Tunable Schottky barrier height of ZnO films by Cu doping

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Abstract. Understanding a mechanism behind photosensitivity in oxide materials is important to realize future photodetector devices. We have studied electrical properties of ZnO:Cu (0-2.5 at.\%) films deposited by a spray technique. Here, Ag-ZnO-Ag planar configuration was used to study the Schottky barrier. Using current-voltage (I-V) characterization, a significant increment in the photocurrent is observed in all samples, indicating a photosensitivity behavior. The Schottky barrier is clearly observed in the doped sample. The Cu concentration of 1.5 at.\% show the highest Schottky barrier height (0.8 eV), which may be originated from carrier trapping under dark and carrier de-trapping under ultraviolet radiation. Thus, our result is essential to improve the functionality of ZnO for photodetector applications.

1. Introduction
Zinc Oxide (ZnO) with excellent optical and electrical properties is an attractive material for wide range applications such as solar cells, light-emitting diodes, gas sensors, flat panel display, and photodetector [1]. ZnO has a direct bandgap and strong exciton binding energy (~60 meV), which is promising for future optoelectronic devices [2]. ZnO films have been prepared using a variety of chemical and physical methods such as pulsed laser deposition [3], magnetron sputtering [4,5], chemical bath deposition [6], sol-gel coating, hydrothermal [7], spray pyrolysis [8], etc. As compared to these methods, spray pyrolysis is very simple, cheap, and easy to control its thickness.

Some efforts have been carried out to improve the photodetector performance, such as surface modification (embedding metal nanoparticle and capping with other metal oxides) [9], making p-n junction [10], post-annealing treatment, formation of composites [11], fabricating low dimension structure (quantum dot, nanowires, etc.) [12], and doping with transitional metal elements [4]. Doping with transition metal elements (Cu, Ti, Fe, Al) is considered as one of the effective ways to improve the photodetector performance [4,13].
In the previous study, ZnO:Cu thin films revealed ferromagnetic and ferroelectric properties in the same sample by controlling Cu dopant and oxygen vacancy [14]. F. M. Li et al. demonstrated that Cu doping induced blue-green emission and increased UV sensitivity [15]. Cu defect complex also induced high UV photocurrent gain via trapping mechanism [16]. The high gain can be achieved by increasing the absorption cross-section, increasing the photocurrent, or decreasing the dark current. However, besides the use of UV photodetector material in our future technology, there are still some issues to be paid further attention such as doping, and the Schottky barrier in the metal-semiconductor interface.

In this paper, the effect of Cu doping on the Schottky barrier of ZnO films is investigated. The films were fabricated using the spray technique. The sensitivity of the film was enhanced by inserting the Cu dopant. The effects of Cu on the sensitivity of UV detector and Schottky barrier height are explained systematically.

2. Experiment Details
Cu-doped ZnO films were fabricated by using the spray technique at 450 °C for 30 seconds. Si substrates were firstly cleaned using acetone, ethanol, and aquades for 5 minutes. The 0.5 M solution was prepared on magnetic stirrer by mixing zinc acetate dehydrate, cupric chloride dehydrate, and ethanol for 60 minutes at the speed of 180 rpm. The distance between nozzle and substrate is ~8 cm. The detail of the experiment is schematically shown in Figure 1. Cu composition in ZnO film was checked using X-ray fluorescence spectroscopy. Furthermore, Ag-ZnO-Ag with planar configuration was prepared to measure the electrical properties. I-V characterizations were performed in the dark and UV illumination (365 nm).

3. Results and Discussion
The elemental composition of the films was characterized using X-ray fluorescence spectroscopy. The variations of Cu content used in this report are from 0 at.% (pure ZnO) up to 2.5 at.%. By applying the deposition temperature of 450 °C, all samples are crystalline that is oriented in (002) plane, as previously reported by E. Nurfani et al. [8].

Furthermore, current-voltage (I-V) characteristics were measured to investigate photodetector performance, as shown in Figure 2. The I-V curves were measured from -8 V to +8 V. Symmetric I-V profile is observed from the negative and positive regions. Comparing to the dark current, the increase of photocurrent under UV illumination indicates a photosensitivity behavior. This low dark current also guarantees a low noise photodetector [17]. Under dark condition, O₂ molecule is adsorbed by ZnO.
surface due to the excess carrier, which it is converted to $\text{O}_2^-$ by capturing electrons. This condition increases the depletion width, a region where carriers flow through the film, resulting in the current suppression under dark. Under UV illumination of 365 nm (3.4 eV), when the incident photon has higher energy than the ZnO bandgap (3.37 eV), the electron is excited from the valence to conduction band. A photoexcited hole is then trapped by $\text{O}_2^-$, and $\text{O}_2$ molecule is released from the film surface. At this stage, the current increases due to the decrease of depletion width. Moreover, the sensitivity ($S$) of the photodetector is expressed by

$$S = \frac{I_{\text{photo}} - I_{\text{dark}}}{I_{\text{dark}}}$$

(1)
where $I_{\text{photo}}$ is the photocurrent, and $I_{\text{dark}}$ is the dark current.

