Carrier concentration tuning of bandgap-reduced *p*-type ZnO films by codoping of Cu and Ga for improving photoelectrochemical response

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In this study, the synthesis of *p*-type ZnO films with similar bandgaps but varying carrier concentrations through codoping of Cu and Ga is reported. The ZnO:(Cu,Ga) films are synthesized by rf magnetron sputtering in O_2 gas ambient at room temperature, followed by postdeposition annealing at 500 °C in air for 2 h. The bandgap reduction and *p*-type conductivity are caused by the incorporation of Cu. The tuning of carrier concentration is realized by varying the Ga concentration. The carrier concentration tuning does not significantly change the bandgap and crystallinity. However, it can optimize the carrier concentration to significantly enhance the photoelectrochemical response for bandgap-reduced *p*-type ZnO thin films. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2888578]

I. 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 photoinduced 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 study on bandgap reduction of these metal oxides has been carried out.

A common method for reducing the bandgap of transition metal oxides is the incorporation of anion impurities such as C, S, and N.[2,10,11] Incorporating these impurities has typically resulted in bandgap-reduced *n*-type thin films. On the basis of our theoretical results,[12] we recently synthesized bandgap-reduced *p*-type ZnO by Cu incorporation.[13] In order to achieve significant bandgap reduction, a high concentration of impurities must be incorporated. However, because most of these impurities are not usually isovalent but are either donors or acceptors, the incorporation of high concentration of impurities often leads to metal oxide films with high carrier concentration. As a result, the metal oxides with significantly reduced bandgap usually exhibit very small depletion widths and therefore show poor photoresponse.[14–17] An optimum carrier concentration is desired to achieve good photoresponse. Furthermore, incorporation of high-concentration impurities also introduces uncompensated charged defects that can act as recombination centers. The recombination can cause additional photocurrent loss.

In this paper, we demonstrate that these two problems can be overcome by codoping with compensating impurities. We have synthesized bandgap-reduced *p*-type ZnO thin films with controlled carrier concentration through Cu and Ga codoping. The ZnO:(Cu,Ga) films were synthesized by rf magnetron sputtering in O_2 gas ambient at room temperature, followed by postdeposition annealing at 500 °C in air for 2 h. The incorporation of Cu is responsible for bandgap reduction, and the incorporation of Ga is responsible for carrier concentration tuning. We found that the carrier concentration tuning does not significantly change the bandgap and crystallinity. However, it can optimize the carrier concentration and thus dramatically enhance PEC response for the bandgap-reduced *p*-type ZnO thin films. The acceptor-donor codoping approach should be applicable to bandgap reduction for other metal oxides.

II. EXPERIMENTAL

ZnO:(Cu,Ga) films were deposited using a reactive rf magnetron sputtering system at room temperature and annealed at 500 °C in air for 2 h. Conducting transparent fluorine-doped tin oxide (FTO) (20–23 $\Omega/\square$)-coated glass was used as the substrate to allow PEC measurements. A Cu source of Cu chips (area: 2×5 mm^2) were dispersed uniformly on the 3-in.-diameter Zn target. Based on our previous results,[13] ten Cu chips were used to produce bandgap-reduced *p*-type ZnO. Gallium oxide (Ga_2O_3) powders were dispersed uniformly on the target as a Ga source. Two sets of ZnO:(Cu,Ga) films were deposited: a low-Ga regime with Ga_2O_3 powders of 0.001 and 0.002 g, and a high-Ga regime with Ga_2O_3 powders of 0.01 and 0.03 g. We refer to these samples as ZnO:(Cu,Ga)0.001, ZnO:(Cu,Ga)0.002, ZnO:(Cu,Ga)0.01, and ZnO:(Cu,Ga)0.03. The samples in the first set are 0.5 μm thick, and the samples in the second set are 1 μm thick. For comparison, pure ZnO and ZnO:Cu films were also deposited under the same sputtering conditions and annealed at 500 °C in air for 2 h. Sputtering was performed at an rf power of 100 W at room temperature.
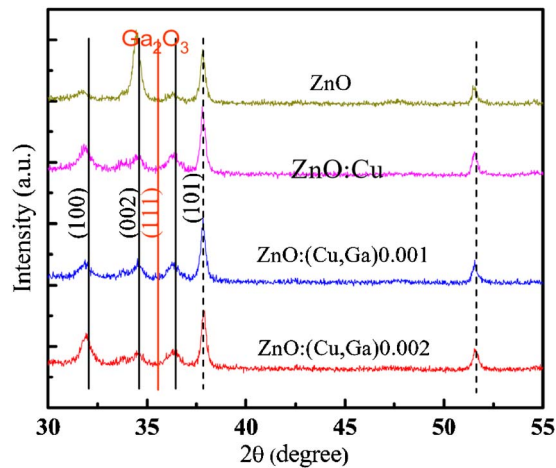
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FIG. 1. (Color online) XRD curves of ZnO:(Cu,Ga)0.001, ZnO:(Cu,Ga)0.002, ZnO:Cu, and ZnO samples with similar thickness of about 0.5 μm. The dotted lines indicate the peaks from FTO substrate.

