substrate absorbs the light and only reflectance spectra can be obtained (see the diagram on the left, Fig. 3). For the measurement of the IB–CB transition, an FTIR spectrometer has been used. In this case, it is possible to obtain reflectance and transmittance spectra (see the diagram on the right, Fig. 3).

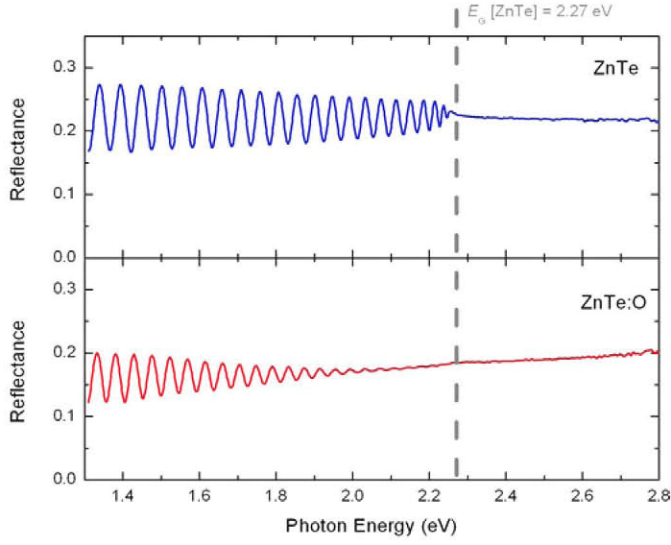


Fig. 4. Measurement of the reflectance of ZnTe and ZnTeO samples.

IV. RESULTS

Fig. 4 shows the reflectance spectra measured in the visible range on a ZnTe and a ZnTeO sample (30° with respect to normal incidence) using the monochromator setup. For ZnTe (upper plot) it can be seen a flat reflectance for energies above the fundamental bandgap and an interference oscillation for energies below it. This is the typical measurement of a semiconductor film around its bandgap. The flat component that is present for any photon energy is the surface reflectance (R_1 in Fig. 3, left) and the interfering components ($R_2 \dots R_n$) appear only for energies at which the layer is transparent.

In the case of ZnTeO (lower plot), the interference is strongly attenuated for subbandgap energies, indicating VB–IB absorption in the layer. Since the absorption is complete in a large part of the range, it is not possible to extract from this measurement an accurate absorption coefficient value. It can be estimated, given the thickness of the layer, that between 2 and 2.3 eV the VB–IB absorption coefficient has to be at least in the order of 10^4 cm^{-1} , which is in agreement with previous reports [10].

Fig. 5 shows the reflectance (R) and transmittance (T) spectra under normal incidence measured in the IR range on the same samples using an FTIR spectrometer. It can be seen a dip around 0.4 eV in the transmittance of the ZnTeO sample which is not present for the ZnTe sample. We interpret that feature as the effect of the absorption in the IB–CB transition. From these measurements, we can obtain the absorbance A of the film as $A = 1 - T - R$. Then, we can extract the absorption coefficient α from the expression $A = 1 - \exp(-\alpha d)$, where d is the thickness of the film.

We have estimated a thickness of $3.5 \mu\text{m}$ for the ZnTe film and $4.0 \mu\text{m}$ for the ZnTeO film using the well-known fact that in the interference pattern T reaches a maximum and R a minimum when $2nd \approx m\lambda$ (n is the refractive index, λ the wavelength, and m an integer). Here, we have assumed for ZnTeO the same n as for ZnTe.

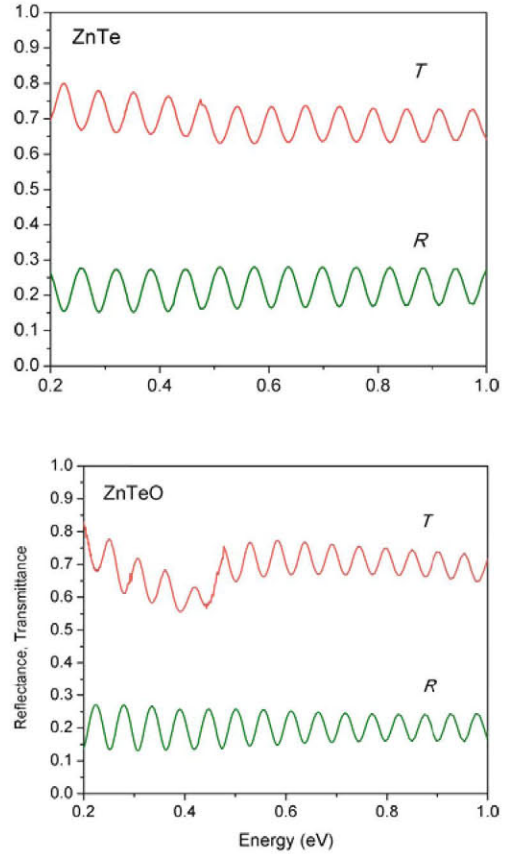


Fig. 5. Reflectance and transmittance spectra in the IR measured with FTIR on the ZnTe (top) and ZnTeO (bottom) samples (same samples as in Fig. 4).

