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Effect of substrate temperature on the photoelectrochemical responses of Ga and N co-doped ZnO films

Sudhakar Shet · Kwang-Soon Ahn · Heli Wang · Ravindra Nuggehalli · Yanfa Yan · John Turner · Mowafak Al-Jassim

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Abstract Ga–N co-doped ZnO thin films with reduced bandgaps were deposited on F-doped tin-oxide-coated glass by radio-frequency magnetron sputtering at different substrate temperatures in mixed N_2 and O_2 gas ambient. We found that Ga–N co-doped ZnO films exhibited enhanced crystallinity when compared to undoped ZnO films grown under the same conditions. Furthermore, Ga–N co-doping ensured enhanced N-incorporation ZnO thin films as the substrate temperature is increased. As a result, Ga–N co-doped ZnO thin films exhibited much improved photoelectrochemical (PEC) response, compared to ZnO thin films. Our results therefore suggest that the passive co-doping approach could be a means to improve PEC response for bandgap-reduced wide-bandgap oxides through impurity incorporation.

Introduction

Photoelectrochemical (PEC) systems based on transition metal oxides, such as TiO_2, zinc oxides (ZnO), and WO_3, have received extensive attention since the discovery of photo-induced decomposition of water on TiO_2 electrodes [1–9]. The drawback of PEC systems using these metal oxides is that they have large bandgaps and cannot efficiently absorb visible light, which is the major fraction of the solar spectrum. Therefore, reducing the bandgap of these metal oxides is a critical issue for improving PEC applications of these oxides. In recent years, intensive studies have been conducted on bandgap reduction of these metal oxides.

A common method for reducing the bandgap of transition metal oxides is the incorporation of anion impurities such as C, S, and N [2, 10–14]. Incorporating these impurities has typically resulted in bandgap-reduced thin films. To achieve significant bandgap reduction, a high concentration of impurities must be incorporated. However, these films usually exhibit poor crystallinity, which is extremely detrimental to the PEC performance. Because most of these impurities are not usually isovalent, but are either donors or acceptors, the incorporation of a high concentration of impurities often leads to metal oxide films with high carrier concentration and recombination centers. As a result, the metal oxides with significantly reduced bandgap usually exhibit very small depletion widths and high recombination rate, and therefore, show poor photoresponse [15–18]. Recently, we proposed to overcome this problem by charge-compensated donor–acceptor co-doping, e.g., Ga and N co-incorporation in ZnO [19, 20]. It is easier to incorporate (N, Ga) pairs than to incorporate sole N atoms because of donor–acceptor interaction [18–22]. The Ga and N co-doped ZnO films have been synthesized by other groups. However, these syntheses involved were sintering mixed GaN and ZnO powders at high temperatures. In these syntheses, the Ga-to-N ratios, which determine the carrier concentration, are not controllable [21, 22]. For a PEC device, an optimum carrier concentration is desired to achieve good photoresponse.

S. Shet (✉) · H. Wang · Y. Yan · J. Turner · M. Al-Jassim
National Renewable Energy Laboratory, Golden, CO 80401, USA
e-mail: sudhakar.shet@nrel.gov

S. Shet · R. Nuggehalli
New Jersey Institute of Technology, Newark, NJ 07102, USA

K.-S. Ahn
School of Display and Chemical Engineering, Yeungnam University Gyeongsan, Gyeongbuk 712-749, South Korea

In this article, we report on the synthesis of enhanced N incorporation at higher substrate temperature by Ga and N co-doping in ZnO films. The Ga–N co-doped ZnO films were synthesized by radio-frequency (RF) magnetron sputtering in mixed N_2 and O_2 gas ambient at increased substrate temperatures from 100 to 500 °C. The co-incorporation of Ga and N enhanced the solubility of Ga and N, leading to significantly reduced bandgap, and compensated for charged defects. The ratio of Ga and N tunes the carrier concentration and optimizes the depletion width. As a result, the Ga and N co-doped ZnO thin films show much enhance PEC response as compared to ZnO thin films grown at similar conditions.

