Solar Energy Materials & Solar Cells 127 (2014) 174–178

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Temperature-resistant high-infrared transmittance indium molybdenum oxide thin films as an intermediate window layer for multi-junction photovoltaics

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ARTICLE INFO

Article history:
Received 27 October 2013
Received in revised form
23 March 2014
Accepted 26 April 2014
Available online 21 May 2014

Keywords:
IMO
CIGS
High temperature
High mobility thin films
Multi-junction cells
TCO

ABSTRACT

For optimal performance, the intermediate window layer in multijunction photovoltaics should transmit as much light as possible to guarantee maximum device efficiency. In this work, we demonstrate that indium molybdenum oxide (IMO) is a more suitable intermediate layer, compared to indium tin oxide (ITO), as it would absorb significantly less infrared light with comparable electrical conductivity once integrated into a multijunction solar cell. In fact, we show that IMO optoelectronic properties are virtually unchanged by the typical thermal budgets used in solar absorber deposition processes used in low-cost high-performance multijunction photovoltaics (e.g. $CuInGaSe_2$). Specifically, IMO and ITO thin films were reactively sputtered onto glass substrates at 150 °C, then subjected to a vacuum annealing process (550 °C, 2 h) identical to that of co-evaporated copper gallium diselenide (CGSe), a candidate material for the top absorber in multijunction cells. We found that annealing substantially reduces the infrared transmittance of ITO starting at 900 nm, reducing by 2.5% per 100 nm, while IMO only started experiencing a reduction at 1400 nm and decaying more slowly at 1.6% per 100 nm. Furthermore, the resistivity of IMO was comparable to that of ITO after annealing. The resilience of IMO to such high temperature processes show that it has potential to enhance the performance of multijunction devices.

1. Introduction

In coherence with the Drude model of electrical conduction as applied to transparent conductive oxide (TCO) [1,2], most of the research done in the past decade on this material class has been concentrated on enhancing electron mobility in order to improve electrical conductivity, as opposed to increasing electron concentration [3–5]. While increasing the electron concentration will in fact increase the conductivity, it will also shift the plasma wavelength (the wavelength below which electromagnetic radiation is strongly reflected) from the infrared (IR) region towards the visible spectrum, making the TCO less transparent. Furthermore, the Drude model also predicts that increasing the mobility of TCO will result in a lower IR absorbance, which is an added value when used in solar cell devices because it allows more photons to pass to the absorber layer.

By exploiting this optical property of TCO, single-junction solar energy devices could potentially benefit from replacing conventional TCO (e.g. indium tin oxide (ITO) and aluminum-doped zinc oxide (AZO)) with high-mobility TCO (HMTCO, e.g. indium molybdenum oxide (IMO) and indium titanium oxide (ITiO)) to receive more IR photons and consequently increase the photocurrent density [4,6]. In fact, Koida et al. have already experimentally shown that μC–Si solar cells with HMTCO, instead of ITO, had a higher device efficiency as a result of an increase in short circuit current [7]. However, we posit that HMTCO are better suited for use in *multi-*, rather than *single-*, junction solar cells where the bottom absorbers rely on IR photons to operate efficiently. Using a conventional TCO as the intermediate layer would significantly decrease IR transmittance, reducing the bottom cell photocurrent hindering device performance on a whole.

As many multi-junction solar devices are fabricated by relatively high temperature ($\geq$ 500 °C) vacuum processes, it is critical to develop TCO thin film materials whose optoelectronic characteristics withstand annealing. Although van Hest et al. [4] have already shown that sputtering IMO at 500 °C produces films with

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http://dx.doi.org/10.1016/j.solmat.2014.04.029
0927-0248/

high IR-transmittance and conductivity, it may be necessary to deposit the intermediate TCO layer at low temperatures to avoid damage to the bottom cell (<200 °C) then subsequently deposit the top cell at high temperatures. From this viewpoint, we were curious to see if low-temperature deposited IMO would also boast high IR transmittance and conductivity after enduring a high-temperature annealing. If so, then why? In accordance, this research compares the optoelectronic properties of low-temperature sputtered ITO and IMO thin films before and after a temperature profile all in an effort to mimic a multi-junction solar cell fabrication process (550 °C maximum temperature).

