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Research Article

The Low-Temperature Crystallization and Interface Characteristics of ZnInSnO/In Films Using a Bias-Crystallization Mechanism

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This study presents a successful bias crystallization mechanism (BCM) based on an indium/glass substrate and applies it to fabrication of ZnInSnO (ZITO) transparent conductive oxide (TCO) films. The effects of bias-crystallization on electrical and structural properties of ZITO/In structure indicate that the current-induced Joule heating and interface diffusion were critical factors for low-temperature crystallization. With biases of 4 V and 0.1 A, the resistivity of the ZITO film was reduced from $3.08 \times 10^{-4}\ \Omega^*$cm to $6.3 \times 10^{-5}\ \Omega^*$cm. This reduction was attributed to the bias-induced energy, which caused indium atoms to diffuse into the ZITO matrix. This effectuated crystallizing the amorphous ZITO (a-ZITO) matrix at a lower temperature (approximately 170°C) for a short period ($\leq$20 min) during a bias test. The low-temperature BCM developed for this study obtained an efficient conventional annealed treatment (higher temperature), possessed energy-saving and speed advantages, and can be considered a candidate for application in photoelectric industries.

1. Introduction

Transparent conductive oxide (TCO) film has been applied in solar cells, light-emitting diodes, and touch panels because of its high conductivity and transmittance [1–3]. The properties of TCO films are critically affected by material compositions, manufacturing methods, and posttreatment techniques [4–7]. This study uses multicompound ZnInSnO (ZITO) material because of its potential application in various optoelectronic devices [8, 9]. In addition, thermal annealing can improve the quality of TCO films. For example, a low-resistivity tungsten-doped tin oxide TCO film was obtained by annealing at 850°C in air [10]. Thermal annealing at 450°C approached a state of minimum resistivity of ZnO-In_2O_3 thin films [5]. However, high-temperature manufacturing consumes substantial energy and is unsuitable for applications requiring flexible substrates.

This study uses the electrical current method (bias testing) instead of high-temperature manufacturing. Biasing is a familiar technique that has been applied in various fields for a long time, such as for electrochemical deposition, spot welding, and wire drawing [11–13]. The proposed bias-crystallization apparatus had no shielding gas, and the entire process was performed at low temperature. This is the first study to investigate the adjustment of ZITO crystallization using a biasing mechanism. The ZITO films used for this study were treated using the proposed BCM. This study examines the effects of the bias-induced Joule heat and diffusion on the crystallization of ZITO film and clarifies its interface characteristics.

2. Experimental Procedures

The experiments in this study involved fabricating the bias-crystallization system (BCS) using metal indium as the current-transmitting layer. An indium layer of 200 nm and a ZnInSnO (ZITO) film of 150 nm were sequentially deposited

