Intermediate Band Solar Energy Conversion in ZnTeO

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Abstract—**Energy conversion in solar cells incorporating ZnTeO base layers is presented. The ZnTeO base layers incorporate intermediate electronic states located approximately 0.4eV below the conduction band edge as a result of the substitution of O in Te sites in the ZnTe lattice. Cells with ZnTeO base layers demonstrate optical response at energies lower than the ZnTe bandedge, a feature that is absent in reference cells with ZnTe base layers. Quantum efficiency is significantly improved with the incorporation of ZnSe emitter/window layers and transition from growth on GaAs substrates to GaSb substrates with a near lattice match to ZnTe.**

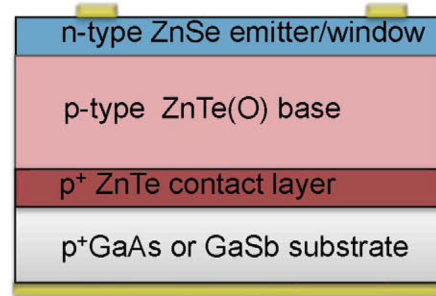
Index Terms—**Photovoltaic cells, heterojunctions, II-VI semiconductor materials, photoluminescence, oxygen.**

I. Introduction

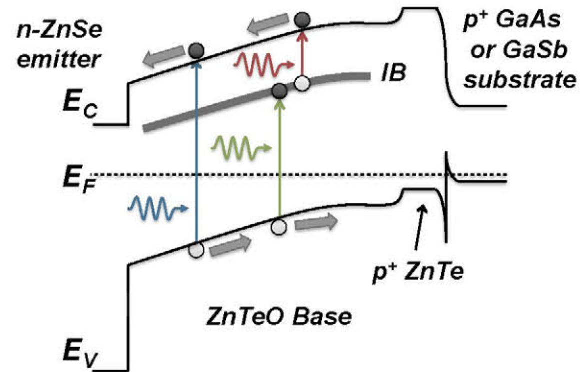
Intermediate energy states or energy bands in a semiconductor provide multiple spectral absorption bands that may be used to enhance solar energy conversion [1], [2]. However, efficient solar energy conversion requires proper positioning of the intermediate states to optimize spectral bands, strong optical transitions, and decoupling of thermal carrier processes in the intermediate states from the conduction and valence bands. Highly mismatched alloys (HMAs) are promising for intermediate band solar cells (IBSC), where the formation of intermediate states may be achieved and is often attributed to band anti-crossing behavior [3]. The use of an alloy system is attractive for an IBSC, offering the potential for a high density of states, strong optical absorption, and a production friendly process technology. ZnTe with dilute oxygen content is one such HMA, where the oxygen-tellurium substitution is known to provide electronic states 0.4 eV below the conduction band [4]. Initial ZnTeO intermediate band solar cells have been demonstrated [5], [6], though device performance has been low due to challenges associated with junction formation and identification of a proper substrate for growth. In this work, the characteristics of solar cells with ZnTeO absorbers will be presented. Improved diode performance is achieved through epitaxial growth on GaSb substrates with a near lattice match and n-ZnSe heterojunction window layers, as well as through use of graded ZnSeTe alloys. Subbandgap response is observed near 1.9 eV corresponding to oxygen states in ZnTe.

II. Experiment

Materials were grown by molecular beam epitaxy (MBE) using solid sources for Zn, Se, Te, and a plasma source for oxygen. P-type ZnTe:N doping was achieved using a plasma source for nitrogen, and n-type ZnSe:Cl doping was achieved using solid source $ZnCl_2$. Epitaxial layers were grown on GaAs (001) and GaSb (001) substrates resulting in a lattice misfit with respect to ZnTe of 7.4% and 0.15%, respectively. The structural and optical properties of the material were measured by x-ray diffraction and photoluminescence spectroscopy.



(a)



(b)

Fig. 1. Schematic diagrams of (a) solar cell device structure and (b) energy band diagram of the ZnTeO solar cell devices studied in this work.

