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Valance band offset of $TiO_2/CuGaO_2$ hetero-structure measured by x-ray photoelectron spectroscopy

R.S. Ajimsha [a,*], Amit K. Das [a], Vikas Kumar Sahu [a], M.P. Joshi [a], L.M. Kukreja [a], Uday P. Deshpande [b], T. Shripathi [b]

[a] Laser Material Processing Division, Raja Ramanna Centre for Advanced Technology, Indore 452013, India
[b] UGC-DAE Consortium for Scientific Research, Indore, India

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ABSTRACT

We studied the band offset and alignment of pulsed laser deposited $TiO_2/CuGaO_2$ hetero-structure using x-ray photoelectron spectroscopy. Valance band offset (VBO) of $TiO_2/CuGaO_2$ interface was calculated using Kraut equation as 2.15 eV, which was in corroboration with VBO obtained directly from valance band onsets. A schematic band alignment diagram for the $TiO_2/CuGaO_2$ interface was constructed which showed a type II band alignment with a significant band bending of 0.48 eV. Interface studies of $TiO_2/CuGaO_2$ hetero-structure, showing type II band alignment, is important for gaining insight to the design of various photovoltaic devices based on such hetero-structures.

1. Introduction

In the case of TiO_2 based dye sensitized solar cells (DSSCs), extensive research has been going on to find out a suitable solid-state hole transport medium to circumvent the issues related to the present TiO_2/liquid electrolyte interfaces [1,2]. Basic requirement for the hole transport medium is that its valance and conduction band positions should be compatible with that of TiO_2, i.e. type II band alignment to drive the charge transport process across the junction [3]. In addition, hole transport material should be transparent and photo-chemically stable with reasonably good carrier mobility. Inorganic p-type materials such as CuI and CuScN have been generally used as hole transport mediums in solid-state DSSCs [1,2]. Various delafossites like $CuAlO_2$, $CuGaO_2$, $AgCoO_2$, $AgGaO_2$, etc. are the known p-type transparent conducting oxides, generally used in transparent electronic applications [4–7]. Among these p-type delafossites, $CuGaO_2$ is a promising p-type transparent conducting oxide (TCO) which can replace the existing hole transport mediums in TiO_2 based DSSCs, due to its high transparency (~80%), better conductivity ($\sim 10^{-1}$ S cm^{-1}) and its stability towards photo-corrosion [8].

Information about the band alignment and offset at the interface of $TiO_2/CuGaO_2$ hetero-structure is essential for the chemical design of sensitizer dye which has to ensure the separation and transport of photo-induced carriers. Valance band offsets and band alignment studies of $TiO_2/CuGaO_2$ interface have not been reported so far. Therefore it becomes essential to study the band offset and hence the band alignment of $TiO_2/CuGaO_2$ hetero-structures. X-ray photoelectron spectroscopy (XPS) has been demonstrated as a direct and powerful tool for determining the valance band offset and hence the band alignment of various hetero-structures [9–11]. In this paper, we report the studies on the band offset and alignment of $TiO_2/CuGaO_2$ hetero-structures using x-ray photoelectron spectroscopy. Results indicate that a type II band alignment with a significant band bending of 0.48 eV is formed at the interface of $TiO_2/CuGaO_2$ hetero-structure.

2. Experimental

All the thin films and hetero-structures were grown using pulsed laser deposition (PLD) on sapphire (0001) substrates. For all the depositions, we used KrF excimer laser with wavelength ~248 nm, pulse duration 20 ns, repetition rate 10 Hz and energy density ~1 J/cm^2. Prior to each deposition, the vacuum chamber was evacuated to a base pressure of $\sim 5 \times 10^{-6}$ mbar. During deposition, oxygen partial pressure was maintained at 10^{-3} mbar for both TiO_2 and $CuGaO_2$ thin films. Sintered pellets of TiO_2 and $CuGaO_2$ were used as targets for respective depositions. The substrate to target distance was kept at ~40 mm for all the depositions. Substrate temperatures were kept at 400 °C for TiO_2 and 600 °C for $CuGaO_2$. Three films were grown on sapphire substrates for XPS studies; ~400 nm TiO_2 thin film (A1), ~400 nm $CuGaO_2$ thin film (A2) and ~5 nm $CuGaO_2$ thin film on ~400 nm TiO_2 thin film (A3).

* Corresponding author. Tel.: +91 731 2488304; fax: +91 731 2488300.
E-mail address: ajimsha@gmail.com (R.S. Ajimsha).

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3. Results and discussions

XPS measurements were performed using ESCA instrument with AlK$_\alpha$ ($h\nu = 1486.6$ eV) as the x-ray radiation source. All XPS spectra were calibrated by the C 1s peak (284.6 eV). Exposure to normal atmosphere may contaminate sample surface and this may affect the precision of the measurement. To solve the issues related to contamination, Ar sputtering was used for five minutes to clean the surface of all the samples prior to XPS measurement. After Ar sputtering, peaks related to contaminations were significantly reduced. All the core-level peak positions were obtained by fitting the respective core-level spectra using Shirley background and Voigt (mixed Gaussian–Lorentzian curve) line shape functions.

