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Ting, M.; Yu, K. M.; Jaquez, M.; Sharp, I. D.; Ye, Yifan; Segercrantz, N.; Greif, R.; Mao, S. S.; Liu, Chao Ping; Walukiewicz, W.

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Published in:
Journal of Applied Physics

DOI:
[10.1063/1.5088852](https://doi.org/10.1063/1.5088852)

Published: 21/04/2019

Document Version
Publisher's PDF, also known as Version of record

Please cite the original version:
Ting, M., Yu, K. M., Jaquez, M., Sharp, I. D., Ye, Y., Segercrantz, N., Greif, R., Mao, S. S., Liu, C. P., & Walukiewicz, W. (2019). ZnO 1-x Te x highly mismatched alloys beyond the dilute alloy limit: Synthesis and electronic band structure. *Journal of Applied Physics*, 125(15), [155702]. <https://doi.org/10.1063/1.5088852>

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$\text{ZnO}_{1-x}\text{Te}_x$ highly mismatched alloys beyond the dilute alloy limit: Synthesis and electronic band structure

Cite as: J. Appl. Phys. **125**, 155702 (2019); <https://doi.org/10.1063/1.5088852>

Submitted: 15 January 2019 . Accepted: 27 March 2019 . Published Online: 16 April 2019

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Note: This paper is part of the Special Topic on: Highly Mismatched Semiconductors Alloys: from Atoms to Devices.

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ABSTRACT

We have synthesized ZnO_{1-x}Te_x highly mismatched alloys (HMAs) with high, up to $x = 0.34$, Te content using pulsed laser deposition. We have found that the film composition is strongly dependent on the growth temperature and background pressure during growth. Lowering the growth temperature and/or increasing the background Ar or N₂ pressure increases the Te content in the film. When grown in O₂ atmosphere, however, oxidation of the Te species occurred, resulting in much less Te incorporation in the O sublattice. While a lower substrate temperature is needed for the incorporation of more Te in the ZnO_{1-x}Te_x film, the crystallinity of the film degrades at low growth temperature. X-ray photoemission, soft x-ray absorption, and x-ray emission measurements reveal that the observed drastic narrowing of the optical bandgap with increasing Te content is primarily due to the modification of the valence band. The experimentally observed evolution of the optical properties of ZnO_{1-x}Te_x HMAs from dilute to mid-composition range ($x > 0.3$) is analyzed within the framework of a modified band anticrossing model with composition dependent coupling parameters describing the anticrossing interaction between the valence band of the matrix and Te localized states. Electrically, we found that adding Te in ZnO increases the film resistivity. When doped with N, a drastic drop in n from mid- 10^{19} to 10^{15} cm⁻³ is observed for ZnO_{1-x}Te_x with ~2%–4% of Te. These electrical behaviors can be understood as the effect of the upward shift of the valence band, which favors the formation of native as well as N acceptors.

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I. INTRODUCTION

As the Si-based solar cell technology approaches its theoretical efficiency limit,¹ increasing efforts have been devoted to the search for new materials and designs for high efficiency solar cell structures. The energy conversion efficiency of the Si single junction solar cell has been stagnant over the past 20 years (24% in 1995 and 25.6% in 2015). The concept of multiple junction solar cells can significantly

increase the power conversion efficiency. For example, a double junction solar cell built on top of a Si bottom cell can potentially achieve efficiency >45% when the top cell material has an optimal bandgap of ~1.7–1.8 eV.^{2–4} As a result, in recent years, much work has been performed to combine the mature Si photovoltaic (PV) technologies with new materials to achieve cost effective and highly efficient double junction solar cells.^{5–9}

ZnO is an attractive material for photovoltaic applications, due to its high natural availability and nontoxic and stable characteristics.^{10–13} Al doped ZnO is a common transparent conductive oxide or window material found in thin film PV technologies such as CdTe and CIGS solar cells.^{14,15} Incidentally, ZnO has its conduction band (CB) well aligned with the valence band of Si, which makes a natural tunnel junction when a layer of n-type ZnO is grown on a p-type Si. This electronic band offset between ZnO and Si favors the fabrication of a ZnO-Si tandem solar cell structure. Unfortunately, the bandgap of ZnO (3.4 eV) is too wide to be considered as the material for the top cell in the Si tandem structure. However, with a proper reduction of the bandgap energy, ZnO-based alloys could be an ideal top cell material in a Si-based tandem solar cell design, provided that the bandgap reduction primarily comes from lifting of the valence band so that the favorable conduction band alignment with the Si valence band is not disturbed. Moreover, a low gap oxide will be of great technological significance for the development of oxide-based electronics.