Pure O_2 gas was used as the sputtering ambient to suppress the formation of oxygen vacancies and enhance the incorporation of Cu and Ga.

The structural and crystallinity characterizations were performed by x-ray diffraction (XRD) measurements, using an x-ray diffractometer (XGEN-4000, SCINTAG, Inc.) operated with a Cu Kα radiation source at 45 kV and 37 mA. The surface morphology was examined by atomic force microscopy (AFM) conducted in the tapping mode with a silicon tip. The UV-vis absorption spectra of the samples were measured by an n&k analyzer 1280 (n&k Technology, Inc.). Hall measurements could not be performed because of the fact that the ZnO:(Cu,Ga) thin films were deposited on conducting substrates. Conventional three-electrode cells were used for the (photo)electrochemical experiments, the details of which are described elsewhere.[18,19] The working electrode was located in front of the reference electrode. The ZnO:(Cu,Ga) films were used as a working electrode and the active surface area was about 0.25 cm^2. Pt mesh and a Ag/AgCl electrode were used as counter and reference electrodes, respectively. A 0.5M Na$_2$SO$_4$ aqueous solution was used as the electrolyte.

III. RESULTS AND DISCUSSION

The two sets of samples exhibited different PEC behaviors. We first show the results obtained from the first set of samples. Figure 1 shows XRD curves for the first set of samples. For comparison, XRD curves of a pure ZnO sample and a ZnO:Cu sample with similar thickness are also shown. The location of the (111) peak of Ga$_2$O$_3$ is indicated by the red line. It is seen that the incorporation of Cu leads to decreased crystallinity as compared to pure ZnO films. The incorporation of additional Ga showed similar crystallinity as compared to ZnO:Cu films. The XRD curves showed no Cu oxides and Ga oxides, thus indicating no phase separation. However, the incorporation of Cu and Ga changed the preferred orientation of the films. For example, with the dopants, the (002) peak was suppressed and the (100) and (101) peaks were enhanced. AFM images also confirmed that the
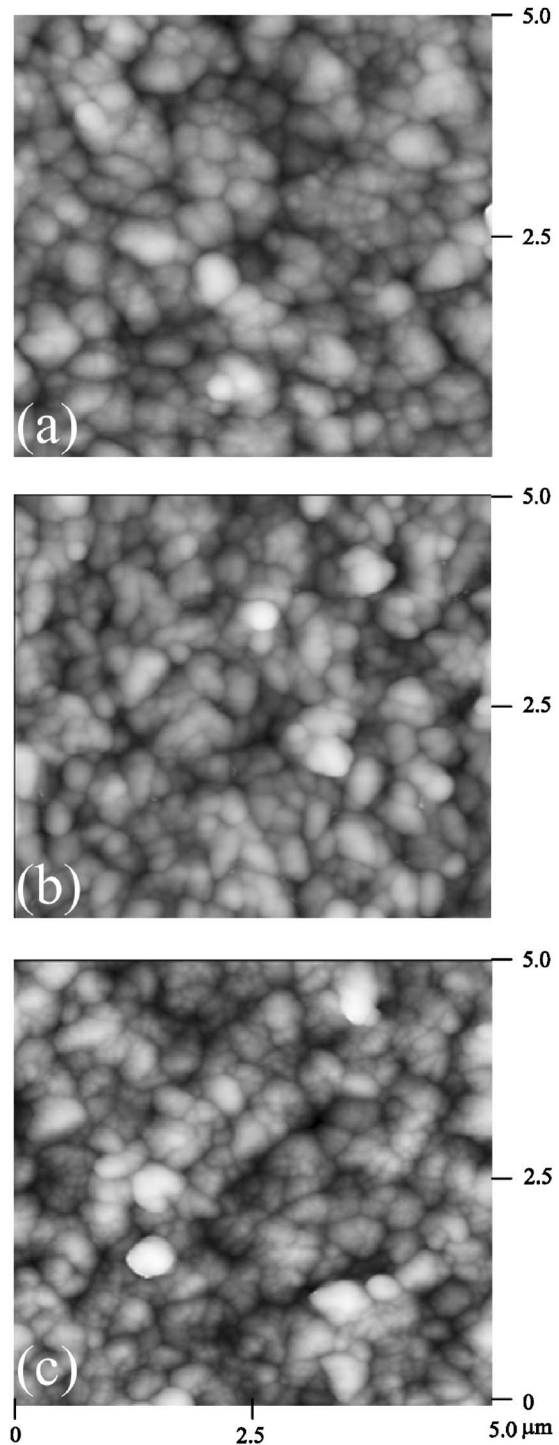

FIG. 2. AFM images taken from (a) ZnO:Cu, (b) ZnO:(Cu,Ga)0.001, and (c) ZnO:(Cu,Ga)0.002 samples.

ZnO:Cu and ZnO:(Cu,Ga) films have similar grain sizes. Figures 2(a)–2(c) show AFM images from the ZnO:Cu, ZnO:(Cu,Ga)0.001, and ZnO:(Cu,Ga)0.002 samples, respectively. The images clearly show that the incorporation of a low concentration of Ga did not significantly change the morphology and average crystallite sizes.

Figures 3(a) and 3(b) show the optical-absorption spectra and absorption coefficients of the first set of samples, pure ZnO, and ZnO:Cu samples with similar thickness. To eliminate the effect from the FTO substrate, the absorbance was calculated by the following equation:[20]
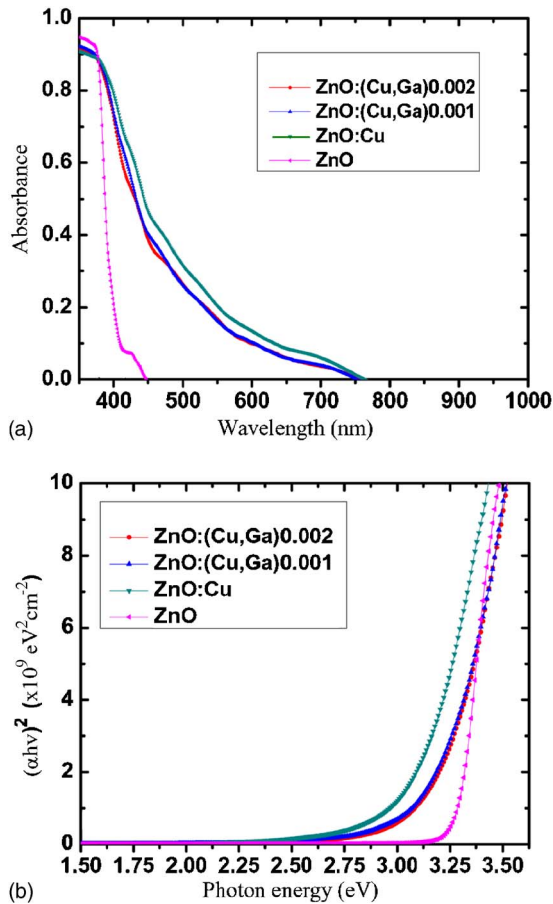
(a)