Solar cells were fabricated using conventional photolithography, metallization, and etching techniques. The heterojunction material and device structure are shown in Fig. 1. The device structure consists of a heavily doped p-ZnTe:N contact layer, undoped ZnTe(O) base layer, and n-ZnSe:Cl emitter and window layer. Electrical characteristics were measured using a semiconductor device parameter analyzer. Optical

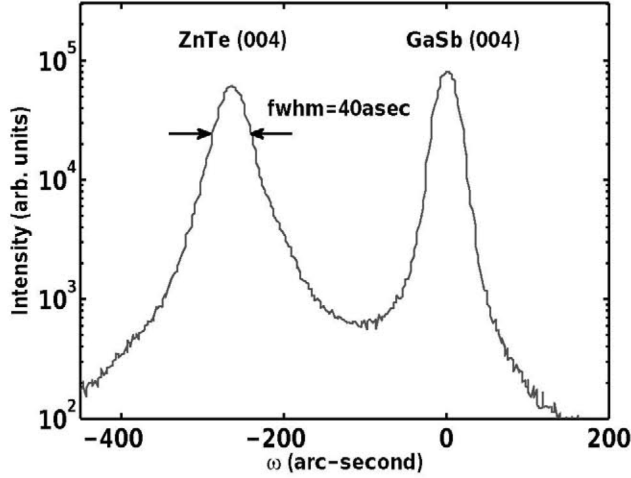


Fig. 2. X-ray diffraction ω-2θ scan for the (004) reflection of ZnTeO grown on GaSb (001).

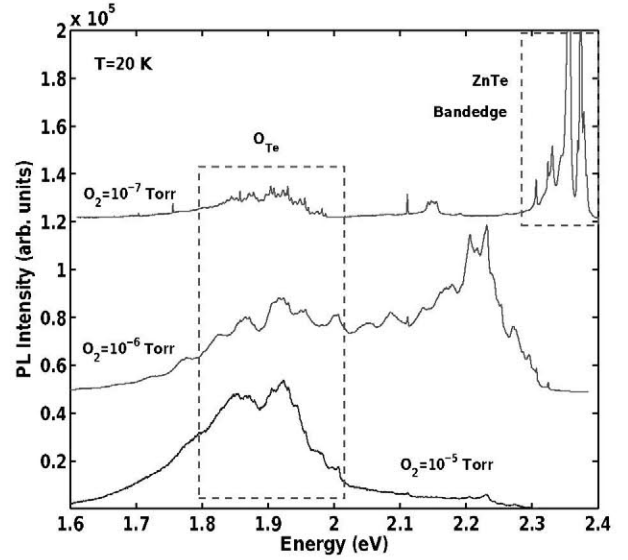


Fig. 3. Photoluminescence spectra of ZnTeO layers grown on GaAs under varying oxygen flow rate.

measurements were performed using either a halogen lamp or calibrated AM1.5 source, as indicated in the text.

III. Results and Discussion

A. Material Properties

The epitaxial materials demonstrate high quality structural and optical properties, with significantly improved behavior for ZnTe(O) grown on GaSb in comparison to ZnTe(O) grown on GaAs. Representative material properties are illustrated by the X-ray diffraction (XRD) and photoluminescence data in Fig. 2 and 3. The XRD ω-2θ scan shown in Fig. 2 illustrates good structural quality on GaSb, with a full width at half maximum (fwhm) of 40 arcsec and a shift relative to the substrate of 264 arcsec corresponding to a lattice misfit of 0.1%. Samples grown on GaAs exhibit broadened XRD peaks of several hundred arcsec due to an increase in dislocation density arising from the large lattice mismatch between ZnTe and GaAs.