Previously, we have demonstrated that the substitution of a small fraction of the anion with a more (less) electronegative isovalent element can result in a dramatic modification in the conduction (valence) band of the original material.^{16–20} Hence, the resulting alloys, highly mismatched alloys (HMAs), have electronic band structures very different from those of the host materials and exhibit many unexpected optoelectronic properties. Several III-V as well as II-VI HMAs such as GaNAs,^{16,17} ZnOS,^{21,22} ZnOSe,^{23,24} and ZnOTe^{25–27} have been studied. The large modification in the conduction and/or valence band in HMAs has been attributed to the anticrossing interaction between the extended band states of the host material and the localized states due to the substitutional species,^{17,18} and is well described by the band anticrossing (BAC) model. The BAC model has been widely adopted to explain the modifications of the electronic band structure as well as the electronic properties of group III-V and II-VI HMAs,^{16,17,22–26,28,29} especially for HMAs with a dilute composition (<10%).

In a recent work, we have synthesized $\text{ZnO}_{1-x}\text{Te}_x$ alloys with tellurium (Te) composition $x < 0.23$ by using pulsed laser deposition (PLD). Using x-ray diffraction (XRD) and scanning transmission electron microscopy, we found that alloys with $x < 0.06$ are crystalline with a columnar growth structure, while samples with a higher Te content are polycrystalline with a random grain orientation. We have also shown that the drastic band structure modification of ZnO by the substitution of tellurium (Te) to the anion sites can be described by the BAC model.²⁶ In this work, we present a systematic investigation on the effects of growth conditions on the properties of $\text{ZnO}_{1-x}\text{Te}_x$ over a large composition range to $x \sim 0.34$. In particular, in addition to optical absorption measurements that determine only the bandgap and the relative locations of the conduction and the valence band edges, modifications of both the conduction and the valence band edges on the absolute energy scale were directly measured by synchrotron x-ray absorption (XAS) and emission (XES) as well as x-ray photoelectron spectroscopy (XPS). Experimental results on the band edge modifications were analyzed with a modified BAC model³⁰ that takes into account the composition dependent coupling parameters of the anticrossing interaction. Furthermore, we show that the changes in the band structure and the large shift of the

valence band edge have a profound effect on the electrical properties of the alloys.

II. EXPERIMENTAL DETAILS

Thin films of $\text{ZnO}_{1-x}\text{Te}_x$ were deposited on glass substrates by pulsed laser deposition (PLD) using a KrF laser ($\lambda = 248$ nm), with 20 ns laser pulse duration. The laser fluence used in this work was fixed at 2.3 J/cm^2 with a laser spot size of 6 mm^2 and a laser repetition rate of 5 Hz. Seven $\text{ZnO}_{1-x}\text{Te}_x$ PLD targets composed of different ZnTe contents were used in this study: $x = 0, 0.026, 0.051, 0.086, 0.14, 0.17$, and 0.275 . The film thickness and the alloy composition were measured by Rutherford backscattering spectrometry (RBS) using a 3 MeV He^{2+} ion beam. Note that RBS measures only the total Te content in the film, not necessarily the Te incorporated in the O sublattice. The amount of substitutional Te in the films was deduced from the lattice parameter of the $\text{ZnO}_{1-x}\text{Te}_x$ films measured by x-ray diffraction (XRD) assuming a linear interpolation between the lattice parameters of ZnO and ZnTe. The absorption coefficient of the $\text{ZnO}_{1-x}\text{Te}_x$ was obtained from transmission and reflection measurements performed in a Perkin Elmer Lambda 950 spectrophotometer in the wavelength range of 250–2500 nm.

Electrical properties of the films were determined by Hall effect measurements in van der Pauw geometry using an Ecopia HMS3000 system with a 1.1 T magnet. The variation in the valence band energy as a function of Te content was studied by x-ray photoelectron spectroscopy (XPS). XPS valence band spectra were measured using a monochromated Al $K\alpha$ X-ray source ($h\nu = 1486.6 \text{ eV}$) with a hemispherical electron analyzer. XPS spectra were charge corrected to the C 1s spectral component binding energy.³¹ The electronic band structure of $\text{ZnO}_{1-x}\text{Te}_x$ films was further investigated using soft x-ray absorption (XAS) and x-ray emission (XES) spectroscopy at room temperature at Beamline 8.0.1 of the Advanced Light Source, Lawrence Berkeley National Laboratory. In an XAS experiment, electrons from the core level are photoexcited to available states in the conduction band (CB), and hence, it probes the CB partial density of states (DOS). Both the total electron yield (TEY) and the total fluorescence yield (TFY) were collected. XES uses a photon beam with energy just above the absorption edge of the element of interest to excite core electrons into the CB. Electrons from the valence band then relax back to fill the core holes with the emission of photons. The collected emitted photon spectrum represents the valence band (VB) partial DOS of the sample.