(b)

FIG. 3. (Color online) (a) Optical absorption curves and (b) absorption coefficients of ZnO, ZnO:Cu, ZnO:(Cu,Ga)0.001, and ZnO:(Cu,Ga)0.002 samples.
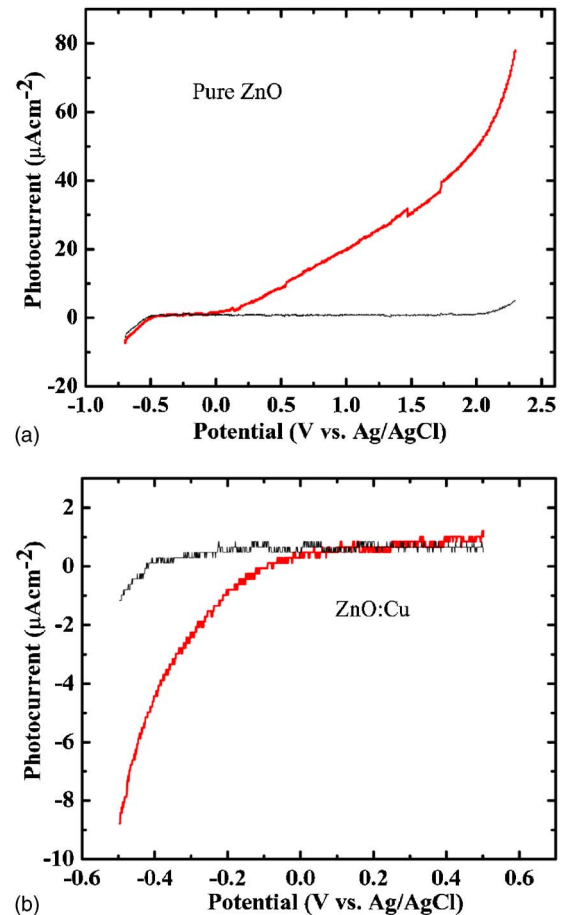

(a)

(b)

FIG. 4. (Color online) Photocurrent-voltage curves under (red curve) continuous illumination, (black curve) dark condition, with an UV/IR filter measured from (a) ZnO and (b) ZnO:Cu films.

$$A = 1 - R(\text{film}) - T(\text{film})/T(\text{substrate}), \qquad (1)$$

where R and T are the measured reflectance and transmittance, respectively. The ZnO:Cu sample exhibits absorption in the visible region due to two main effects: (1) The strong d-p coupling between Cu and O upshifts the O $2p$ orbital, which narrows the fundamental bandgap; and (2) the Cu $3d$ orbital creates impurity bands above the ZnO valance band. The bandgap for the ZnO:Cu sample is calculated to be about 3.05 eV. Based on our previous compositional study,[13] this bandgap corresponds to about 10 at. % Cu in the film. The incorporation of Ga does not significantly change the absorption spectrum as compared to that of ZnO:Cu due to low Ga concentration. This ensures that the effect of Ga incorporation is mainly to tune the carrier concentration of Zn:Cu films. However, small blueshifts are observed for the sample codoped with Ga as compared to the ZnO:Cu sample. The measured bandgaps are about 3.12 eV for ZnO:(Cu,Ga)0.001 and ZnO:(Cu,Ga)0.002 samples. The blueshift can be understood as follows. The impurity band generated by Cu in ZnO is partially occupied. When Ga is incorporated, the Ga $4s^2 4p^1$ electrons will fill some of the unoccupied states in the Cu-induced impurity band. Such filling will lower the energy of the system through a downward shift of the Cu-induced impurity band. This downward shift, therefore, leads to the observed blueshift in the optical absorption spectra.