Photoluminescence spectra for samples with varying oxygen flow rate are shown in Fig. 3. The maximum oxygen content corresponding to the O_2 partial pressure of 10^{-5} Torr was determined to be approximately 0.5% ($ZnTe_{0.995}O_{0.005}$) based on independent SIMS and NRA measurements. The PL spectra at T=20 K for low oxygen flow demonstrate strong ZnTe bandedge emission near 2.38 eV and emission from O_{Te} substitutional impurities near 1.9 eV [4]. The increase of oxygen flow rate results in an increase in the PL emission intensity and quenching of the ZnTe bandedge PL. The integrated PL intensity remains relatively unchanged, suggesting that the increase in oxygen content is not introducing any appreciable increase in non-radiative recombination pathways in the material. The quenching of the bandedge PL may be attributed to fast electron relaxation from the conduction band to the O_{Te} states, as described from previous time-resolved optical measurements [7]. Optical absorption as a result of the O_{Te} states has similarly been reported [8], and is the origin of intermediate band solar energy conversion. Temperature dependent photoluminescence measurements indicate an internal quantum efficiency of approximately 5 %, estimated from the ratio of PL emission at room temperature relative to low temperature.

B. Current-Voltage Characteristics

The ZnTeO solar cell devices exhibit strong rectifying behavior and photovoltaic response, as shown in the current-voltage (J-V) characteristics in Fig. 4. Significant reduction in leakage current and enhancement in short circuit current are observed for samples grown on GaSb substrates. The short circuit current is improved by more than a factor of 10 using the same device structure on differing substrates. We believe that these improvements are primarily due to reduction in dislocation density, and therefore reduction in non-radiative recombination pathways in the material. The performance of these devices is still substantially below the ideal ZnTe diode, where an increase in open circuit voltage by approximately a factor of two can be expected for ideal material. The reduced open circuit voltage may be attributed to the highly-mismatched p-ZnTe/n-ZnSe heterojunction, where a high dislocation density is expected for the lattice mismatch of approximately 7%. Further improvements in open circuit voltage will require breakthrough technologies to achieve reliable n-type ZnTe and/or to significantly reduce the defect density at the p-ZnTe/n-ZnSe heterojunction interface.

C. Spectral Response

The influence of the intermediate band response cannot be effectively observed in the J-V characteristics due to variability in device performance that is likely due to variations in material quality and defect density. We have in fact observed all combinations of increased/decreased current

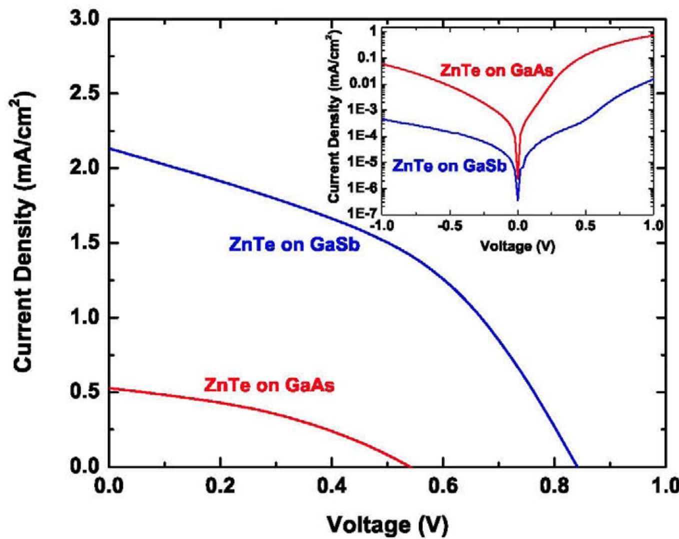


Fig. 4. Current-voltage response under illumination by a halogen lamp, comparing n-ZnSe/p-ZnTeO heterojunction diodes on GaAs and GaSb substrates