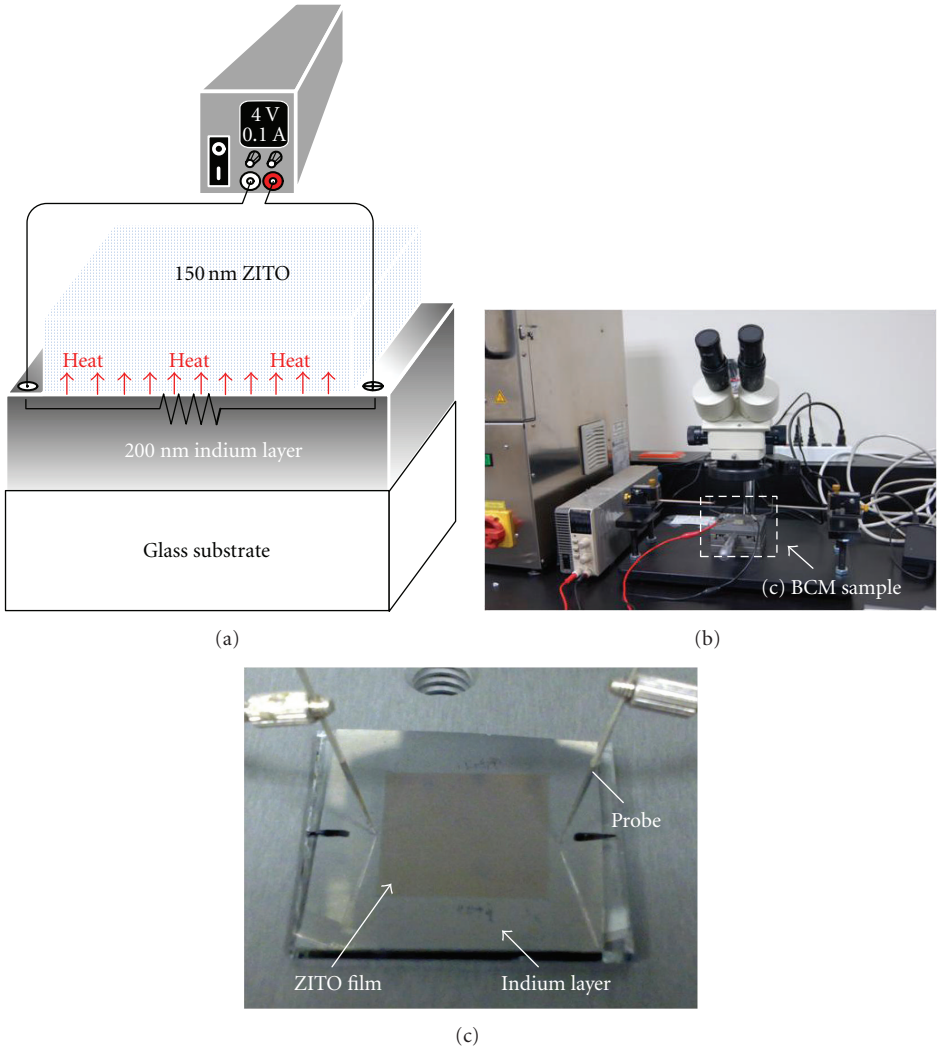

Figure 1: (a) Schematic illustration, (b) a photograph of full view, and (c) localization for the bias-crystallization mechanism (BCM) of ZITO/In sample.

onto a glass substrate by a DC magnetron sputter deposition (Helix/HLLS-87) and a cosputtering system (VAC/Model ACS-4000-C3), respectively [14]. A DC power supply (KIKUSUI, PAK60-6A) provided the electrical current. The ZITO film was adjusted by the thermal energy derived from the current passing through the metal indium. Figure 1 shows a schematic illustration of the BCS, and photographs of a full view and a close-up shot view.

The BCS also was used in our previous research [15]. Figure 2 shows an optical transmittance and a low magnification TEM image of ZnO/In/ZnO tri-layer thin film. Each layer thick of ZnO/In/ZnO trilayer film was 200 nm, 15 nm and 200 nm, respectively (inset of Figure 2), and its average transmittance in visible range (390∼800 nm) was about 80%. Briefly, a conductive metal film was suitable for a candidate of current-transmitting layer and can not affect the transmittance of TCO films. In present study, the indium layer with 200 nm thick was expressly designed to enhance the efficiency of BCM. Figure 3 plots the bias-induced thermal energy as a function of varied biasing durations under a bias voltage of 4 V. The surface temperature of the ZITO layer was measured by noncontact infrared with a laser marker thermometer. With increasing the biasing duration, the temperature of the sample surface rapidly increased from room temperature to 170°C, before tending toward saturation. This result indicates that the bias-induced joule heat in the interface zone can adjust the upper ZITO quality. Therefore, a biasing duration of 20 min was used to treat the ZITO/In sample by applying the proposed BCM.

This study investigates the structural properties of the ZITO/In sample using X-ray diffraction technique (XRD, Rigaku). Electrical measurements were conducted using the Hall system. Finally, a detailed composition of the ZITO structure was examined using high-resolution thermal field emission transmission electron microscopy (HR-TEM, JEOL/JEM-2100F) and energy-dispersive X-ray analysis (EDX).

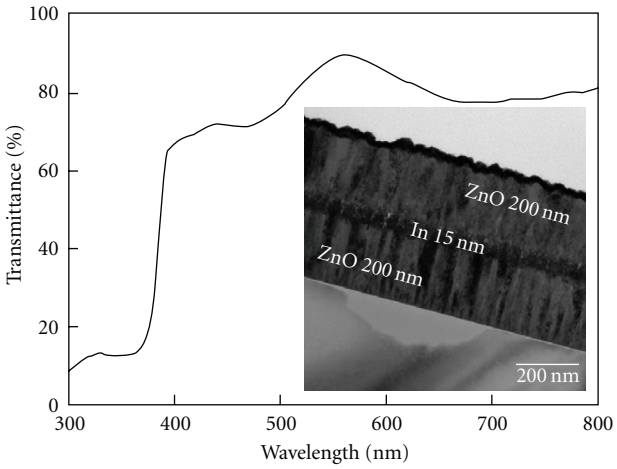

Figure 2: Optical transmittance and low magnification TEM image of ZnO/In/ZnO film.