III. RESULTS AND DISCUSSION

A. PLD growth of $\text{ZnO}_{1-x}\text{Te}_x$

Figure 1(a) shows the composition of the $\text{ZnO}_{1-x}\text{Te}_x$ films using PLD targets with different ZnTe contents as measured by RBS for films grown at 200°C in vacuum ($<10^{-7}$ Torr), 5 mTorr and 15 mTorr of Ar pressure. Previously, we have reported that the RBS and XRD measured compositions of $\text{ZnO}_{1-x}\text{Te}_x$ films agree well for films with a low Te content up to $x \sim 0.06$.²⁶ This suggests that all Te atoms are in substitutional group VI sites forming random alloys. With a Te content $>10\%$, no clear diffraction peak can be observed, indicating an amorphous structure. For films grown in vacuum and low Ar pressure (5 mTorr), a reasonably

FIG. 1. (a) The correlation of Te content between the PLD target and the resulting film deposited in vacuum and in Ar (5 and 15 mTorr). The dotted line shows 1:1 ratio. (b) Dependence of film Te content on the background pressure of N₂, O₂, or Ar gas for the PLD target with 5.1% Te.

good correspondence of film and target composition is observed. In high Ar pressure, the films have a significantly higher Te content than that in the target. The increase of the Te content with increasing Ar pressure is consistent with the increased scattering of ablated species by Ar ions. As an inert gas, Ar is not expected to react with the deposited species during the deposition. However, Ar atoms will scatter the ablated species traveling from the target to the substrate. Since the heavy elements are affected less by the scattering, the incorporation of Te is expected to be higher as the Ar pressure increases. For example, with a 2.6% Te PLD target, the films with a Te content of 0.3%, 1.6%, and 4% were obtained for growths under vacuum, 5 mTorr, and 15 mTorr of Ar pressure, respectively.

Figure 1(b) shows the Te content in the films as a function of the background pressure of N₂, O₂, or Ar gases during deposition with the 5.1% Te target. The Te content in the film first increases linearly from ~2% to ~10% when the chamber pressure increases from the base pressure 10^{-7} Torr to 10 mTorr and then with a slower increase in the Te incorporation rate for a pressure higher than 10 mTorr. The highest Te content ~13% was obtained for the background pressure reaching 50 mTorr. It is interesting to note that this Te incorporation rate is dependent only on the background pressure but is independent of the gas species introduced during deposition.

Absorption coefficient α spectra for ZnO_{1-x}Te_x samples grown with PLD targets with different Te contents (2.6%, 5.1%, 8.6%, 17%, and 27.5%) in vacuum, 5 mTorr, and 15 mTorr of Ar pressure are shown in Fig. 2. Similar results were also obtained for films grown in a different N₂ pressure. The results in Fig. 1 show that although the same targets were used, film compositions were considerably different when the growth was carried out in different gas pressures. The RBS measured Te contents in the films are shown in the figure legends. As has been reported previously, replacing the small, electronegative O atoms with large metallic group VI atoms (Te) in ZnO produces localized levels above the valence band of ZnO.²⁶ In ZnO_{1-x}Te_x,

anticrossing interaction of these Te levels with the extended valence band states of the host matrix results in the formation of a narrow, fully occupied subband, leading to a large reduction of the energy gap.^{26,28–30} Figure 2 reveals that the optical bandgap of the alloy decreases with increasing Te content, in agreement with expectation and observations reported previously.²⁶ Note that the absorption coefficient spectra are similar for samples with a similar composition irrespective of the Ar growth pressure. While bandgap reduction with increasing Te content is observed for films grown under different Ar and N₂ pressures, consistent with the substitution of Te in the O sublattice, a bandgap increase was observed for films grown in O₂ atmosphere with increasing O₂ pressure. This suggests that Te atoms in the film are less likely to substitute O sublattice sites as the ambient O₂ pressure increases. Some of the ablated Te species may react with O₂ before deposition on the substrate and hence small clusters of TeO₂ may be present in the film.²⁶ We note that when the O₂ pressure is 50 mTorr, the bandgap of the film is essentially the same as that of ZnO, although ~13% of Te was detected by RBS in the film.