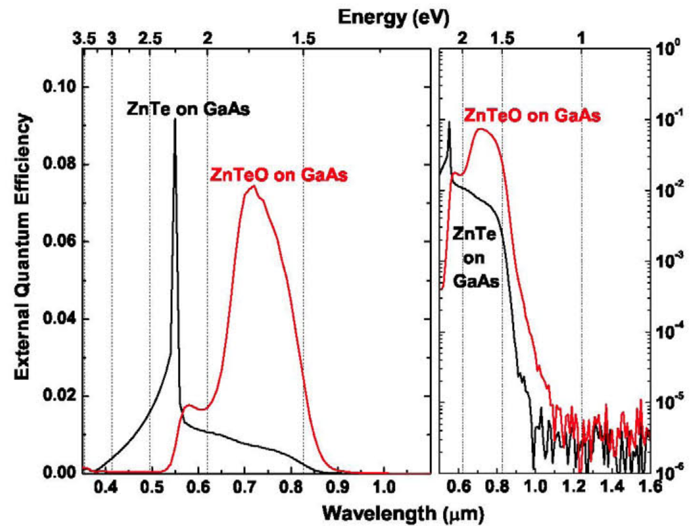


Fig. 5. External quantum efficiency of a p-ZnTe(O) base layer on n-GaAs demonstrating enhanced response below the ZnTe bandedge.

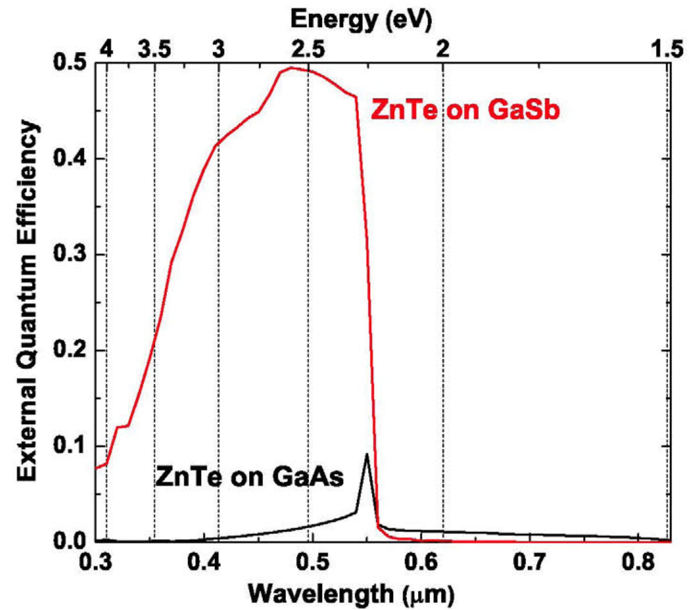


Fig. 6. External quantum efficiency comparing a p-ZnTe/n-GaAs solar cell on GaAs substrate to an n-ZnSe/p-ZnTe solar cell on GaSb substrate

and increased/decreased voltage when comparing cells with ZnTeO base layers to reference cells with ZnTe base layers. A more obvious means of detecting the intermediate band response is through the external quantum efficiency. Enhanced response is observed at wavelengths below the bandedge for cells with ZnTeO base layers, as shown in Fig. 5. The devices shown in Fig. 5 were taken from the same samples that were reported in 2009 [5] and measured two years later, illustrating the stability of the intermediate band transition over time. One feature of note in the quantum efficiency for the ZnTeO sample is the turn-on for the response corresponding to the ZnTe bandedge. In this device, the response is dominated by subbandgap processes. While the subbandgap response is desirably observed, the drop in response above ZnTe bandgap is sacrificed, suggesting a degradation in carrier transport and lifetime parameters that must be improved in order to make this material a viable technology.

Significant improvements in performance for response above the bandgap are realized through growth on GaSb substrates and incorporating an n-ZnSe emitter/window layer. The resulting EQE is shown in Fig. 6 for one of these devices and compared to the prior p-ZnTe/n-GaAs reference cell in Fig. 5. An increase in the overall quantum efficiency is observed, likely due to reduced defect density and corresponding increase in minority carrier lifetime and minority carrier diffusion length. The EQE also maintains a relatively high value above the ZnTe bandedge, which can be attributed to the proper function of the ZnSe window layer in isolating the ZnTe(O) base layer from the surface. An inflection point and drop off in EQE is observed near 2.7 eV, corresponding to the ZnSe bandgap, further supporting this conclusion.

