Journal of Ceramic Processing Research. Vol. 18, No. 9, pp. 687~690 (2017)

J O U R N A L O F
Ceramic Processing Research

Measurement of band offsets in $MgO/InGaZnO_4$ heterojunction by X-ray photoelectron spectroscopy

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Amorphous $InGaZnO_4$ (α-IGZO) thin film transistors (TFTs) are one of the most promising candidates for switches in the active-matrix and driver-integrated circuits of transparent liquid crystal displays and flexible displays. The stability and overall performance of amorphous IGZO TFTs depend to a great extent on the band offsets in gate dielectric/α-IGZO heterojunction. The energy discontinuity in the valence band (ΔE_V) and conduction band (ΔE_C) in MgO/IGZO heterojunctions were systematically examined by using X-ray photoelectron spectroscopy (XPS). The MgO gate dielectric was found to have a straddled type band offset alignment on the IGZO. The valence band offset value for the MgO/IGZO heterojunction was determined as 0.81 ± 0.17 eV using the Ga $2p_{3/2}$, Zn $2p_{3/2}$ and In $3d_{5/2}$ energy levels as references. The bandgap energy difference between the MgO and IGZO led to a corresponding conduction band offset (ΔE_C) of ~3.79 eV and a nested interface alignment.

Key words: $MgO/InGaZnO_4$ heterojunction, Band offsets, XPS, Interface alignment.

Introduction

Amorphous oxide semiconductors thin film transistors (TFTs) have recently shown very exceptional potential for switches in the active-matrix and driver-integrated circuits of transparent displays due to their optical transparency in the visible range and superior electrical characteristics compared to conventional amorphous Si TFTs [1-5]. In addition to high optical transparency, field-effect mobility higher than 3-5 $cm^2 \cdot V^{-1} \cdot sec^{-1}$, low threshold voltage, high on/off ratios and high frame rate are needed in the large area transparent active-matrix liquid crystal displays and organic light emitting diode displays. Amorphous $InGaZnO_4$ (IGZO) TFTs deposited at low temperature are one of the most promising candidates which can meet those requirements. IGZO has shown very high electron mobility in the amorphous state (10-50 $cm^2 \cdot V^{-1} \cdot sec^{-1}$), the possibility to control the conductivity through the oxygen partial pressure during deposition, and its ability for device fabrication over a wide range of novel flexible substrates [6-10]. A major remaining issue with IGZO is a better understanding of the appropriate choice of compatible gate dielectrics for TFTs fabricated using IGZO channels. Band offsets in the gate dielectric/IGZO heterojunction are of critical importance for designing heterostructure TFT devices since the stability and overall performance of IGZO TFTs depend to a great extent on the dielectric layer. High-k dielectrics generally have smaller band offsets are expected to lead to a low breakdown voltage and high leakage current due to the excitation of electrons or holes by Schottky emission into the oxide conduction or valence band [11]. MgO is one of the promising gate dielectrics for IGZO TFTs due to its high dielectric constant and relatively low leakage current and good thermal stability [12,13].

In this paper, we report the energy discontinuity in the valence band (ΔE_V) and conduction band (ΔE_C) of MgO/IGZO heterostructures determined from X-ray photoelectron spectroscopy (XPS) measurements. The valence band offset was determined to be ΔE_V = 0.81 ± 0.17 eV from X-ray photoelectron spectroscopy (XPS) measurements by using the Ga $2p_{3/2}$, Zn $2p_{3/2}$ and In $3d_{5/2}$ energy levels as references, leading to a conduction band offset (ΔE_C) of 3.79 eV.

Experimental

The MgO films were grown on IGZO/Si and Si substrates by pulsed laser deposition with a 248 nm KrF excimer laser at room temperature in 5×10^{-3} Torr oxygen. The IGZO films were deposited by RF magnetron sputtering on both Si and glass substrates (Corning EAGLE 2947) using a commercial 3-inch diameter $InGaZnO_4$ target. The RF power was 140 W and the process pressure was maintained at 10 mTorr in a pure Ar ambient. The grown IGZO films were

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amorphous and had the same composition with the IGZO target. The carrier concentration of the grown IGZO film was measured as 4.14×10^{17} cm^{-3} and optical transmittance of ~80% in the visible range was obtained. From the latter and assuming parabolic density of states within the a-IGZO, an optical energy gap of ~3.2 eV was determined from Tauc plots [14] and this is consistent with previous reports [15, 16]. Three kinds of samples were examined by XPS to obtain the band offsets in MgO/IGZO system, a 2000 Å thick IGZO layer grown on Si, a 400 Å thick MgO/IGZO and a 20 Å thick MgO/IGZO. In the XPS measurements, low-resolution survey scans were initially performed in order to examine the surfaces of the films and to determine elemental composition. And then, very high resolution spectra were acquired in order to determine the binding energy of specific elements observed in the survey spectra. A Physical Electronics PHI 5100 XPS with an aluminum x-ray source (energy 1486.6 eV) was used in these experiments. The source power was 300 W and the analysis region was 10 mm × 4 mm, with an exit angle of 45 °. The entrance slit width was 4 mm and the electron pass energy was 35.75 eV. The approximate escape depth (3λ sin θ) of the carbon electrons was 80 Å. Charge correction was performed using the known position of the C-(C,H) line in the C 1*s* spectra at 284.5 eV. The total energy resolution was 0.10 ± 0.01 eV and charge neutralization was performed with an electron flood gun. A core-level photoemission-based method was used to determine the valence band offset [17-19]. The valence band maximum (VBM) was determined by using a linear extrapolation method. Core-level peaks were referenced to the top of the valence band for the thick $InGaZnO_4$ and the thick film of MgO. To determine the valence band offset, the binding energy differences between the valence band maximum and the selected core peaks for the single thick layers were combined with the core-level binding energy differences for the heterojunction sample. This is a standard method for determining band-offsets [20-22]. 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 ± 0.002 and 0.00 ± 0.02 eV, respectively. The binding energy range of 0-100 eV is accurate on an absolute scale within 0.02-0.03 eV.