In general, the sensitivity is proportional to the voltage. By inserting Cu dopant of 1 at.%, the sensitivity at 8 V increases 35 times higher compared to the pure ZnO. Cu concentration of 1.5 at.% shows the most sensitive detector, which is $\sim$300 times higher than the pure ZnO. Increasing the Cu concentration above 1.5 at.% is not effective, even though the sensitivity is still higher than that of pure ZnO. On the other hand, Cu dopant acts as an acceptor in the ZnO host, resulting in electron trapping in the defect state in the dark and de-trapping under UV illumination. Cu doping also can trigger another native defect such as oxygen vacancy and zinc interstitial. This condition decreases the dark current and increases photocurrent simultaneously, resulting in the enhancement of the sensitivity.

Nonlinear I-V curves and current suppression indicate the presence of the Schottky barrier. Smaller barrier is found in the pure ZnO, as indicated by current suppression below $\sim$1 V. Wider Schottky barrier is found in the CZO samples, as demonstrated by the current suppression up to $\sim$3 V. The main reason of Schottky barrier is due to the difference in the work function of Ag and electron affinity energy of ZnO (4.1 eV) [15]. Regarding the theory of thermal electron emission, the diffusion current between metal and semiconductor can be expressed as [18]

$$ I = A \exp \left( -\frac{q\Phi_B}{kT} \right) \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right], $$

$$ I_0 = A \exp \left( -\frac{q\Phi_B}{kT} \right), $$

where $A$, $A'$, $q$, $\Phi_B$, $n$, $k$, $T$, $V_D$ are the area of Schottky contact, Richardson constant (32 A.K⁻²), electron charge, Schottky barrier, ideality factor, Boltzmann constant (8.617×10⁻⁵ eV.K⁻¹), absolute temperature, and built-in potential at the barrier.

By conducting linear extrapolation on the voltage versus ln[$I$] exp[$qV/kT$] (exp[$qV/kT$] - 1), $I_0$ can be obtained to calculate the barrier height as shown in Figure 3(a). The obtained $I_0$ is -25 (0 at.%), -26 (1 at.%), -30 (1.5 at.%), -27 (2 at.%), and -28 (2.5 at.%). Relationship between Schottky barrier height and width of the depletion layer ($W$) is described by [18]

$$ W = \sqrt{\frac{2\varepsilon_0\varepsilon_1}{qN_d}} (\Phi - \Phi_0 + V - \frac{kT}{q}), $$

where $\varepsilon_0$, $\varepsilon_1$, $\Phi_0$, and $N_d$ are absolute dielectric constant, the relative dielectric constant, the distance between the conduction band and Fermi level, and donor concentration, respectively. From equation (4), the depletion layer is proportional to the barrier. It means that the increase in the barrier can reduce the electric field. Figure 3(b) shows the calculated Schottky barrier height. The Schottky barrier from Ag-ZnO is 0.67 eV, showing the lowest value. The barrier increase by increasing Cu content up to 1.5 at.%. Above this concentration, the barrier tends to decrease but it is still higher than that of pure ZnO. This tendency is similar to photosensitivity. The Schottky barrier may give a significant contribution to photosensitivity.

Previous study showed that native point defects play an essential role in the Schottky barrier [19,20]. Also, oxidation state of Cu dopant should be considered. The common oxidation state of Cu is +1 and +2. When the oxidation state is +2, Cu can replace Zn sites substitutionally. For +1 oxidation state, the formation of oxygen vacancy is possible to maintain a charge neutrality. However, the previous study showed that the oxygen vacancy tend to decrease the barrier height [20]. Thus, we argue that Cu-related complex defect should be responsible for the increase the barrier height.
4. Conclusions
In summary, Cu-doped ZnO films were fabricated with Cu concentrations of 0-2.5 at.% to realize the ideal UV detector. The effect of Cu content on the Schottky barrier height has been studied. Generally, the Cu dopant increases the Schottky barrier height. The Cu content of 1.5 at.% shows the highest barrier, which may due to carrier traps promoting by the dopant. Further study is underway to fabricate high-performance photodetector using the simple deposition technique.

