

## Measurement of Band Offsets in (Ce,Tb)MgAl<sub>11</sub>O<sub>19</sub>/InGaZnO<sub>4</sub> Heterostructure System

Jong Cheon Park<sup>a</sup>, Kyeong-Won Kim<sup>b</sup>, Jae Woong Lee<sup>b</sup>, Brent P. Gila<sup>b</sup>, David P. Norton<sup>b</sup>, Fan Ren<sup>c</sup>, Stephen J. Pearton<sup>b</sup>, Ok Geun Jeong<sup>a</sup>, Tae Gyu Kim<sup>d</sup>, Jin Kon Kim<sup>d</sup>, and Hyun Cho<sup>d,\*</sup>

<sup>a</sup>Department of Nano Fusion Technology, Pusan National University, Miryang, Korea

<sup>b</sup>Department of Materials Science and Engineering, University of Florida, Gainesville, USA

<sup>c</sup>Department of Chemical Engineering, University of Florida, Gainesville, USA

<sup>d</sup>Department of Nanomechatronics Engineering, Pusan National University, Miryang, Korea

The energy discontinuity in the valence band ( $\Delta E_V$ ) and conduction band ( $\Delta E_C$ ) of (Ce,Tb)MgAl<sub>11</sub>O<sub>19</sub> (CTMA)/InGaZnO<sub>4</sub> (IGZO) heterostructure was obtained from X-ray photoelectron spectroscopy measurements. The CTMA exhibited a band gap of  $\sim 7.02 \pm 0.2$  eV from absorption measurements. Determination of the band offsets using Ga 2p<sub>3/2</sub>, Zn 2p<sub>3/2</sub> and In 3d<sub>5/2</sub> energy levels as references shows a valence band offset of  $\sim 0.55$  eV. This implies a conduction band offset  $\Delta E_C$  of  $\sim 3.27$  eV in CTMA/IGZO heterostructures and a nested interface alignment.

**Key words:** Band offsets, (Ce,Tb)MgAl<sub>11</sub>O<sub>19</sub>/IGZO heterostructure, X-ray photoelectron spectroscopy, Valence band offset.

### Introduction

Recently, amorphous oxide semiconductors have attracted much attention for flat panel displays and flexible thin film transistors (TFTs) because they are optically transparent in the visible range and exhibit superior electrical characteristics compared to amorphous Si which is dominantly used in TFTs [1-5]. In particular, InGaZnO<sub>4</sub> (IGZO) deposited at low deposition temperature has shown very high electron mobility in the amorphous state ( $10\text{--}50\text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$ ) and the possibility to control the conductivity through the oxygen partial pressure during deposition. Moreover, its ability to be deposited at room temperature allows for use of novel flexible substrates such as plastic or even paper, which raises the possibility of making low-cost electronics on a very wide range of arbitrary surfaces [6-11]. Amorphous IGZO TFTs have potential applications as switches in the active-matrix and driver-integrated circuits of low cost flexible displays. A major remaining issue with IGZO is a better understanding of the appropriate choice of compatible gate dielectrics for TFTs fabricated using IGZO channels. (Ce,Tb)MgAl<sub>11</sub>O<sub>19</sub>(CTMA) has shown promising performance as a gate dielectric oxide for electric field gated structures with ZnO. This complex oxide has a relatively high dielectric constant ( $k \approx 10$ ) and exhibited low leakage current characteristics on ZnO [12]. In this letter we report the band offsets in PLD deposited

CTMA/IGZO heterojunctions. The valence band offset was determined to be  $\Delta E_V = 0.55 \pm 0.23$  eV from X-Ray Photoelectron Spectroscopy (XPS) measurements, leading to a conduction band offset of  $\Delta E_C$  of 3.27 eV.