Due to the large differences in atomic size and electronegativity, the equilibrium solubility of Te in ZnO is expected to be low. In order to overcome the miscibility gap, relatively low temperatures are needed to grow ZnO_{1-x}Te_x films with a substantial fraction of Te. This is similar to cases for the growth of III-V HMAs such as GaN_{1-x}As_x²⁸ and GaN_{1-x}Sb_x.²⁹ Figure 3 shows the effects of the substrate temperature on ZnO_{1-x}Te_x films grown with the 5.1% Te PLD target in the substrate temperature range of 120–425 °C in vacuum. Figure 3(a) shows that the wurtzite ZnO_{1-x}Te_x (0002) diffraction peak shifts continuously to a lower angle as the growth temperature decreases. This suggests that the ZnO_{1-x}Te_x lattice parameter expands due to the incorporation of more Te in the O sublattice at a lower growth temperature. Figure 3(b) shows that the Te concentration measured by RBS reveals a monotonic increase from 0.5% to ~7.5% as the growth temperature decreases from 425

FIG. 2. Absorption coefficient (α) spectra for $\text{ZnO}_{1-x}\text{Te}_x$ samples grown with PLD targets with different Te contents (2.6%, 5.1%, 8.6%, 17%, and 27.5%) in vacuum (a), 5 mTorr of Ar (b), and 15 mTorr of Ar (c).

to 120 °C. Note that, as is shown in Fig. 3(b), for most samples, the XRD results yield higher Te contents than those of RBS. This discrepancy may be due to stress in the films. The absorption edge (not shown) exhibits a monotonic shift to lower energy with decreasing growth temperature, confirming an improved incorporation of substitutional Te. The grain size in the films was estimated from the width of the (0002) diffraction peak using the Scherrer equation, and the results are shown in Fig. 3(c). The average grain size increases from ~15 nm when grown at 120 °C to ~30 nm when

grown at 425 °C. Note that high quality ZnO films are typically grown at a substrate temperature >600 °C.^{11,12} Hence, as a lower substrate temperature is needed for the incorporation of more Te in the $\text{ZnO}_{1-x}\text{Te}_x$ film, the crystallinity of the film degrades.

B. Electronic band structure

The main critical absorption edges of $\text{ZnO}_{1-x}\text{Te}_x$ films were determined by spectrophotometry, while the conduction and the

FIG. 3. (a) XRD patterns, (b) Te composition measured by RBS and XRD, and (c) the XRD peak width and the corresponding grain size from $\text{ZnO}_{1-x}\text{Te}_x$ samples grown in vacuum using the 5.1% Te PLD target at a different substrate temperature.

valence band edge energies on the absolute scale were measured using synchrotron X-ray absorption (XAS) and emission (XES) as well as x-ray photoelectron spectroscopy (XPS). The results are analyzed in terms of the BAC model for highly mismatched alloys.

The absorption coefficient of the $\text{ZnO}_{1-x}\text{Te}_x$ HMA films was derived by the Beer–Lambert Law from the transmittance and reflectance measurements in the spectral range of 250–2500 nm and has been discussed previously in Ref. 26. In brief, as the Te content in the film increases, we observe that the absorption spectra shift to lower energy, suggesting that the minimum absorption edge of $\text{ZnO}_{1-x}\text{Te}_x$ HMA films decreases with x . A detailed analysis of the absorption coefficient using the BAC model has been reported previously.²⁶

1. Valence band position measured by x-ray photoelectron spectroscopy

It has been demonstrated that the surface Fermi level of semiconductors is pinned to a universal energy level, known as the Fermi level stabilization energy E_{FS} , located at ~ 4.9 eV below the vacuum level.^{32–34} This corresponds to the Fermi level at which the formation energy of acceptor and donor native defects is the same.³² In order to correct for the surface E_F pinning at E_{FS} , a 3.5 mW laser with $\lambda = 405$ nm was used to flatten the surface band bending. The band bending energy is determined by the shift of the carbon 1s XPS peak under dark and laser excitation conditions.