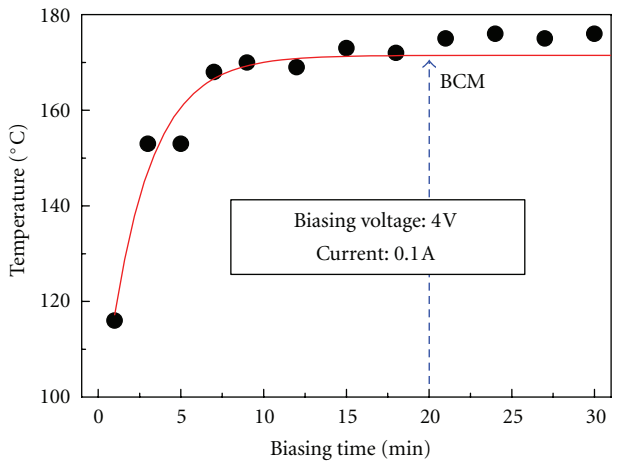

Figure 3: The relation of biasing duration and the bias-induced temperature at the biased of 4 V. (BCM: bias-crystallization mechanism).

3. Results and Discussions

Figure 4 shows the resistivity of unbiased ZITO/In sample and those biased at 4 V for 20 min. In the biased sample, film resistivity decreased from $3.08 \times 10^{-4}\,\Omega^*$ cm to $6.62 \times 10^{-5}\,\Omega^*$ cm. The bias-induced joule heat caused the indium atoms to diffuse into the ZITO film, and this diffusion decreased film resistivity. The bias-induced thermal energy in the interface between the ZITO and indium layer reduced film resistivity by improving ZITO crystallization. XRD analysis was performed to determine the influence of indium atoms diffusion on structural characteristics (inset of Figure 4). The present ZITO crystallization was attributed to an amorphous-like structure [14]. However, the as-grown ZITO/In sample exhibited a polycrystalline structure, and the In_2O_3 phase dominated the ZITO crystallization [16]. The In_2O_3 phase primarily resulted from the formation of In_2O_3 structures in the interface between the ZITO film and the indium layer during the deposition process. XRD

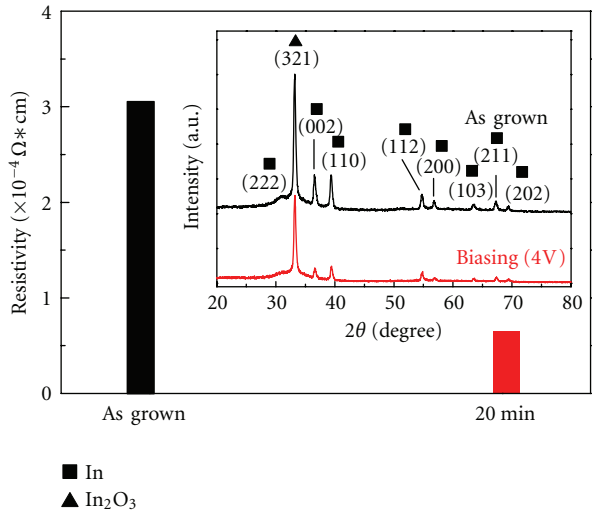

Figure 4: The resistivity and crystallization of unbiased ZITO/In sample and ZITO/In sample with biased of 4 V for 20 min.

analysis revealed the existence of a metal indium layer, which improved the crystallization in the ZITO/In sample. The intensities of indium phases decreased as the ZITO/In sample was biased at 4 V for 20 min. The BCM promoted the formation of In_2O_3 structures, which consequently decreased the thickness of the indium layer. Briefly, the indium crystal dominated the structural crystallization in the ZITO/In sample.

This study includes TEM observation and EDS analysis to determine the detailed composition of the ZITO structure and the contribution of bias-crystallization to its crystallization (Figure 5). Figure 5(a) shows a TEM image of the as-grown ZITO/In sample; the image in the lower right corner displays the structure of the indium layer, and the image in the upper left corner displays that of the ZITO film. The ZITO film was approximately 145 nm-thick, and its formation was continuous and uniform. The select area electron diffraction (SAED) pattern (inset of Figure 5(a)) confirmed that the unbiased ZITO film was an amorphous structure, which is in agreement with previous research [14]. The oxygen, indium, zinc, and tin concentrations from points A to B (180 nm) were examined by EDS (Figure 5(b)). The O/In/Zn/Sn concentration of the ZITO/In sample included three zones. Though indium should be the only element in Zone I, oxygen atoms were also present in this zone. This is primarily because the sputter-induced thermal energy during deposition caused the indium atoms to react with the oxygen atoms in the ZITO crystallization, forming In_2O_3 structures. This thermal energy also enhanced the formation of InZnO (IZO) structures (Zone II), and this thermal diffusion path was approximately 18 nm. In Zone III (ZITO layer), the concentration of all the elements resulted in uniform distribution, which was confirmed with TEM observation (Figure 5(a)). Figure 5(c) shows a TEM image and SAED pattern of ZITO film after bias crystallization at 4 V for 20 min. The ZITO film possessed an unregulated structure, and its SAED pattern