### Experimental

The CTMA films were deposited in a conventional pulsed laser deposition system (base pressure  $\sim 3 \times 10^{-7}$  Torr) using a KrF 248 nm excimer laser as an ablation source at room temperature in  $5 \times 10^{-3}$  Torr oxygen. The ablation target was prepared from commercial Ce<sub>0.33</sub>Tb<sub>0.67</sub>MgAl<sub>11</sub>O<sub>19</sub> phosphor powders (Stanford Materials). The powders were pressed into 1 inch targets and annealed in air at 1400 °C for 14 h. The CTMA layers were grown on IGZO and Si at room temperature in  $5 \times 10^{-3}$  Torr oxygen. The target displayed bright green luminescence when exposed to 248 nm ultraviolet light and the strong absorption yields an efficient laser ablation process with virtually no particular ejection from the target. The IGZO was deposited by sputtering on both Si and glass substrates (Corning EAGLE 2947) using an RF magnetron system with a 3-inch diameter single target of InGaZnO<sub>4</sub>. The temperature at the substrate was  $\sim 40$  °C after the  $\alpha$ -IGZO deposition. The RF power was 150 W, while the working pressure was held constant at 10 mTorr in a pure Ar ambient. The carrier concentration in the resulting films was  $4.14 \times 10^{17}\text{ cm}^{-3}$  from Hall data. The In/Ga/Zn ratio was measured by X-ray microprobe. The films were amorphous as determined by powder x-ray diffraction (XRD), and showed optical transmittance of  $\sim 80\%$  in the visible range. Assuming parabolic density of states within the

\*Corresponding author:  
Tel : +82-55-350-5286  
Fax: +82-55-350-5289  
E-mail: hyuncho@pusan.ac.kr

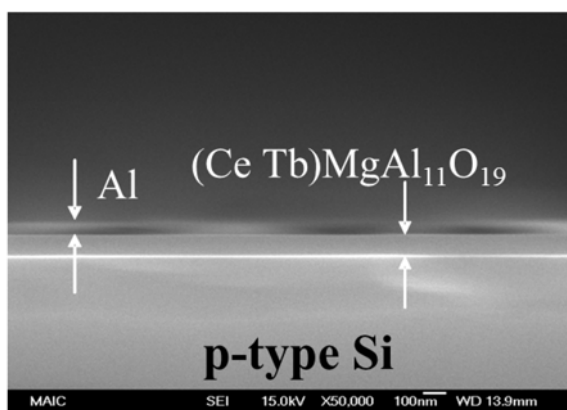
$\alpha$ -IGZO, we determined an optical energy gap of  $\sim 3.2$  eV from Tauc plots [13], similar to previous reports [14-19]. To obtain the band offsets from XPS measurements, three samples were characterized: a 2000 Å thick IGZO layer grown on Si, 2000 Å CTMA/IGZO and 25 Å CTMA/IGZO.

To obtain the valence band offset, high resolution XPS spectra were measured to determine the chemical state of the Ga, In and Zn. A Physical Electronics PHI 5100 XPS with an aluminum x-ray source (energy 1486.6 eV) with source power 300 W was used, with an analysis area of  $10 \text{ mm} \times 4 \text{ mm}$  and exit angle of  $45^\circ$ . The electron pass energy was 35.75 eV. The approximate escape depth ( $3\lambda \sin \theta$ ) of the electrons was 80 Å. Using the known position of the C-(C,H) line in the C 1s spectra at 284.5 eV, charge correction was performed. The total energy resolution was  $0.10 \pm 0.01$  eV. The valence band offset was obtained from the usual core-level photoemission-based approach [20-22], with charge neutralization performed with an electron flood gun. We did not observe significant charging even without this precaution since the IGZO is conducting.