2. Experimental

For side-by-side comparisons of the thin film materials under investigation in this study, batches of ITO and IMO (5 substrates per batch) were deposited by RF magnetron reactive sputtering on the tin-free side of cleaned soda lime glass substrates. The substrates were cleaned by scrubbing them in 1% alconox solution followed by 5 min of sonication in an isopropanol bath then blown dry with nitrogen gas. The cleaned substrates were then placed in the deposition chamber in a "cross" configuration. The chamber was then evacuated to a pressure between 1 and 5 μTorr by a rough pump and cryo pump in sequence at which point the temperature of the substrate was increased to 150 °C (measured at the front side of one of the substrates). An In_2O_3(90 wt%)–SnO_2(10 wt%) and an In_2O_3(98 wt%)–Mo(2 wt%) sputtering targets were used for ITO and IMO, respectively. With the shutter closed, the target was pre-sputtered for 10–15 min (50 W steps every 2 min up to 200 W). Three different tanks of gas were used to create the TCO deposition environment: (1) oxygen, (2) argon and (3) 1 vol% oxygen and 99 vol% argon mix. For ITO films, 109.0 and 22.0 sccm were used from tanks 2 and 3, respectively, at a pressure of 8.0 mTorr. For IMO films, 1.1 and 170.0 sccm were used from tanks 1 and 2, respectively at a pressure of 6.0 mTorr. Films were sputtered at 200 W of RF power until a quartz crystal monitor measured 100 nm. After the deposition was finished, the shutter was closed and RF power was stepped down in a pure argon environment for 5–10 min. All gas was then shut off and samples were allowed to cool down under high vacuum to at least 60 °C before exposing to atmosphere. At this point, selected samples of ITO and IMO were subjected to a vacuum (5 μTorr) annealing process resembling a 3-stage copper gallium diselenide (CGSe, $Eg=1.7$ eV) evaporation deposition, consisting of a first stage at 420 °C and the subsequent stages at 550 °C [8]. To make this study time-independent, each temperature setting was held for 120 min, a duration that exceeds that of each individual step in a 3-stage process.

Several measurements were performed on un-annealed and annealed ITO and IMO to observe the change in microstructural, chemical and optoelectronic properties. The thickness of each film was measured with a stylus profilometer (Tencor, alpha step 200). For each film, six thickness measurements were taken at different locations. The six measurements were then averaged to give an overall average thickness for the film. Only ITO and IMO films with similar average thicknesses (typically 100 nm $\pm$ 10 nm) were selected for comparison. X-ray photoelectron spectroscopy (XPS) was performed on a VG 220i-XL ESCALAB spectrometer equipped with a monochromatized AlKα source (1486.6 eV). Once deposited, thin films were kept under vacuum to prevent contamination. However, during the transfer from the substrate holder to the spectrophotometer, films were exposed to air for a few minutes. All XPS spectra have been realigned on C1s at 284.8 eV. A custom-made Van der Pauw and Hall measurement setup done at 16 °C under a magnetic field of 9500 Gauss was used to measure the electrical properties of sheet resistance R_s, resistivity ρ, majority carrier concentration N and hall mobility μ. The crystal structure was analyzed by an X-ray diffractometer (XRD) (Rigaku, Mini-flex 2) using Cu Kα_1 radiation (1.54059 nm) at a scan rate of 0.025°/s.

3. Results

3.1. Optical properties

Transmittance curves from 250 to 2500 nm before and after annealing of IMO and ITO are shown in Fig. 1. There are essentially three regions that noticeably change due to annealing. In the visible to near-IR (vis-NIR) region, both materials experienced small increases ($\leq 5\%$) in transmittance after annealing. Averaged over 500–900 nm, annealed ITO experienced an increase of 3.6% relative to un-annealed ITO. In contrast, IMO experienced a slightly smaller increase of 2.4% of transmittance averaged over a more stretched out range from 500 to approximately 1400 nm.

In the ultraviolet (UV) region distinct features were observed for both ITO and IMO samples (Fig. 2). In the case of ITO, a set of 2 peaks with different amplitudes was observed at 395 and 370 nm on the as-deposited sample. Upon annealing, both peaks were attenuated to a similar level. In the case of IMO, a new peak appeared to the left of the original peak after annealing with both peaks at the same transmittance level. Incidentally, both the ITO and IMO annealed samples showed nearly identical peaks at approximately the same wavelength. From the resemblance

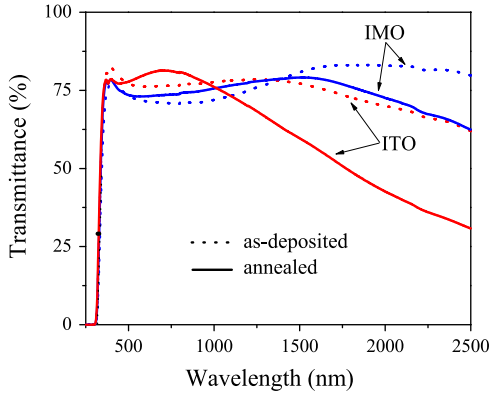

Fig. 1. Optical transmittance of typical IMO and ITO samples measured from 250 to 2500 nm. Infrared transmittance of IMO remains high even after annealing whereas that of ITO has decreased significantly.

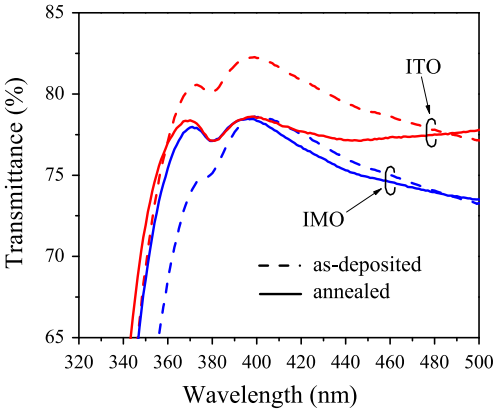

Fig. 2. Optical transmittance of typical IMO and ITO samples measured from 320 to 500 nm. Annealing increases the UV absorption edge and affects the UV transmittance peaks in both materials.