D. Inverted p-ZnTe/ZnTeO/n-ZnSe Devices on GaAs

One concern with the improved n-ZnSe/ZnTe(O)/p-ZnTe diodes is the location of the junction near the surface, which poses difficulty in carrier collection for subbandgap response where absorption is located further from the surface. An inverted device structure has been investigated that places the junction near the substrate interface, using an n-ZnSe buffer layer and intermediate graded n-ZnSeTe alloy, as shown in Fig. 7. The graded ZnSeTe layer is approximately 100 nm thick, and is intended to reduce dislocation formation in transitioning from the ZnSe lattice constant to the ZnTe lattice constant. The J-V characteristics of the inverted structure is shown

in Fig. 8 in comparison to a representative n-ZnSe/ZnTe/p-ZnTe/GaSb solar cell. One note on these measurements is the use of AM1.5 illumination for the data in Fig. 8, where photovoltaic response is lower than shown in Fig. 4 where halogen illumination is used due to the larger compenent of UV/visible light above the ZnTe bandgap for the halogen spectrum relative to AM1.5. The performance of the inverted structure with ZnTeO on GaAs actually exceeds the performance of the ZnTe on GaSb, despite the large lattice mismatch for GaAs substrates and associated increase in dislocation density. This behavior demonstrates the importance of the n-ZnSe/p-ZnTe junction in determining diode performance, where the graded ZnSeTe layer appears to be desirable for improving the electrical junction. Another key observation for the inverted diode structure is that the performance is maintained using a ZnTeO base layer, implying that the solar cell performance is not dramatically degraded by the presence of oxygen.

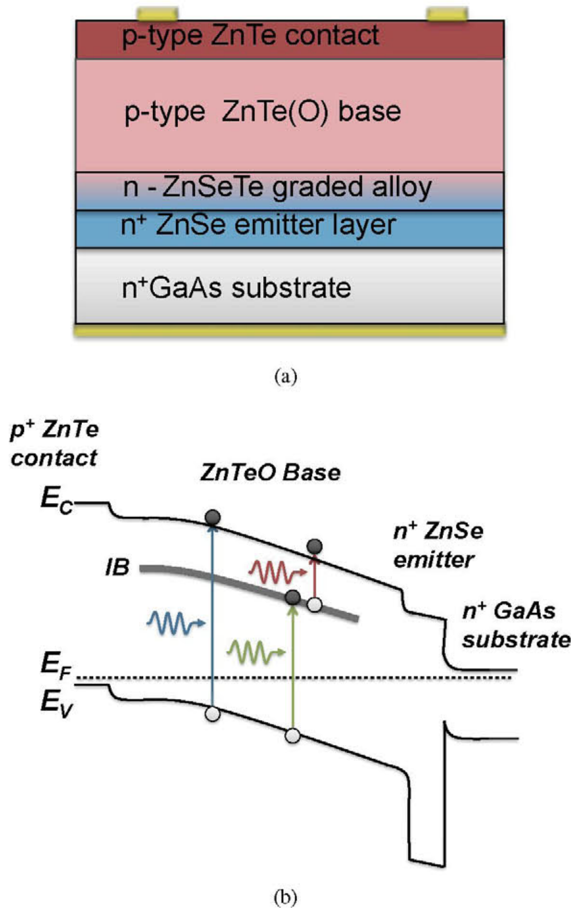


Fig. 7. Schematic diagrams of (a) solar cell device structure and (b) energy band diagram of the ZnTeO solar cell devices studied in this work.

Subbandgap response is also observed in the inverted structure, as demonstrated by the J-V characteristics in Fig. 9 with varying light excitation. Illumination with a red laser (λ = 635 nm) and power density of 375 mW/cm^2 results in a photogenerated current and open circuit voltage of 0.3 V. In comparison to response with white light excitation with a halogen source, the addition of the red laser shows a small, but measurable, increase in response through addition contributions from subbandgap excitation.