Figure 4 shows the valence band maximum (VBM) positions obtained from fitting the XPS valence band spectra using a Gaussian function and the Fermi level E_F positions determined from the shift of the C 1s peak under laser irradiation for six

FIG. 4. Valence band maximum (VBM) positions as determined by fitting the XPS valence band spectra using a Gaussian function and the Fermi level E_F positions as determined from the shift of the C 1s peak under a 403 nm laser irradiation for six selected samples with Te = 0.6%–32%. The inset shows XPS valence band spectra and the Gaussian fits (solid black lines) for the six samples with increasing Te content.

selected samples with the Te content ranging from 0.6% to 32%. The VBM energies were determined by fitting the VB spectra with a convolution of a step function and a Gaussian function (cumulative distributed Gaussian function),

$$A(E) = \frac{K}{2} \left[1 - \operatorname{erf} \left(\frac{E - E_s}{\sqrt{2}\sigma} \right) \right], \quad (1)$$

where K is the step function amplitude, E_s is the step function transition energy, and σ is the Gaussian function broadening. The transition energy of the step function is determined as the position of the VBM. The inset shows XPS valence band spectra for samples with increasing Te. Two trends are clearly observed: an increasing spectral weight and the upward shift of the highest valence band edge with increasing Te content. The solid black lines in the inset of Fig. 4 show the fitting for all six spectra. The XPS measurements show that the valence band edge moves up as Te is incorporated in ZnO with the upward shift >1.5 eV for the alloy with $\sim 30\%$ Te. These results will be further analyzed with the modified BAC modeling calculations in Sec. III B 3.

2. Band edges measured by synchrotron x-ray absorption/emission spectroscopies

To directly probe the conduction band and valence band movement as the alloy composition changes, we carried out synchrotron soft x-ray absorption and emission measurements of the oxygen partial density of states in the conduction and valence bands of $\text{ZnO}_{1-x}\text{Te}_x$ alloys, respectively, with increasing Te contents.³⁴ In order to avoid surface effects, the bulk sensitive total fluorescence yield (TFY) XAS data were used here. Figure 5(a) shows the XES and XAS spectra obtained for seven samples ranging from pure ZnO to ZnTe with 32% Te. An enlarged view of the VBM and conduction band minimum (CBM) regions is shown in Fig. 5(b). It can be seen that as the Te content increases in the film, the VBM energy increases, while the CBM remains relatively unchanged.

The VBM and CBM energies are determined using a linear extrapolation near the onset of the XES and XAS spectra, respectively, and the results are shown in Fig. 6. Both the VBM and the CBM for $\text{ZnO}_{1-x}\text{Te}_x$ films with $x > 0$ are determined with reference to the positions of pure ZnO. Despite the uncertainty in the exact value of the XES band edges, the measurement shows an initial rapid shift of the valence band edge at a low Te content followed by a slow monotonic upward shift of VBM at higher Te contents. These results are in good agreement with the XPS measurements. Figure 6 also shows the CBM and VBM over the entire composition calculated using the modified BAC model, and these will be discussed in Sec. III B 3.

3. Theoretical calculations of the $\text{ZnO}_{1-x}\text{Te}_x$ dispersion relation

The BAC model has been widely accepted for describing the electronic band structure in HMA systems.^{22,24–26,28,29} The model was initially developed for alloys in the dilute composition limits by treating the abrupt changes at the CBM and VBM as new bands formed through the interaction of the mismatched

FIG. 5. (a) Normalized x-ray emission (XES) and x-ray absorption (XAS) in total fluorescent yield spectra for $\text{ZnO}_{1-x}\text{Te}_x$ samples with Te content from $x=0\%$ to 32% ; (b) magnified energy scale plots of the XES/XAS spectra showing a monotonic shift of VBM to higher energy with increasing Te content.

minority anion localized levels and the extended host band states.^{16–18} For $\text{ZnO}_{1-x}\text{Te}_x$ in ZnO-rich and ZnTe-rich regimes, the valence band and the conduction band are split into $E_V^\pm$ and $E_C^\pm$, respectively, and are given by

$$E_V^\pm(k) = \frac{1}{2} \left\{ [E_{V,\text{ZnO}}(k) + E_{\text{Te}}] \pm \sqrt{(E_{\text{Te}} - E_{V,\text{ZnO}}(k))^2 + 4C_{\text{Te}}^2 x} \right\}, \quad (2)$$

FIG. 6. Conduction band minimum (CBM) and valence band maximum (VBM) determined from XAS/XES measurements. The VBM positions measured by XPS are also plotted for comparison. The solid lines are CBM and VBM over the entire $\text{ZnO}_{1-x}\text{Te}_x$ composition range calculated using the modified BAC model.

$$E_C^\pm(k) = \frac{1}{2} \left\{ [E_{C,\text{ZnTe}}(k) + E_{\text{O}}] \pm \sqrt{(E_{\text{O}} - E_{V,\text{ZnTe}}(k))^2 + 4C_{\text{O}}^2 (1-x)} \right\}, \quad (3)$$

where E_{Te} and E_{O} are the Te and the O localized level located above the ZnO valence band and below the ZnTe conduction band, respectively. $E_{V,\text{ZnO}}(k)$ and $E_{C,\text{ZnTe}}(k)$ are the dispersions of the ZnO valence band and the ZnTe conduction band, while C_{Te} and C_{O} are the coupling parameters describing the interaction strength between the extended ZnO VB and ZnTe CB states and the localized Te and O states, respectively. Hence, Eq. (2) gives the VB dispersion relation under the valence band anticrossing (VBAC) interaction for ZnO-rich ZnOTe alloys, whereas Eq. (3) gives the CB dispersion relation under conduction band anticrossing (CBAC) interaction for ZnTe-rich ZnOTe alloys.