Experimental

The Ga–N co-doped ZnO films were deposited by reactive RF magnetron sputtering of a zinc metal target using mixed oxygen and nitrogen gas. F-doped SnO_2-coated transparent glasses (20–23 Ω/□) were used as substrates. The distance between the target and substrate was 8 cm. The base pressure was below 5×10^{-6} torr and the working pressure was 2×10^{-2} torr. The chamber ambient was mixed N_2 and O_2 with an oxygen gas ratio $O_2/(N_2 + O_2) = 20\%$. This low O_2 gas ratio was found to be necessary because the chemical activity of O_2 is much higher than that of N_2. Prior to sputtering, a pre-sputtering process was performed for 30 min to eliminate any contaminants from the target. Sputtering was then conducted at a RF power of 100 W at substrate temperatures of 100, 300, and 500 °C. Ga_2O_3 powders (0.006 g) were dispersed uniformly on the 3-inch-diameter Zn metal target as the Ga source. For comparison, a ZnO film was deposited at an RF power of 100 W in pure O_2 gas ambient. All the sputtered samples were controlled to have a similar film thickness of 500 nm as measured by stylus profilometry.

PEC measurements were performed in a three-electrode cell with a flat quartz-glass window to facilitate illumination to the photoelectrode surface [23–25]. The sputter-deposited films were used as the working electrodes with an active surface area of about 1.2 cm^2. Pt mesh and an Ag/AgCl electrode were used as counter and reference electrodes, respectively. A 0.5-M Na_2SO_4 aqueous solution with a pH of 6.8 was used as the electrolyte for the PEC measurements and the scan rate was 5 mV/s in this experiment. The PEC response was measured using a fiber-optic illuminator (150-W tungsten-halogen lamp) with an ultraviolet/infrared (UV/IR) cut-off filter (cut-off wavelengths: 350 and 750 nm) and combined UV/IR and green band-pass filter (wavelength: 538.33 nm, full width at half maximum [FWHM]: 77.478 nm). The light intensity was measured by a photodiode power meter. The total light intensity with the UV/IR filter only was fixed at 125 mW/cm^2.

Because our films were deposited on conducting substrates, measurements of electrical property by the Hall Effect were not possible. Instead, the electrical properties were measured by Mott–Schottky plots, which were obtained by alternating current (AC) impedance measurements. AC impedance measurements were carried out with a Solartron 1255 frequency response analyzer using the above three-electrode cells. Measurements were performed under dark conditions with an AC amplitude of 10 mV and frequency of 5000 Hz were used for the measurements taken under dark condition, and the AC impedances were measured in the potential range of −0.7 to 1.25 V (vs. Ag/AgCl reference). The series capacitor–resistor circuit model was used for Mott–Schottky plots [25].

For crystallinity characterization, X-ray measurements were performed using an X-ray diffractometer (XGEN-4000, SCINTAG Inc.) operated with a Cu Kα radiation source at 45 kV and 37 mA. The ultraviolet–visual (UV–VIS) absorption spectra of the samples were measured by an n&k analyzer 1280 (n&k Technology, Inc.). To evaluate the N concentrations in the Ga–N co-doped ZnO films, X-ray photoelectron spectroscopy (XPS) was performed. Monochromatic Al Kα radiation was used for all data sets, and the analyzer was set to 59-eV pass energy. Argon ion sputtering (3 keV, 0.8 μAmm^{-2}, 120 s) was used to clean samples prior to analysis. Other aspects of the photoemission system are described in detail elsewhere [26].