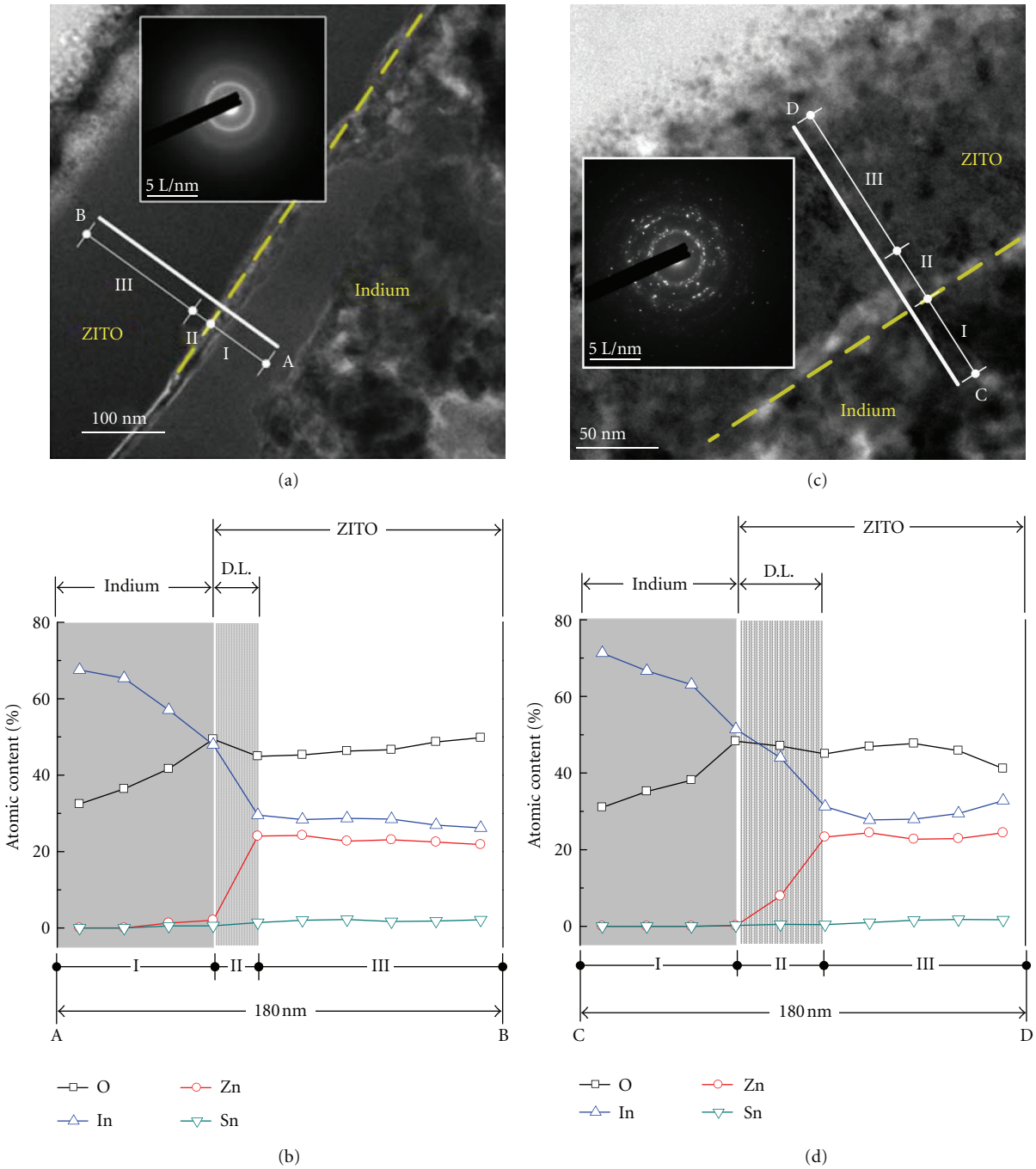

Figure 5: (a) TEM and SAED images of unbiased ZITO/In sample, (b) the profile of oxygen, zinc, indium, and tin contents from point A to B in (a); (c) TEM and SAED images of the ZITO/In sample with the biased of 4 V for 20 min, (d) the profile of oxygen, zinc, indium, and tin contents from point C to D in (c). (D. L.: diffusion layer).