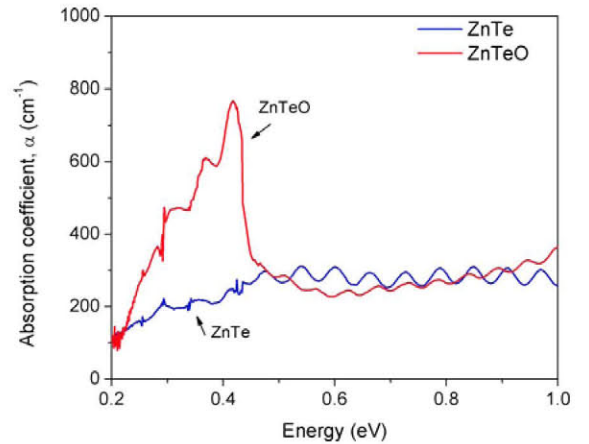


Fig. 6. Absorption coefficient associated to the IB–CB transition in ZnTeO extracted from the data in Fig. 5.

The resulting absorption coefficients are shown in Fig. 6. Since the absorption peak observed at 0.3–0.4 eV for ZnTeO is clearly above the amplitude of the interference oscillations, this measurement constitutes a good approximation to the real bulk absorption coefficient of the material. If the absorption peak was of the same order than the amplitude of the interference oscillations, modeling would be required to distinguish the real absorption coefficient from the magnitude α that we have defined above. It is also remarkable that this absorption has been

detectable at room temperature. The absorption baseline measured for ZnTe determines the level of inaccuracy introduced by the nonideal surfaces of the grown samples (scattering).

The IB–CB absorption reaches 700 cm^{-1} at the highest point, being at least over an order of magnitude lower than the absorption for the VB–IB transition. It has to be taken into account that an FTIR spectrometer sample is illuminated with a light of a broadband spectrum, including those wavelengths that produce VB–IB transitions in ZnTeO. This illumination is not as high as to produce a situation of large photofilling of the IB, but can still provide the IB with a sufficient carrier population that allows the measurement of this IB–CB absorption. On the other hand, it is not established yet whether the position of the Fermi level in the practical ZnTeO material is the same than in ZnTe. It has to be noted that the amount of oxygen introduced is huge. Assuming an O incorporation of 10^{19} cm^{-3} , if 1% of the O atoms, for example, do not occupy Te-substitutional sites, there would be 10^{17} cm^{-3} potential dopants, which may produce complexes that are not necessarily acceptors. In these considerations it should not be forgotten the self-compensation effects that prevent the achievement of a notable n -doping in ZnTe [14]. In order to evaluate the real impact on the performance of solar cells in future studies, this empirical absorption coefficient needs to be inserted in a theoretical model to estimate the effective absorption values during normal cell operation where the illumination gives rise to an IB population very different from that in the FTIR spectroscopy measurements.

Finally, it is worth mentioning the IB–CB transition in ZnTeO shows an abrupt selective character: no absorption is recorded for energies higher than 0.5 eV. As explained in the introduction, this is a positive feature from the point of view of IBSC implementation (selectivity of the absorption coefficients), although it will probably need to be accompanied by a blue-shift of the IB–CB gap to render the potential for really high-conversion efficiencies. The theoretical results in [7], [12], and [13] indicate that this blue-shift can be produced by increasing the O content. Furthermore, this behavior has been experimentally demonstrated in [7] and [15].

V. CONCLUSION

We have presented the first report to our knowledge of absorption in both subbandgap transitions in an IBSC material at room temperature. The material was ZnTeO grown by MBE and, in particular, it was possible to measure using an FTIR spectrometer the less energetic IB–CB transition. The extracted absorption coefficient for that transition is 700 cm^{-1} . That low value is not surprising taking into account the natural p -character of the ZnTe material (the IB is expected to be empty

under equilibrium), where determination of the optical cross section (oscillator strength) independent of carrier population would be of great value. The absorption shows a peak at about 0.4 eV and is negligible for energies above 0.5 eV. Therefore, it is concluded that the absorption coefficients for the VB–IB transition and IB–CB transition do not overlap in energies but the energy of the IB–CB transition is too low for an efficient IBSC operation. It is important to shift that energy to higher values.

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