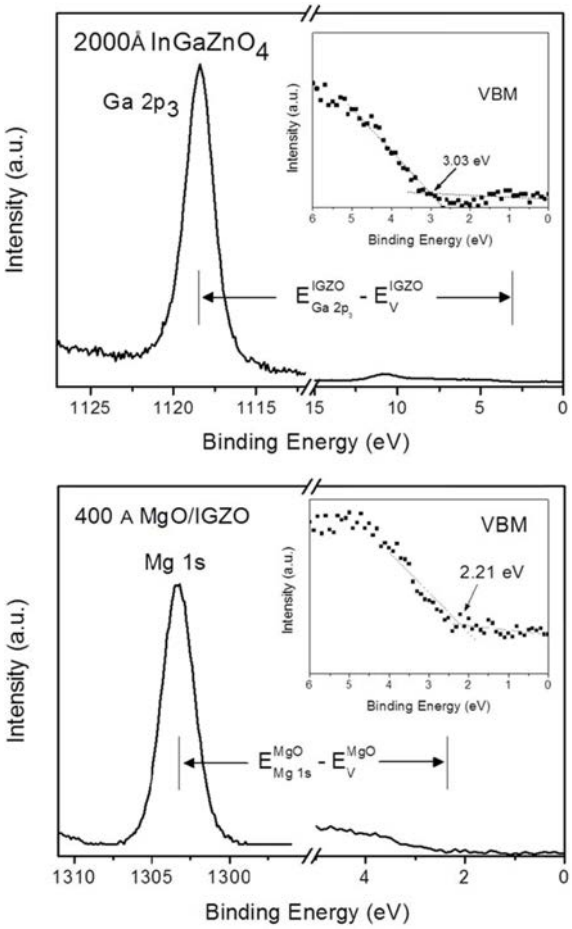

Fig. 1. XPS narrow scans of Ga $2p_3$, Mg *1s*, and valence band spectra of the 2000 Å IGZO/Si substrate and the 400 Å MgO/IGZO/Si.

Results and Discussion

Fig. 1 (top) shows the XPS narrow scan of Ga $2p_3$ and valence band spectrum acquired from the 2000 Å thick IGZO layer on Si substrate using a pass energy of 35.75 eV and a step size of 0.01 eV. 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. The resultant VBM of 3.03 eV was obtained for the 2000 Å thick IGZO layer. Fig. 1 (bottom) shows the XPS Mg *1s* narrow scans along with valence band spectra from the 400 Å MgO/IGZO. The position of core level peak of Mg *1s* was found at the binding energy of

Table 1. Values of band offsets for the MgO/IGZO determined in these experiments (eV).

Metal Core	IGZO VBM	Metal Core level	Metal core-IGZO VBM	MgO VBM	Mg *1s*	Mg 1s-MgO VBM	Metal core-Mg *1s*	Valence band offset (ΔE_V)
Ga $2p_3$	3.03	1118.44	1115.41	2.21	1303.31	1301.1	–186.61	0.92
In $3d_5$	3.03	445.24	442.21	2.21	1303.31	1301.1	–859.5	0.61
Zn $2p_3$	3.03	1022.45	1019.42	2.21	1303.31	1301.1	–282.57	0.89

1303.31 eV and VBM of the MgO was determined as 2.21 eV.

Fig. 2 shows the core level survey spectra of the 400 Å MgO layer on IGZO, 20 Å layer of MgO on IGZO and 2000 Å IGZO/Si substrate at a pass energy of 89.45 eV and a take-off angle of 45 °. Table 1 presents a summary of the XPS band offset results for the MgO/IGZO heterojunctions. As a further check on the results, the valence band offsets (ΔE_V) were also determined for core level peaks for In $3d_{5/2}$, Ga $2p_{3/2}$, and Zn $2p_{3/2}$. These values were then inserted into the following equations to calculate ΔE_V for the MgO/IGZO material system.