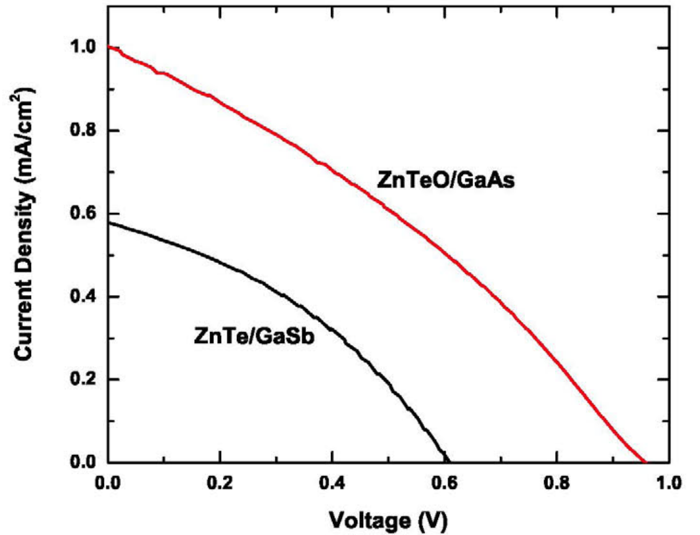


Fig. 8. Current-voltage response under AM1.5 illumination of inverted p-ZnTe/ZnTeO/n-ZnSe/GaAs structure in comparison to n-ZnSe/ZnTe/p-ZnTe/GaSb.

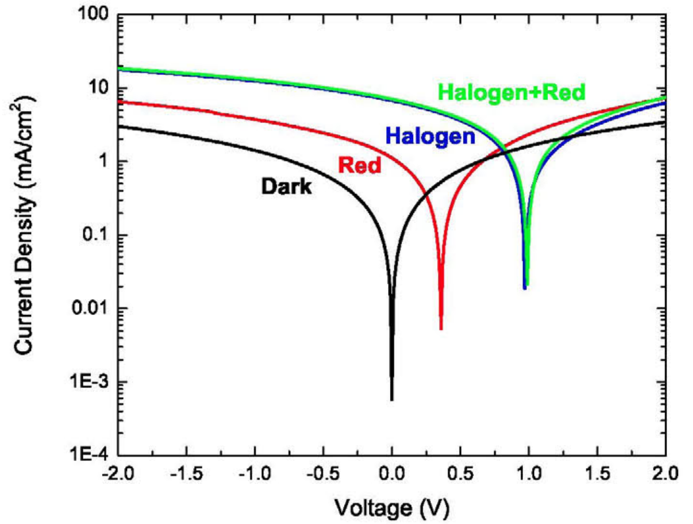


Fig. 9. Current-voltage characteristics of inverted p-ZnTe/n-ZnSe/GaAs diode with graded ZnSeTe layer comparing response under dark, subbandgap illumination with a red laser (λ = 635 nm), halogen lamp, and halogen lamp with red laser.

IV. Conclusion

The introduction of O_{Te} substitutional impurities in ZnTe provides a path for sub-bandgap optical absorption without a significant sacrifice in the optical and electronic properties of the material. These transitions may be effectively utilized for an intermediate band solar cell material. Presently, the performance of solar cells utilizing ZnTeO base layers are limited by the ability to obtain a high-quality rectifying

junction. The ability to grow on substrates with a near lattice match, the incorporation of wide-bandgap window layers, and graded ZnSeTe layers at the electrical junction have all shown improvement in the electrical performance of ZnTe heterojunction solar cells. An inverted diode structure on GaAs utilizing a ZnTeO base exhibits good performance relative to typical ZnTe heterojunction reference cells and demonstrate that oxygen does not dramatically decrease performance, while also providing subbandgap response to potentially increase conversion efficiency. Further improvements to produce a more ideal junction and to understand the energy conversion process associated with oxygen levels in ZnTe are critical in realizing the potential of ZnTeO intermediate band solar cells.

ACKNOWLEDGMENT

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