Results and discussion

Figure 1 shows the X-ray diffraction curves for ZnO and Ga–N co-doped ZnO films deposited at substrate

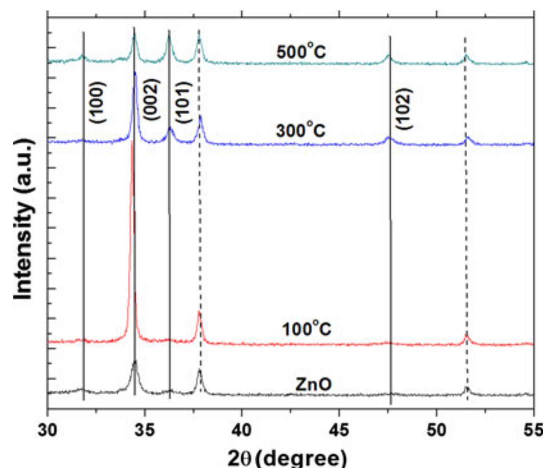

Fig. 1 XRD curves of a ZnO film deposited at 100°, and Ga–N co-doped ZnO films deposited at 100, 300, and 500 °C

temperatures of 100, 300, and 500 °C. The ZnO film exhibited poor crystallinity due to deposition at low temperatures. However, Ga–N co-doped ZnO film deposited at 100 °C showed sharper peaks. As the substrate temperature is increased to 300 and 500 °C, the peak intensities are decreased, indicating the incorporation of more N in the films. It is known from recent reports that incorporated N atoms can deteriorate the crystal structure and modify the growth mode [11, 27, 28]. The crystallite size of the ZnO film, estimated according to the Scherrer equation, is about 21 nm. The Ga–N co-doped ZnO films deposited at 100 °C exhibited much better crystallinity (crystallite size: 44 nm). This is because the deposition is carried out at the increased substrate temperature of 100 °C, and very low concentration of N incorporated in the film, whereas ZnO film was deposited at room temperature. Such significantly enhanced crystallinity could be because Ga_2O_3 powders were used as the Ga source. The ionic radius of substitutional Ga^{3+} is close to that of Zn^{2+}. The size mismatch between them is very small. Furthermore, the Ga_2O_3 source provides more oxygen during the sputtering process [11], leading to decreased oxygen vacancies and enhanced crystallinity. A similar effect of the Ga oxide source on ZnO crystallinity has also been reported by other groups [26]. The crystallite size of Ga–N co-doped ZnO films deposited at a substrate temperature of 300 and 500 °C is 35 and 24 nm, respectively, indicating that more N is incorporated in these films. XPS results confirmed that very low concentration nitrogen (0.19 at.%) is present in the Ga–N co-doped ZnO films grown at 100 °C, whereas films deposited at 300 and 500 °C contain 0.8 and 1.4 at.% N, respectively. ZnO films with high crystallinity can be synthesized at high temperatures, but a significant amount of nitrogen is very difficult to be incorporated into ZnO films at these substrate temperatures. However, with Ga–N co-doping, a significant amount of N can be incorporated into ZnO even at higher substrate temperatures.

Figure 2 shows optical absorption spectra of ZnO films and Ga–N co-doped ZnO films deposited at a substrate temperature of 100–500 °C. The ZnO films showed optical absorption on light with wavelengths below 450 nm because of their wide bandgap. However, Ga–N co-doped ZnO film could absorb lower-energy photons, up to 750 nm as the substrate temperature increased from 100 to 500 °C, indicating that the bandgap was narrowed by Ga–N incorporation in ZnO [29, 30].

Figure 3 shows the optical absorption coefficients for the samples used in this experiment. The direct electron transition from valence to conduction bands was assumed for the absorption coefficient curves, because ZnO films are known as direct-bandgap materials. The optical bandgap of the films was determined by extrapolating the linear portion of each curve. The bandgap of the ZnO film is