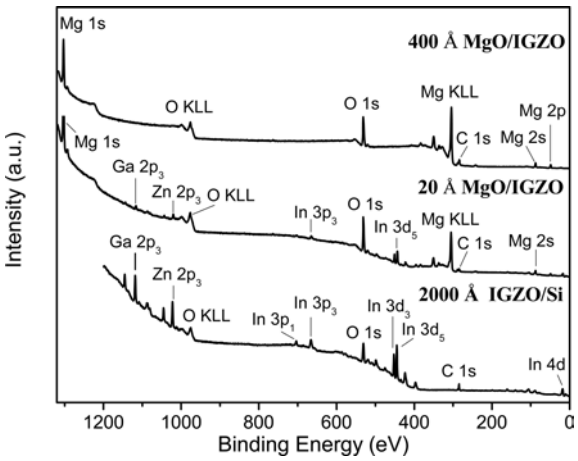

Fig. 2. Core level survey spectra of the 400 Å MgO, 20 Å layer of MgO on IGZO, and 2000Å IGZO/Si at a pass energy of 89.45 eV and a take-off angle of 45 °.

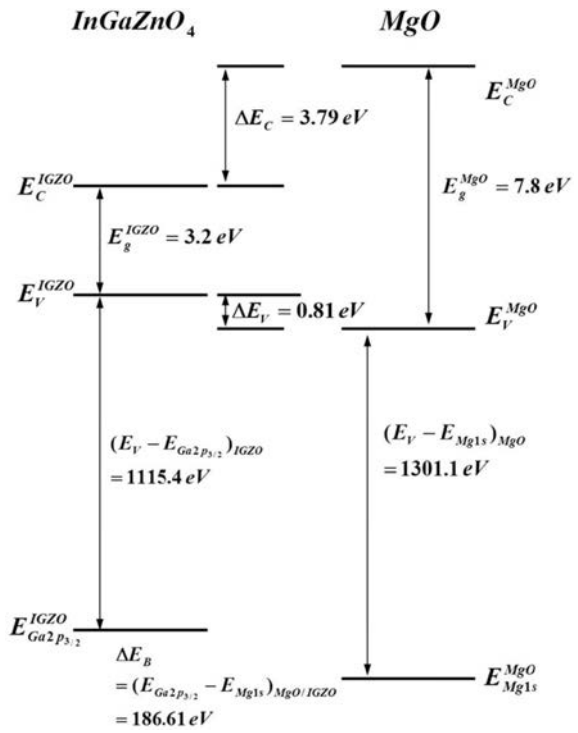

Fig. 3. Energy band diagrams of a thin MgO/IGZO heterojunction interface, ΔE_B is the corresponding core level separation measured across the interface.

$$\Delta E_V = (E_{Core\ Level\ Peak} - E_V)_{IGZO} - (E_{Mg\ 1s} - E_V)_{MgO} - (E_{Core\ Level\ Peak} - E_{Mg\ 1s})_{MgO/IGZO} \quad (1)$$

Where $(E_{Core\ Level\ Peak} - E_V)_{IGZO}$ is the energy difference between the metal core levels (In $3d_{5/2}$, Ga $2p_{3/2}$, and Zn $2p_{3/2}$) and the VBM in the thick IGZO layer, $(E_{Mg\ 1s} - E_V)_{MgO}$ is the energy difference between the Mg *1s* and the VBM in the thick MgO, and $(E_{Core\ Level\ Peak} - E_{Mg\ 1s})_{MgO/IGZO}$ is the energy difference between the metal core levels and the Mg *1s* in the MgO/IGZO heterojunction, respectively. The resulting ΔE_V value was 0.81 ± 0.17 eV for the MgO/IGZO oxide heterojunction. This is an excellent value for heterojunction field effect transistor device applications in which a strong carrier confinement is needed.

The conduction band offset (ΔE_C) in the MgO/IGZO heterojunction was determined by using the following equation;

$$\Delta E_C = E_g\,(MgO) - E_g\,(IGZO) - \Delta E_V \quad (2)$$

The bandgap energy of the IGZO here is ~3.2 eV at room temperature, as mentioned earlier. The bandgap differences of ~4.6 eV between the MgO [23] and IGZO lead the conduction band offset of ~3.79 eV, which is more than sufficient to provide a strong carrier confinement in the IGZO channel. Fig. 3 shows a schematic of the energy band lineup in the MgO/IGZO heterojunction, with all of the energy scales included. It was found that the MgO/IGZO heterojuncion has a straddled type band offset alignment with an almost 4.7 : 1 ratio between and an almost 4.7 : 1 ratio between the conduction band offset (ΔE_C) and the valence band offsets (ΔE_V).

Conclusions

The band offsets in the MgO/IGZO heterojunction were studied by XPS measurements. The valence band offset in the MgO/IGZO heterojunction was determined to be 0.81 ± 0.17 eV. Given the bandgap differences between the MgO and IGZO, this translates to a straddled type interface band alignment with a conduction band offset of 3.79 eV. This shows that the MgO is a promising candidate as a gate oxide material for the amorphous IGZO-based TFTs since the MgO/IGZO heterojunction can provide good valence and conduction band offsets.

Acknowledgments

The work at University of Florida was supported in part by National Science Foundation (J.M. Zavada). The use of the Major Analytical Instrument Center facilities at University of Florida is appreciated.

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