The conductivity of ZnO films is n type, whereas it is p type for ZnO:Cu with ten Cu chips. The different type of conductivity was confirmed by photocurrent-voltage curves. Figures 4(a) and 4(b) show measured photocurrent-voltage curves under illumination with the UV/IR filter and dark currents for a pure ZnO film and ZnO:Cu, respectively. Figure 4(a) shows that the photocurrent increases with an increase of applied potential, which is characteristic of n type conductivity. Figure 4(b) shows that the photocurrent increases with a decrease of applied potential, which is characteristic of p type conductivity. Thus, the ZnO film is n type and the ZnO:Cu film is p type. However, the photocurrent of the ZnO:Cu film is very low. The poor PEC performance can be attributed to the high concentration of Cu, which is necessary for sufficient bandgap reduction. The high concentration of Cu results in very high carrier concentration and, therefore, very small depletion width.[14,16] In addition, the high concentration of Cu also introduces a large number of charged defects, which can act as recombination centers. These two effects are probably the main reasons for poor PEC performance. We found that these two undesired effects can be overcome by codoping of Ga, which is a shallow donor in ZnO.

We now show how the codoping of Ga can improve the PEC performance of ZnO:Cu films. Figure 5 shows the measured photocurrent-voltage curves under illumination with
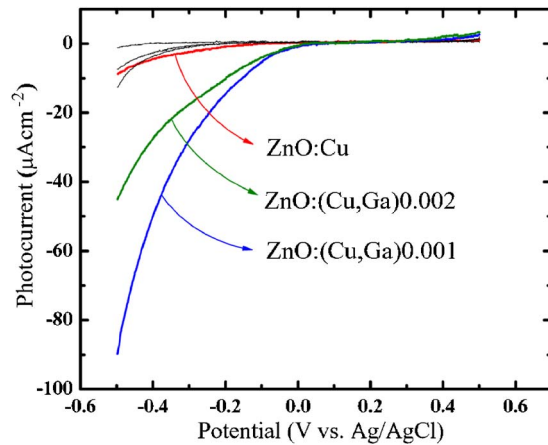
FIG. 5. (Color online) Photocurrent-voltage curves under (arrowed) continuous illumination, (black curve) dark condition, with an UV/IR filter measured from ZnO:Cu, ZnO:(Cu,Ga)0.001, and ZnO:(Cu,Ga)0.002 films.

FIG. 6. (Color online) XRD curves of ZnO:(Cu,Ga)0.01, ZnO:(Cu,Ga)0.03, ZnO:Cu, and ZnO samples with similar thickness of about 1 μm. The dotted lines indicate the peaks from FTO substrate.

the UV/IR filter and dark currents for ZnO:Cu, ZnO:(Cu,Ga)0.001, and ZnO:(Cu,Ga)0.002. Both ZnO:(Cu,Ga)0.001 and ZnO:(Cu,Ga)0.002 films showed *p*-type conductivities, indicating that the role of Ga in these films is to reduce the hole concentration that is generated by Cu incorporation. The reduction of hole concentration increases the depletion width so that more photon-generated electron-hole pairs can be collected. Furthermore, the incorporation of Ga will neutralize charged Cu ions, so that recombination will also be suppressed. Thus, ZnO:(Cu,Ga)0.001 and ZnO:(Cu,Ga)0.002 films showed significantly increased photocurrents as compared to the ZnO:Cu film. The photocurrent at a potential of −0.5 V for the ZnO:(Cu,Ga)0.001 sample improved by almost one order of magnitude. The ZnO:(Cu,Ga)0.002 sample showed lower photocurrents than the ZnO:(Cu,Ga)0.001 sample, indicating that an optimum carrier concentration exists. If the carrier concentration of a film is very low, the film will become very resistive and the photocurrent will begin to decrease. The incorporation of more than a certain level of Ga may even cause *p*-type ZnO:Cu film to become *n* type.