To obtain the band edge positions for HMAs over the whole composition range, a simple method of compositionally weighting the BAC results obtained in the dilute limits was adopted.^{19,24,26,28,29} However, this simplistic approach significantly overestimated the bandgap reductions for the alloys in the midrange composition.^{26,28,29} One of the main deficiencies of the model is its assumption for constant coupling parameters over the entire composition.³⁰ To address this, we recently developed a modified BAC model where composition dependent coupling parameters were used and the model was demonstrated to fit well the experimental data obtained for the $\text{GaN}_{1-x}\text{Sb}_x$ HMAs.³⁰

In the following, we adopt the modified BAC model using coupling parameters with linear composition dependence to analyze $\text{ZnO}_{1-x}\text{Te}_x$ HMAs. The absorption coefficient was calculated by considering the transitions between the various valence and conduction subbands. Moreover, to account for the band broadening inherent to the BAC model,¹⁷ the optical Joint Density of States (JDOS) is convoluted with a Gaussian function at each wave vector $\mathbf{k}$.^{26,30}

Figure 7(a) shows an example of the band structure calculated using the modified BAC model for a $\text{ZnO}_{1-x}\text{Te}_x$ with $x=0.23$. The total calculated optical absorption (dashed) and the

FIG. 7. (a) BAC calculated electronic band structure of a $\text{ZnO}_{0.77}\text{Te}_{0.23}$ alloy showing the various conduction and valence subbands due to interactions of O states with the matrix CB and Te states with the matrix VB. (b) The total calculated optical absorption (dashed) and the individual contributions from the eight optical transitions from various VB to CBs.

individual contributions from the eight optical transitions from various VBs to CBs are shown in Fig. 7(b). By fitting the experimentally measured absorption coefficient with the BAC calculations, we obtain the following VBAC parameters: $C_{\text{Te}}(x=0) = 1.65 \text{ eV}$ and $E_{\text{Te}} = 0.99 \text{ eV}$, and the broadenings for the various bands range from $\Delta_{\text{V}}^+ = 0.01 - 0.3 \text{ eV}$, $\Delta_{\text{V}}^- = 0.01 - 0.3 \text{ eV}$, $\Delta_{\text{SO}}^- = 0.01 - 0.2 \text{ eV}$, $\Delta_{\text{C}}^+ = 0.05 - 0.5 \text{ eV}$, and $\Delta_{\text{C}}^- = 0.1 - 0.4 \text{ eV}$. Combining these VBAC parameters with the CBAC parameters reported in the literature,²⁵ the compositional dependence of the band edges of the $\text{ZnO}_{1-x}\text{Te}_x$ alloy is calculated across the whole composition range and the results are shown as solid lines in Fig. 6. Experimental bandgap data obtained in this work for $\text{ZnO}_{1-x}\text{Te}_x$ HMAs with x up to 0.34 using XAS/XES and optical absorption are

shown together with the calculated minimum gap in Fig. 8. The results from the absorption coefficient α were obtained by the conventional method of extrapolating α^2 to the baseline. Hence, the experimental bandgap values represent the minimum gap (i.e., transition from E_{V}^+ to E_{C}^-). Also included for comparison is the bandgap for ZnTe-rich dilute ZnTe HMAs reported in the literature.^{25,35,36} Figure 8 reveals that calculated bandgaps based on the modified BAC model are in excellent agreement with experimental values both for dilute alloys and for alloys with high composition. As illustrated in Fig. 6, the drastic bandgap reduction on the ZnO-rich side of the alloy system is primarily due to the upward shift of the valence band due to the interaction with the Te localized level located at 0.99 eV above the VBM of ZnO.