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References
[1] Özgür Ü, Alivov Y I, Liu C, Teke A, Reshchikov M A, Doğan S, Avrutin V, Cho S J and Morkoç H 2005 A comprehensive review of ZnO materials and devices J. Appl. Phys. 98 1–103
[2] Anand V, Sakthivelu A, Arun K D, Valanarasu S, Kathalingam A and Ganesh V 2018 Rare earth Sm3+ co-doped AZO thin films for opto-electronic application prepared by spray pyrolysis Ceram. Int. 44 6730–8
[3] Kim H, Horwitz J S, Qadri S B and Chrisey D B 2002 Epitaxial growth of Al-doped ZnO thin films grown by pulsed laser deposition Thin Solid Films 420–421 107–11
[4] Nurfani E, Satrya C D, Abdurrahman I, Suťahja I M, Winata T, Takase K, Rusydi A and Darma Y 2018 Weakening of excitonic screening effects in TiZn1-xO thin films Thin Solid Films 645
[5] Nurfani E, Purbayanto M A K, Aono T, Takase K and Darma Y 2018 Origin of fast-response photocurrent in ZnO thin film Opt. Mater. (Amst). 84 453–8
[6] Soundarrajan P, Sankarasubramanian K, Logu T, Sethuraman K, Gupta A, Kumar S M S, Jeganathan K and Ramamurthi K 2018 The degree of supersaturation dependent ZnO nano/micro rod arrays thin films growth using chemical bath deposition and hydrothermal methods Phys. E Low-dimensional Syst. Nanostructures 106 50–6
[7] Cheng D, He M, Li W, Wu J, Ran J, Cai G and Wang X 2019 Hydrothermal growing of cluster-like ZnO nanoparticles without crystal seeding on PET films via dopamine anchor Appl. Surf. Sci. 467–468 534–42
[8] Nurfani E, Kadja G T M, Purbayanto M A K and Darma Y 2020 The role of substrate temperature on defects, electronic transitions, and dark current behavior of ZnO films fabricated by spray technique Mater. Chem. Phys. 239 122065
[9] Gong Y, Andelman T, Neumark G F, O’Brien S and Kuskovsky I L 2007 Origin of defect-related green emission from ZnO nanoparticles: Effect of surface modification Nanoscale Res. Lett. 2 297–302
[10] Klason P, Rahman M M, Hu Q, Nur O, Turan R and Willander M 2009 Fabrication and characterization of p-Si/n-ZnO heterostructured junctions Microelectronics J. 40 706–10
[11] Alamdari S, Sasani M, Afarideh H and Mohammadi A 2019 Preparation and characterization of GO-ZnO nanocomposite for UV detection application Opt. Mater. (Amst). 92 243–50
[12] Law J B K and Thong J T L 2006 Simple fabrication of a ZnO nanowire photodetector with a fast photoresponse time Appl. Phys. Lett. 88 133114
[13] Shewale P S, Lee N K, Lee S H, Kang K Y and Yu Y S 2015 Ti doped ZnO thin film based UV photodetector: Fabrication and characterization J. Alloys Compd. 624 251–7
[14] Herng T S, Wong M F, Qi D, Yi J, Kumar A, Huang A, Kartawidjaja F C, Smadici S, Abbamonte P, Sánchez-Hanke C, Shannigrahi S, Xue J M, Wang J, Feng Y P, Rusydi A, Zeng K and Ding J 2011 Mutual ferromagnetic-ferroelectric coupling in multiferroic copper-doped ZnO Adv. Mater. 23 1635–40
[15] Li F M, Zhu C T, Ma S Y, Sun A M, Song H S, Li X B and Wang X 2013 Investigation of the blue-green emission and UV photosensitivity of Cu-doped ZnO films Mater. Sci. Semicond. Process. 16 1079–85
[16] Sarkar S and Basak D 2013 Defect controlled ultra high ultraviolet photocurrent gain in Cu-
doped ZnO nanorod arrays: De-trapping yield Appl. Phys. Lett. 103 1–5

[17] Duan Y, Cong M, Jiang D, Zhang W, Yang X and Shan C 2019 ZnO Thin Film Flexible UV Photodetectors: Regulation on the ZnO/Au Interface by Piezo-Phototronic Effect and Performance Outcomes Adv. Mater. Interfaces 6 1–8

[18] Guo Z, Jiang D, Hu N, Yang X, Zhang W, Duan Y and Gao S 2018 Significant Enhancement of MgZnO Metal- Semiconductor-Metal Photodetectors via Coupling with Pt Nanoparticle Surface Plasmons Nanoscale Res. Lett. 13 4–9

[19] Brillson L J, Dong Y, Tuomisto F, Svensson B G, Kuznetsov A Y, Doutt D, Mosbäcker L, Cantwell G, Zhang J, Song J J, Fang Z and Look D C 2016 Interplay of native point defects with ZnO Schottky barriers and doping Interplay of native point defects with ZnO Schottky barriers and doping J. Vac. Sci. Technol. B 30 050801

[20] Hwang J D, Lin Y L and Kung C Y 2013 Enhancement of the Schottky barrier height of Au / ZnO nanocrystal by zinc vacancies using a hydrothermal seed layer 115709