This is exactly the case for our second set of samples. Figure 6 shows XRD curves for the second set of samples. For comparison, XRD curves of a pure ZnO sample and a ZnO:Cu sample with similar thickness are also shown. All the peaks have higher intensities than that of the first set of samples due to larger thickness. Similar to the first set of samples, the incorporation of Cu changes the preferred orientation as compared to ZnO. The incorporation of additional Ga did not significantly change the crystallinity as compared to ZnO:Cu films. AFM images (not shown here) also confirmed this conclusion. The XRD curves showed no Cu oxides or Ga oxides, thus indicating no phase separation. However, the incorporation of Cu and Ga changed the preferred orientation of the films.

Figures 7(a) and 7(b) show the optical-absorption spectra and absorption coefficients of the second set of samples and ZnO:Cu samples with similar thickness. The bandgap for the ZnO:Cu sample is calculated to be about 3.0 eV, which corresponds to about 11 at.% Cu in the film. As in the first set of samples, blue shifts are also observed for the second
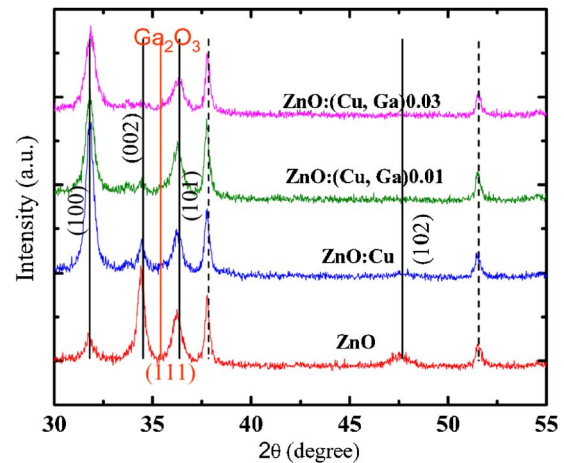
set of samples; however, the shift is much more significant. The measured bandgaps are very similar for ZnO:(Cu,Ga)0.01 and ZnO:(Cu,Ga)0.03 samples, (about 3.15 eV). This indicates that more unoccupied states are now filled by the electrons from Ga, as more Ga_2O_3 powders were dispersed on the target.

Figures 8(a) and 8(b) show measured photocurrent-voltage curves under illumination with the UV/IR filter and
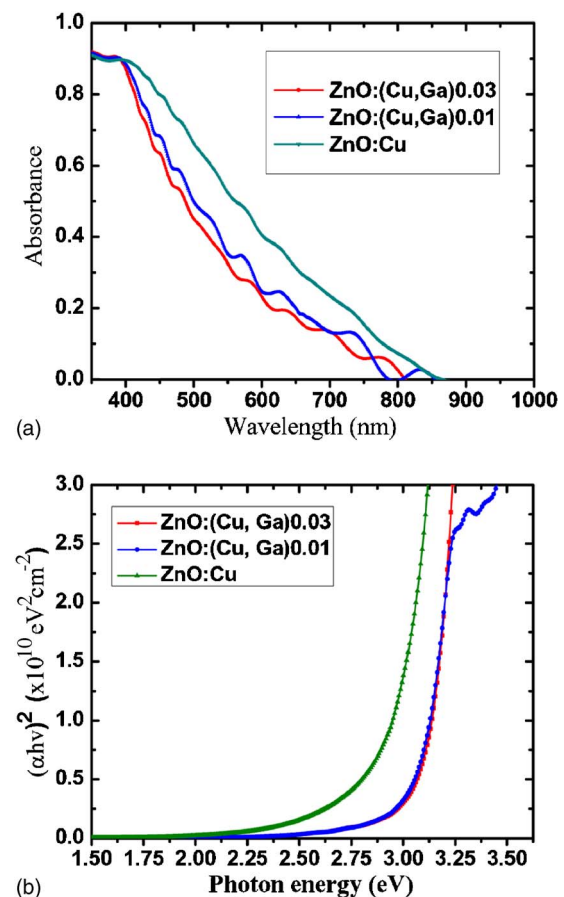