C. Electrical properties of $\text{ZnO}_{1-x}\text{Te}_x$ HMAs

It is now well established that a propensity of semiconductor materials for n-type (p-type) doping is determined by the location of the CBM (VBM) energy relative to the Fermi level stabilization energy, E_{FS} ,^{37,38} which is a common energy reference located at 4.9 eV below the vacuum level. As can be seen in Fig. 7, ZnO with its CBM located at only about 0.1 eV above and the VBM more than 3 eV below E_{FS} is always n-type and there is no reliable evidence of p-type doping.^{13,39–42} On the other hand, ZnTe with its VBM less than 1 eV below and the CBM more than 1 eV above E_{FS} is easy to dope p-type, although a limited n-type doping is possible. It has been shown previously that alloying of GaN with GaSb can produce a p-type GaNSb.⁴³ This effect was explained by a rapid upward shift of the VBM upon introduction of Sb into GaN. Since as we have shown in the Sec. III B, the alloying of ZnO with ZnTe leads to a dramatic upward shift of the VBM closer to E_{FS} , the question arises whether this effect could be used to produce a p-type ZnOTe. To address this issue, we have studied the effects of adding N acceptors on the electrical properties of ZnOTe.

All the undoped $\text{ZnO}_{1-x}\text{Te}_x$ films synthesized by PLD in this work show n-type conductivity. In order to focus on the effect of Te alloying on the electrical properties of the $\text{ZnO}_{1-x}\text{Te}_x$ films, a series of samples with similar grain sizes but different Te contents ranging from 0.6% to 13.4% were studied. Figure 9 shows electrical

FIG. 8. A comparison of the bandgap obtained by the BAC model and experimentally determined values from the absorption coefficient α and XAS/XES data in this work as well as the bandgap obtained for dilute ZnTe HMAs from the literature.^{25,35,36}

FIG. 9. (a) Electron concentration n and mobility μ and (b) resistivity ρ of ZnO_{1-x}Te_x samples with a similar grain size of ~ 20 nm but different Te contents from 0.6% to 13.4%.

transport properties of the selected samples with a similar grain size of ~ 20 nm. As shown in the figure, both the electron concentration n and the mobility μ decrease and hence the resistivity ρ increases with increasing Te content. The resistivity increases over three orders of magnitude with increasing Te content from 0.6% to 13.4%. Since the grain size of these films is about the same, the lowered n is related to the increase in carrier compensation with increasing Te content, while the decrease in μ may be the effects of both compensation and random alloy scattering. As discussed in Sec. III B, the introduction of Te causes a drastic upward shift of VB, which favors the formation of acceptorlike native defects,³² which in turn compensate the native donors, resulting in a lowered n and μ . A similar increase in resistivity with the incorporation of Te in ZnO has also been reported for epitaxial ZnOTe films by Porter *et al.*⁴⁴

The above results indicate that the upward shift of the VBM closer to E_{FS} affects the balance between donorlike and acceptorlike native defects. Here, we attempt a p-type doping of ZnO_{1-x}Te_x with nitrogen by introducing different amounts of N₂ gas during the deposition. Nitrogen has been proposed to be one possible p-type dopant for ZnO.^{13,42,45,46} However, given the deep N level in the ZnO bandgap (>300 meV above VB)^{47,48} and the extremely low

location of the ZnO VBM, no reliable p-type ZnO:N has been reported. Figure 10 shows the electrical properties (n and μ) of ZnO_{1-x}Te_x films deposited with a different N₂ pressure with a 5.1% Te target. Notice that all the doped films shown in Fig. 10 are still n-type, with the electron concentration decreasing over five orders of magnitude (from 10²⁰ to 10¹⁵/cm³) with increasing N₂ pressure from 0 Torr to 5 mTorr. At the same time, the electron mobility decreases from 22 to 3 cm²/V s.

As discussed in Sec. III A (Fig. 1), the Te content in ZnO_{1-x}Te_x also increases with increasing background gas pressure irrespective of the gas species (Ar, N₂, or O₂). The Te content for the samples studied in Fig. 10 increases from 1.8% to 3.4% as the N₂ gas pressure increases. Figure 9 shows that such variation in the Te content will decrease the electron concentration by approximately a factor of 3. Hence, the 5 orders of magnitude decrease in n shown in Fig. 10 with increasing N₂ cannot be explained by the increase in the Te content in the film. In order to isolate the effect

FIG. 10. Electron concentration (a) and mobility (b) variation with respect to N₂ background pressure for ZnO_{1-x}Te_x samples grown by PLD using the target with 5.1% Te.