X-ray diffraction pattern (XRD) of TiO_2 thin film showed only an anatase phase with (101) peak at $2\theta = 25.4°$. Only (001) diffraction peaks were observed in the XRD pattern of $CuGaO_2$ thin film, which indicated highly *c*-axis oriented growth (not shown here). Optical band gaps of TiO_2 and $CuGaO_2$ were found to be 3.2 eV and 3.60 eV respectively. Figs. 1 and 2 show the core levels and VBM of TiO_2, $CuGaO_2$, and $TiO_2/CuGaO_2$ hetero-structure obtained using x-ray photoelectron spectroscopy (XPS). Fig. 1(a) and (b) shows the Ti 2p peak in TiO_2 (A1) and $TiO_2/CuGaO_2$ (A3) respectively. Ti 2p peak can be deconvoluted mainly to two peaks, $2p_{1/2}$ at ~464.40 eV and $2p_{3/2}$ (Ti^{4+}) at ~459.33 eV with a separation of ~5.07 eV. These are consistent with previously reported XPS data of TiO_2 [12]. An additional shoulder peak was found at ~457.34 eV which can be assigned to Ti^{3+} state according to previous data [13]. This indicates the formation of small amount of reduced oxidation states during Ar sputtering [13]. We used $2p_{3/2}$ (Ti^{4+}) peaks of samples A1 and A3 for the calculation of valance band offset in the present work. Fig. 1(b) shows the deconvoluted peaks positioned at ~459.19 eV ($2p_{3/2}$ (Ti^{4+})), ~457.62 eV ($2p_{3/2}$ (Ti^{3+})) and ~464.23 eV ($2p_{1/2}$) in the case of sample A3. Peaks at ~933.22 eV and ~932.88 eV in Fig. 1(c) and (d) represent the $Cu2p_{3/2}$ lines of samples A2 and A3 respectively. Fig. 2(a) and (b) shows the XPS valance band (VB) spectra of $CuGaO_2$

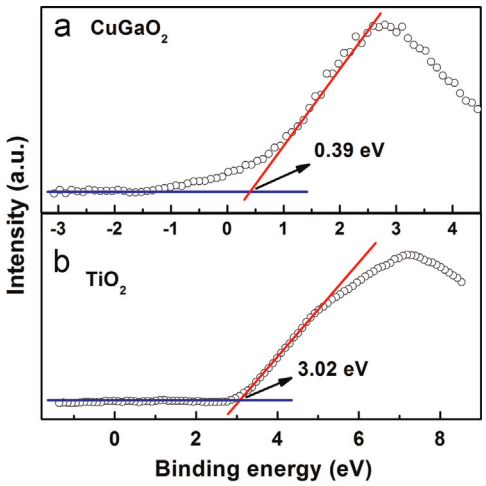

Fig. 2. Valance band edge of (a) $CuGaO_2$ (A2) and (b) TiO_2 (A1) thin films.

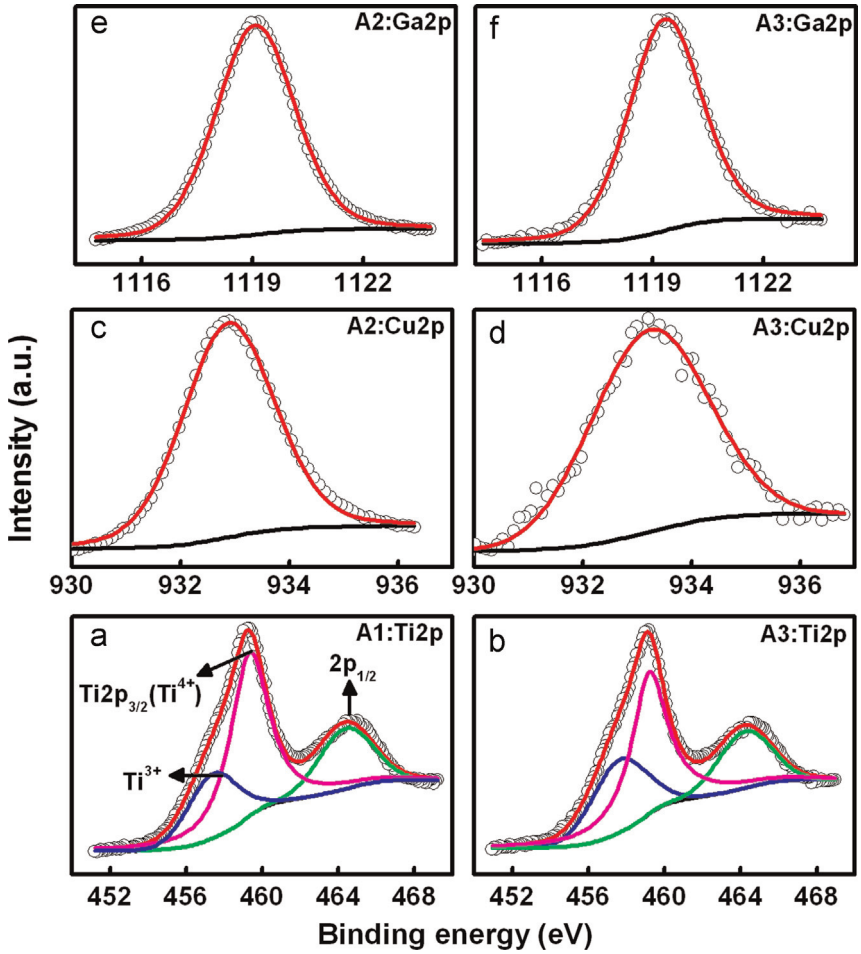

Fig. 1. XPS core level spectra of all samples. Ti2p peaks (a) in A1 and (b) in A3, $Cu2p_{3/2}$ peaks (c) in A2 and (d) in A3, $Ga2p_{3/2}$ peaks (e) in A2 and (f) in A3. Fitting of XPS core-level spectra (circles) using Shirley background (solid black line) and Voigt line shape functions (solid red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)