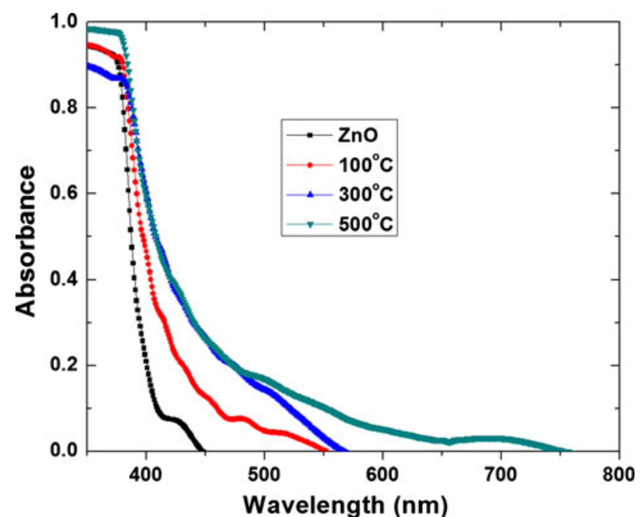

Fig. 2 Optical absorption curves of a ZnO film deposited at 100°, and Ga–N co-doped ZnO films deposited at 100, 300, and 500 °C

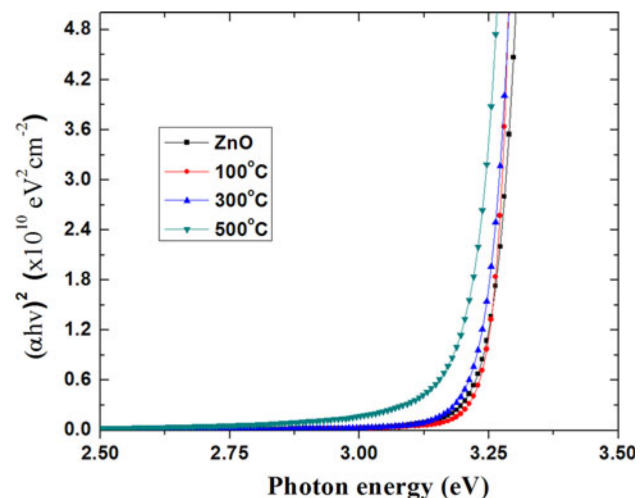

Fig. 3 Optical absorption coefficients of a ZnO film deposited at 100°, and Ga–N co-doped ZnO films deposited at 100, 300, and 500 °C

3.26 eV, which is consistent with the results reported elsewhere [31]. The direct optical bandgaps measured for Ga–N co-doped ZnO films deposited at a substrate temperature of 100–500 °C gradually decreased from 3.25 to 3.22 eV. This small bandgap reduction is due to N-induced upshifting of the valence-band maximum. It is shown theoretically that the incorporated N would generate an impurity band above the valence band. The absorption from this impurity band cannot be characterized by direct band transitions and typically results in an absorption tail in the measured optical absorption coefficients curve. Such an absorption tail is clearly evident in Fig. 3 for the Ga–N co-doped ZnO film. This tail can be considered further bandgap reduction, which enables light harvesting in the

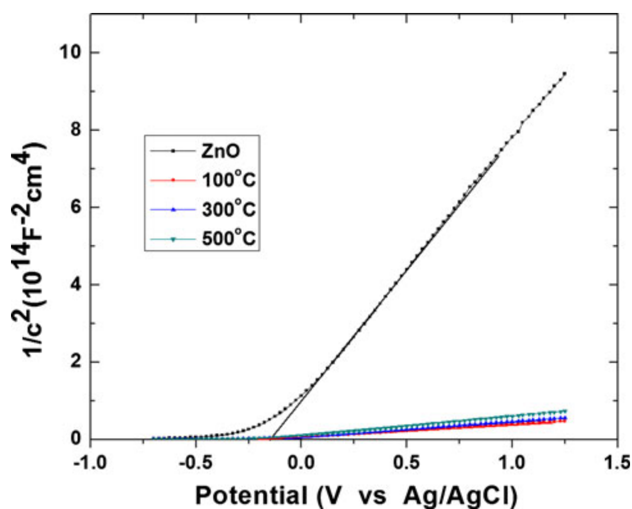

Fig. 4 Mott–Schottky plots of the ZnO film deposited at 100°, and Ga–N co-doped ZnO films deposited at 100, 300, and 500 °C