was attributed to a polycrystalline structure. These results indicate that the proposed BCM transformed amorphous ZITO (a-ZITO) into a polycrystalline ZITO (poly-ZITO) crystal. The variations of all elements concentrated from points C to D (180 nm) were also detected (Figure 5(d)). Figure 5(d) shows that indium atom concentration in Zone rose after bias-crystallization. The main reason is that the bias-induced thermal effect caused the diffusion of indium atoms. In addition, the indium atoms were thermally diffused into the ZITO film, which resulted in the increment of carrier concentration that dominated ZITO resistivity. Compared with unbiased ZITO film (Zone II), the bias-induced mechanism increased the diffusion path of indium atoms from 18 nm to 35 nm (see the diffusion layer shown in Figures 5(b) and 5(d)). The increased thickness of the IZO structure mainly resulted in the reduction of ZITO resistivity.

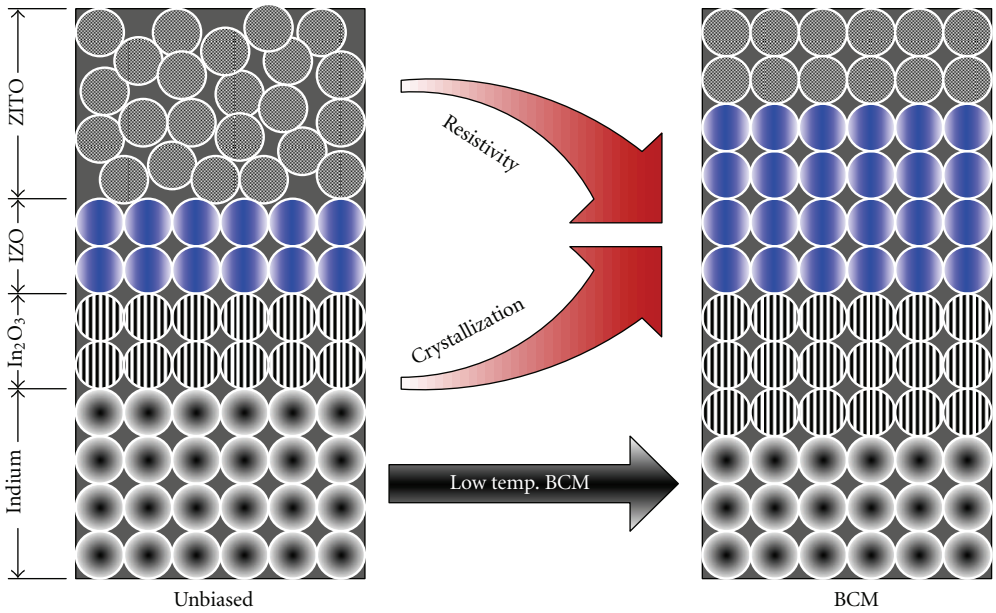

Figure 6: Schematic illustrations of interface characteristics for ZITO/In sample with the bias-crystallization mechanism.

In accordance with the results, Figure 6 presents a schematic illustration of interface characteristics of the ZITO/In sample with the BCM. For the unbiased ZITO/In sample, the sputter-induced thermal energy in the interface (ZITO/In) formed the In_2O_3 and IZO structures. The thermal energy was insufficient to crystallize the a-ZITO structure. When the bias-crystallization was performed, the bias-induced joule heat caused intense diffusion that increased the content of IZO and In_2O_3 phases. The a-ZITO was crystallized to form poly-ZITO, and the thickness of In_2O_3 thin film increased to enhance the film transmittance. The metal indium had good conductivity, promoting the bias-crystallization process. Moreover, the formation of the In_2O_3 structure did not deteriorate optical transmittance [17]. In brief, the BCM improved ZITO crystallization and enhanced its conductivity after only a short duration. This technique is a candidate for posttreatment applications that require low-temperature manufacturing.

4. Conclusions

This study proposed a BCM that enhanced ZITO crystallization at a lower temperature after a short bias time. The bias-induced joule heat caused indium diffusion to form In_2O_3 structures in the interface between the ZITO film and the indium layer. The In_2O_3 structures dominated the crystallization of the ZITO/In sample. The transformation of the ZITO matrix from amorphous to polycrystalline indicated that the proposed biasing treatment enhanced low-temperature crystallization. The bias-induced thermal diffusion also increased the number of In_2O_3 and IZO structures, increasing film conductivity and transmittance.

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