FIG. 7. (Color online) (a) Optical absorption curves and (b) absorption coefficients of ZnO:Cu, ZnO:(Cu,Ga)0.01, and ZnO:(Cu,Ga)0.03 samples.
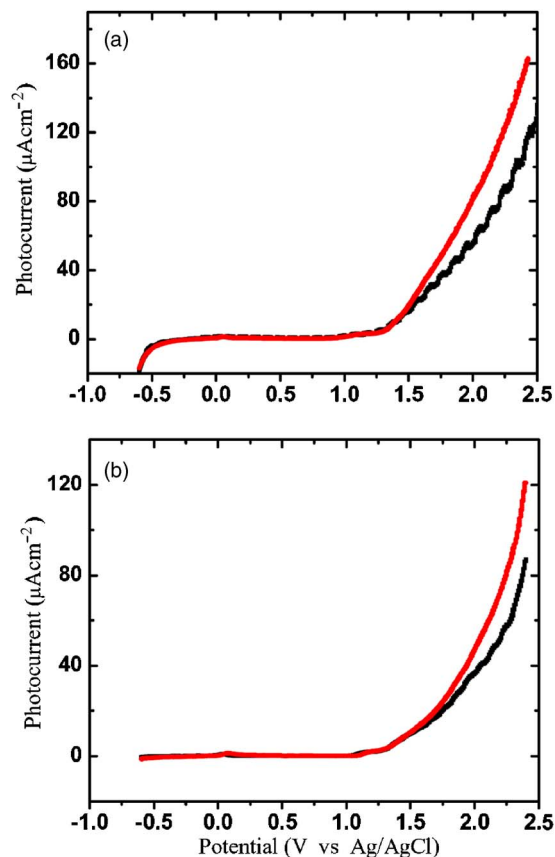
FIG. 8. (Color online) Photocurrent-voltage curves under (red curve) continuous illumination, (black curve) dark condition, with an UV/IR filter measured from (a) ZnO:(Cu,Ga)0.01 and (b) ZnO:(Cu,Ga)0.03 films.

dark currents for ZnO:(Cu,Ga)0.01 and ZnO:(Cu,Ga)0.03, respectively. We see that both ZnO:(Cu,Ga)0.01 and ZnO:(Cu,Ga)0.03 films are no longer *p* type, but are *n* type. Thus, the Ga concentration is so high in these samples that holes are completely compensated and the films become *n* type. Both ZnO:(Cu,Ga)0.01 and ZnO:(Cu,Ga)0.03 films showed very high dark currents indicating poor quality, which may be the result of incorporation of too much Ga. Because the photocurrent-voltage curves indicate that both ZnO:(Cu,Ga)0.01 and ZnO:(Cu,Ga)0.03 are *n* type, the bottom of the conduction bands of these materials may be filled with electrons, which partially contribute to the large blue-shift seen in Fig. 7.

IV. CONCLUSIONS

We have synthesized bandgap-reduced *p*-type ZnO thin films with various carrier concentrations through Cu and Ga codoping. The ZnO:(Cu,Ga) films were synthesized by rf magnetron sputtering in O_2 gas ambient at room temperature and then annealed at 500 °C in air for 2 h. We found that the carrier concentration tuning does not significantly change the bandgap and crystallinity of the ZnO:Cu films. However, it can optimize the carrier concentration and thus dramatically enhance PEC response for the bandgap-reduced *p*-type ZnO thin films. Carrier concentration tuning by acceptor-donor co doping should be applicable to bandgap reduction for other metal oxides.

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