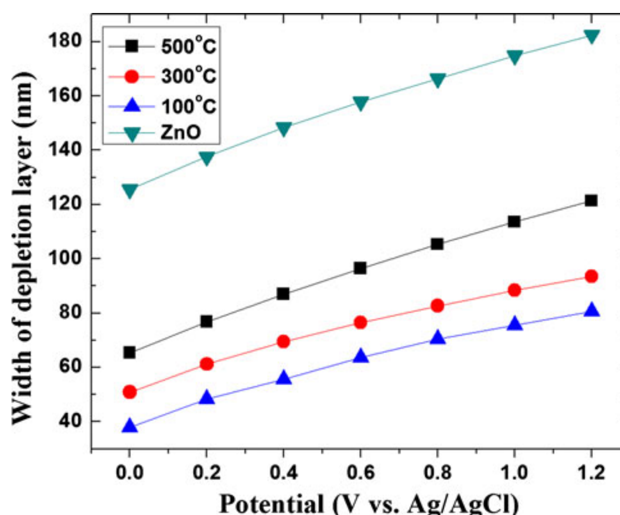

Fig. 5 *W* values with the potential, estimated from Fig. 4 for the ZnO film deposited at 100°, and Ga–N co-doped ZnO films deposited at 100, 300, and 500 °C

much longer-wavelength regions when compared to the ZnO film.

Figure 4 shows Mott–Schottky plots of ZnO, and of Ga–N co-doped ZnO films grown at substrate temperatures of 100, 300, and 500 °C. All the samples exhibited positive slopes, indicating *n*-type semiconductors. Our previous studies [19, 32–34] reported that ZnO/N films deposited under a N_2/O_2 plasma showed *n*-type behaviors, due to substitutional N_2 molecules that act as shallow double-donors. For Ga–N co-doped samples, Ga atoms are shallow donors. The Ga concentration in the films tunes the donor (free electron) concentration. The donor concentrations of the films, calculated from the slopes of the Mott–Schottky plots [16, 34] were about 8.6×10^{16}, 2.85×10^{17}, 2.74×10^{17}, and 2.52×10^{17}/cm^3 for ZnO, and Ga–N co-doped ZnO films deposited at 100, 300, and 500 °C, respectively. The Ga–N co-doped ZnO film exhibited nearly similar donor concentration when compared to ZnO/N film grown at 500 °C reported elsewhere [17], indicating that the co-doped film is a highly compensated system.

The depletion width is an important factor for the PEC application of semiconductors. In general, a larger depletion layer (*W*) is preferred to promote photo-generated carrier separation. Figure 5 shows the *W* values with the potential for the samples, which were calculated from the results of Fig. 4 [16]. It shows that ZnO showed much wider *W* when compared to the Ga–N co-doped ZnO films. The Ga–N co-doped ZnO film exhibited increased *W* values as the substrate temperature is increased, due to lower donor concentration.

Figure 6 shows the photocurrent–voltage curves of ZnO and Ga–N co-doped ZnO films under illumination with an UV/IR filter. It shows clearly that the Ga–N co-doped ZnO films exhibited increased photocurrents, compared to the