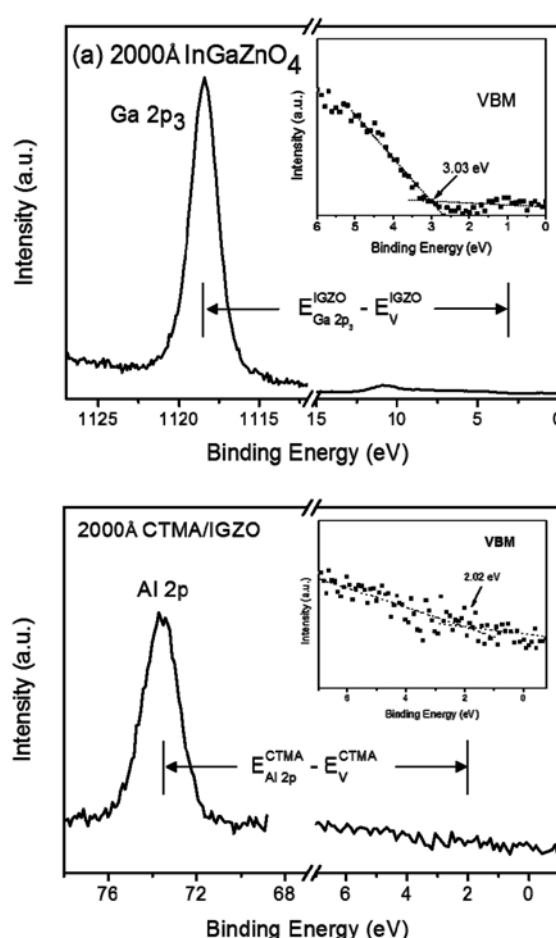
The valence band maximum was determined by using a linear extrapolation method. Core-level peaks were referenced to the top of the valence band for the thick InGaZnO and the thick film of CTMA. To determine the valence band offset, the binding energy differences between the valence band minimum and the selected core peaks for the single thick layers were combined with the core-level binding energy differences for the heterojunction sample [20-27]. The XPS spectrometer was calibrated using a polycrystalline Au foil. The peak position and Fermi-edge inflection point for the Au  $f_{7/2}$  peak were determined to be  $84.00 \pm 0.002$  and  $0.00 \pm 0.02$  eV, respectively. The binding energy range of 0-100 eV is accurate on an absolute scale within 0.02-0.03 eV.

## Results and Discussion

Fig. 1 shows the cross-sectional SEM image of an



**Fig. 1.** Cross-sectional SEM micrograph of the Al/CTMA/Si multilayer structure.



**Fig. 2.** XPS narrow scans of Ga 2p<sub>3</sub>, Al 2p and valence band spectra of (a) 2000 Å IGZO/Si substrate and (b) 2000 Å CTMA/IGZO/Si.

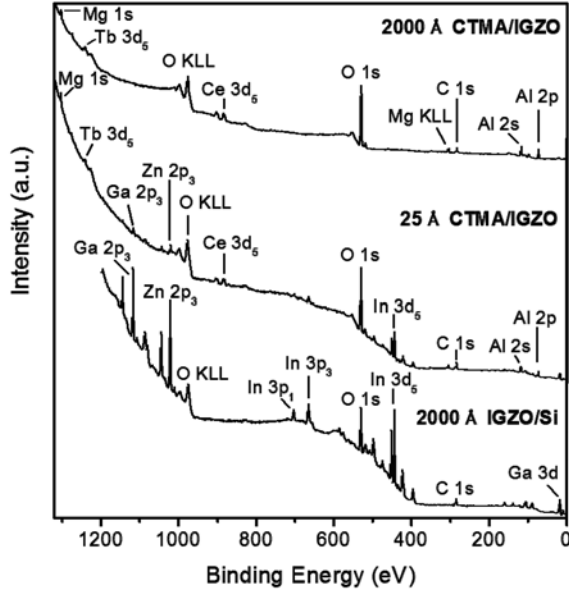
Al/CTMA/Si multilayer structure. The layers are smooth and well-defined. This structure was used for separated measurements of interface state density and was determined to be  $1 \times 10^{10} \text{ eV}^{-1} \text{ cm}^{-2}$  near the conduction band edge.

The XPS narrow scan of Ga 2p<sub>3</sub> and valence band spectrum from the 2000 Å IGZO/Si substrate samples using a pass energy of 35.75 eV and step size of 0.01 eV is presented in Fig. 2(a). The valence band value ( $E_V$ ) was determined by linearly fitting the leading edge of the valence band and linearly fitting the flat energy distribution and finding the intersection of these two lines, as shown in the insets of the figure. Fig. 2(b) shows the XPS Al 2p narrow scan and valence band spectrum from the 2000 Å CTMA/IGZO.