FIG. 11. A comparison of the electron concentration of $\text{ZnO}_{1-x}\text{Te}_x$ and ZnO deposited in various Ar and N_2 background pressures.

of N incorporation on the electrical properties of $\text{ZnO}_{1-x}\text{Te}_x$, control experiments were performed with the samples deposited under Ar background pressure so that samples with a similar composition can be compared. Figure 11 shows the electron concentration of both ZnO and $\text{ZnO}_{1-x}\text{Te}_x$ under Ar (empty symbols) and N_2 (solid symbols) background pressure. For ZnO, under Ar background pressure from 0 to 15 mTorr, the electron concentration remains high (10^{19} – 10^{20} cm^{-3}). In contrast, with 15 mTorr N_2 pressure, n for ZnO dropped to $3 \times 10^{17} \text{ cm}^{-3}$. A much more drastic drop in n from mid- 10^{19} to 10^{15} cm^{-3} is observed for $\text{ZnO}_{1-x}\text{Te}_x$ with 5 mTorr of N_2 during deposition. At 15 mTorr of N_2 , the $\text{ZnO}_{1-x}\text{Te}_x$ film becomes insulating.

The drop in electron concentration in ZnO due to N incorporation shown in Fig. 11 is consistent with compensation due to N acceptors. At the same time, the compensation necessarily increases the ionized impurity scattering and hence also lowers the carrier mobility (as shown in Fig. 10). Such compensation by N acceptors is even more drastic in $\text{ZnO}_{1-x}\text{Te}_x$. This confirms the picture in which the Te content induces an upward shift of the VBM in ZnOTe shown in Fig. 6 and greatly reduces the formation energy of native acceptor defects, shifting the balance toward p-type conductivity. However, as is seen in Fig. 6, this shift may not be sufficient as the VBM is more than 1 eV below E_{FS} and the CBM is still close to E_{FS} . This is in contrast to GaNSb alloys where p-type conductivity was achieved when both VBM and CBM were separated by about 0.5 eV from E_{FS} .⁴³

IV. CONCLUSION

We have carried out a systematic investigation on the synthesis as well as structural, electrical, and electronic band structure properties of $\text{ZnO}_{1-x}\text{Te}_x$ highly mismatched alloys with a ZnTe mole fraction up to 34%. The effect of key PLD growth parameters (ambient gas pressure, gas type, and substrate temperature) on the various properties of this material was studied. We found that films grown

with high (>5 mTorr) Ar and N_2 pressure result in a significantly higher Te incorporation. In O_2 ambient, however, oxidation of the Te species occurred, resulting in much less efficient Te incorporation on the O sublattice. In order to overcome the miscibility gap, a relatively lower temperature is needed for the growth of $\text{ZnO}_{1-x}\text{Te}_x$ films with a substantial fraction of Te. While a lower substrate temperature is needed for the incorporation of more Te in the $\text{ZnO}_{1-x}\text{Te}_x$ film, the crystallinity of the film degrades. Calculations based on a modified BAC model using compositionally dependent coupling parameters reveal that the drastic bandgap reduction on the ZnO-rich side of $\text{ZnO}_{1-x}\text{Te}_x$ HMA is primarily due to the upward shift in the valence band caused by the interaction with the Te states located at $\sim 0.9 \text{ eV}$ above the valence band of ZnO. The upward shift of the valence band is experimentally confirmed by XPS and XES/XAS results. A good agreement between experimental CBM and VBM as well as minimum bandgap values with the electronic band structure described by the BAC model was achieved for $\text{ZnO}_{1-x}\text{Te}_x$ both for HMA in the dilute limits and for a composition up to $\sim 34\%$ Te. $\text{ZnO}_{1-x}\text{Te}_x$ alloys with $x = 0.2$ have a direct energy gap of about 1.8 eV. This provides a good candidate as the top cell material in a Si-based double junction tandem solar cell. In addition to the optimum energy gap, this alloy also has its CBM energy at about $\sim 4.9 \text{ eV}$ below the vacuum level, which provides a good band alignment with the VBM of Si located at 5.1 eV below the vacuum level.

Electrically, we found that adding Te in ZnO increases the film resistivity due to the upward shift of the VBM that favors the formation of native acceptors. When doped with N via increased N_2 background pressure during the growth, a drastic drop of n from mid- 10^{19} to 10^{15} cm^{-3} is observed for $\text{ZnO}_{1-x}\text{Te}_x$ with $\sim 2\%$ – 4% of Te. The results are interpreted in terms of location of the VBM and CBM relative to the Fermi level stabilization energy, E_{FS} .

ACKNOWLEDGMENTS

The materials synthesis and characterization were performed in the Electronic Materials Program at LBNL and were supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, under Contract No. DE-AC02-05CH11231. K.M.Y. acknowledges the support of the General Research Fund of the Research Grants Council of Hong Kong SAR, China, under Project No. CityU 11303715 and CityU SGP 9380076.

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