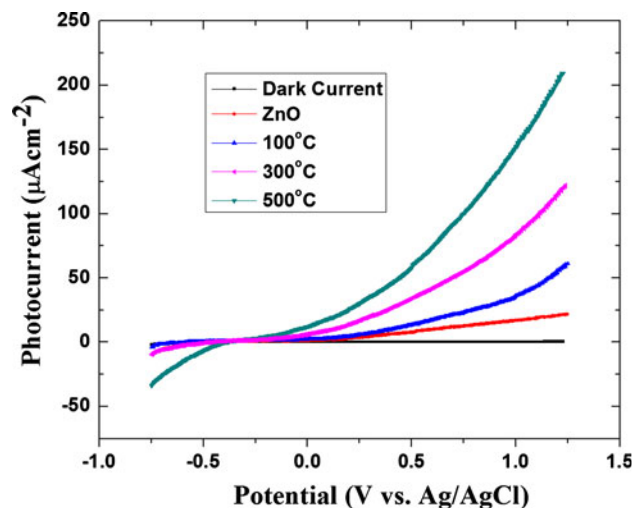

Fig. 6 Photocurrent–voltage curves of the ZnO film deposited at 100°, and Ga–N co-doped ZnO films deposited at 100, 300, and 500 °C, respectively, under illumination with an UV/IR filter

ZnO film. Furthermore, as the substrate temperature is increased for Ga–N co-doped ZnO film, the photocurrents increased accordingly. At the potential of 1.25 V, the photocurrents were 20, 56, 115, and 203 μAcm^{-2} for the ZnO, Ga–N co-doped ZnO films deposited at 100, 300, and 500 °C, respectively. It indicates that a very high recombination rate of the photogenerated electrons and holes is present in the ZnO film, despite its wider *W* value; this may be due to its inferior crystallinity combined with wider bandgap. To investigate the photoresponses in the long-wavelength region, a green-color filter was used in combination with the UV/IR filter, as shown in Fig. 7. The ZnO film exhibited no clear photoresponse, due to its wide

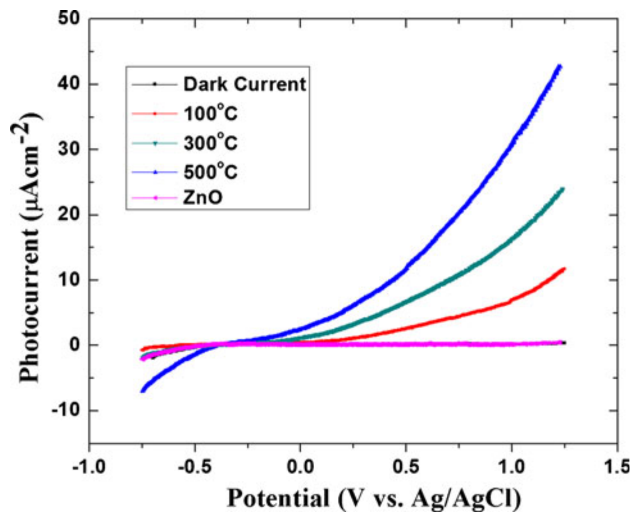

Fig. 7 Photocurrent–voltage curves of the ZnO film deposited at 100, and Ga–N co-doped ZnO films deposited at 100, 300, and 500 °C, respectively, under illumination with the combined green and UV/IR filters

bandgap. The Ga–N co-doped ZnO films exhibited photocurrent, despite much less light absorption. It is evident that the Ga–N co-doped ZnO films exhibited increased crystallinity, good *W* value, reduced bandgap, and compensated charge, which led to an enhanced photocurrent when compared to the ZnO film. The results demonstrate clearly that photocurrents can be obtained from the impurity band-induced absorption tail. The co-doping of Ga and N in ZnO can shift photoresponse of ZnO into the visible-light region, which is the main component of sunlight. We expect that further enhanced photocurrents should be possible when more N is incorporated in ZnO by the co-doping approach.

Conclusions

The Ga–N co-doped ZnO films were deposited by sputtering at different substrate temperatures. We found that the Ga–N co-doped ZnO films exhibited enhanced crystallinity when compared to ZnO film. Ga–N co-doped ZnO films showed increased N-incorporation as the substrate temperature is increased. As a result, the Ga–N co-doped ZnO films showed higher photocurrents than the ZnO film. Our results suggest that substrate temperature plays an important role in the co-doping approach for synthesizing metal oxides with both improved crystallinity and impurity incorporation, which should help to improve their PEC performance.

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