Fig. 3 shows the core level survey spectra of CTMA, 25 Å layer of CTMA on IGZO, and IGZO/Si at a pass energy of 89.45 eV and a take-off angle of  $45^\circ$ . A summary of the XPS band offset results are shown in Table 1. As a further check on the results, the valence band offsets were also determined for core level peaks for In ( $3d_{5/2}$ ), Ga ( $2p_{3/2}$ ), and Zn ( $2p_{3/2}$ ). These values

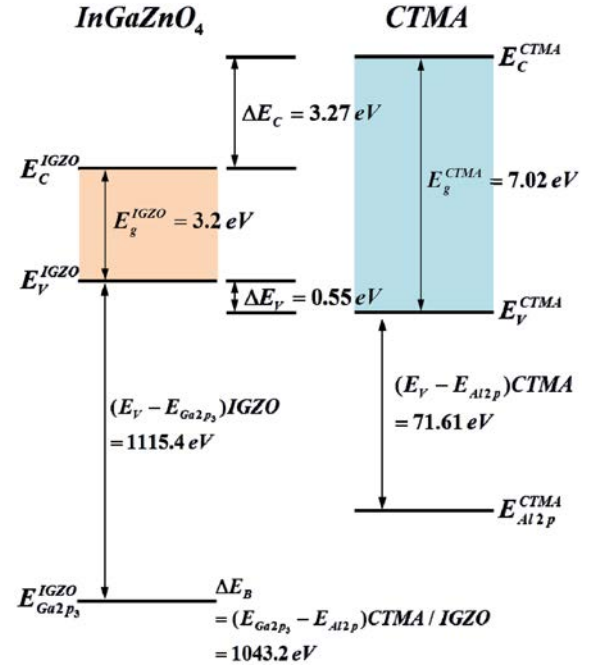
**Table 1.** Values of band offsets determined in these experiments (eV).

Metal core	IGZO VBM	Metal core level	Metal core IGZO VBM	CTMA VBM	Al 2p	Al 2p-CTMA VBM	Metal core-Al 2p	Valence band offset ( $\Delta E_V$ )
Ga 2p <sub>3</sub>	3.03	1118.44	1115.41	2.02	73.63	71.61	1043.22	0.58
In 3d <sub>5</sub>	3.03	445.24	1115.41	2.02	73.63	71.61	370.3	0.3
Zn 2p <sub>3</sub>	3.03	1022.45	1115.41	2.02	73.63	71.61	947.04	0.77

**Fig. 3.** Core level survey spectra of 2000 Å CTMA, 25 Å layer of CTMA on IGZO, and 2000 Å IGZO/Si at pass energy of 89.45 eV and a take-off angle of 45°.

were then inserted into the following equations to calculate  $\Delta E_V$ , namely  $\Delta E_V = (E_{\text{Core Level Peak}} - E_V)_{\text{IGZO}} - (E_{\text{Al2p}} - E_V)_{\text{thick CTMA}} - (E_{\text{Core Level Peak}} - E_{\text{Al2p}})_{\text{CTMA/IGZO}}$ . The resulting  $\Delta E_V$  was  $0.55 \pm 0.23$  eV for the CTMA/IGZO oxide heterojunction, with all three core level peaks falling within the experimental error. To determine the conduction band offset, we need the bandgap of the CTMA, which was measured experimentally since oxide bandgaps reported in the literature often show a dependence on deposition conditions due to compositional and impurity effects. The optical energy band gap,  $E_{\text{gap}}$ , for the 6000 Å CTMA deposited on a transparent sapphire was determined from the sharply increasing absorption region according to Tauc and Menth's law [13]. The optical energy band gap was determined by extrapolating the linear portion in the high energy region of the transmittance spectra. The estimated optical band gap is  $\sim 7.02 \pm 0.2$  eV.

Fig. 4 shows a schematic of the energy band lineup in the CTMA/IGZO heterostructure system, with all of the energy scales included. The band gap of the IGZO used here is 3.2 eV at room temperature, as mentioned earlier. The band gap difference of  $\sim 3.82$  eV between the CTMA and IGZO gives a ratio of 6:1 between the conduction band offset ( $\Delta E_C$ ) and valence band offset ( $\Delta E_V$ ). A conduction band offset of 3.27 is more than

**Fig. 4.** Energy band diagram of a thin CTMA/IGZO heterojunction interface.  $\Delta E_B$  is the corresponding core level separation measured across the interface.

sufficient to provide a significant electron confinement potential in the IGZO channel.

## Conclusions

The valence band offset of CTMA/IGZO heterostructure was determined to be  $\sim 0.55$  eV from XPS measurements. Given the band gap difference of  $\sim 3.82$  eV between these two materials, this translates to a nested interface band alignment with a conduction band offset of  $\sim 3.27$  eV. This indicates excellent conduction band offset can be obtained in this materials system.

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