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Research paper

Influence of Cr doping on Schottky barrier height and visible light detection of ZnO thin films deposited by magnetron sputtering

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ABSTRACT

A comparative study of the electrical and photodetection properties of ZnO and Cr doped ZnO thin films are being reported here. The films were deposited using magnetron sputtering. X-ray diffraction (XRD) revealed hexagonal crystal structure of the films with (002) preferred orientation. Pt/ZnO/Pt and Pt/Cr doped ZnO/Pt Schottky diodes were fabricated for photodetection studies. The Schottky barrier height was lowered for Cr doped ZnO film as compared to ZnO film. The ideality factor was improved upon Cr doping. Pt/ZnO/Pt diode was unresponsive to visible light, however, Pt/Cr doped ZnO/Pt diode showed response to visible light with short response and recovery times. The response of the Pt/Cr doped ZnO/Pt diodes to visible light is attributed to the reduction in band gap of the Cr doped ZnO thin film.

1. Introduction

Photodetectors can be used in environmental monitoring, space research, optical communications, flame detection and many other applications [1]. Therefore, in recent years photodetection properties of various wide band gap materials such as SiCN [2], GaN [3], AlGaN [4] and diamond [5] have been extensively studied to overcome problems associated with silicon based low band gap materials [1]. Among wide band gap semiconductors, ZnO has been largely investigated as solar cells [6], UV photo detectors [7] and gas sensors [8] because of its low cost, direct band gap (3.3 eV) [9] and high exciton binding energy (60 meV) at room temperature [10]. Pure ZnO has shown weak responsivity for visible light [11], due to its wide band gap. Different techniques such as doping with suitable dopants [12,13], decorating with gold nanoparticles and by making different heterostructures have been employed to improve photodetection characteristics of ZnO [14].

In this work, we aim to reduce the band gap of ZnO to improve its responsivity for visible light by doping of ZnO with a suitable element. Chromium (Cr) is a potential candidate to be used as a dopant for ZnO to improve photodetection properties of ZnO. Cr^{+3} has ionic radius (0.063 nm) closer to that of Zn^{+2} (0.074 nm) [15]. Due to a smaller difference in ionic radii, it is expected that Cr may substitute Zn in the crystal lattice. Cr doped ZnO has already been used to improve other properties of ZnO [15–18]. However, the effect of Cr doping on the Schottky parameters of Pt/ZnO/Pt diodes and the use of these diodes for visible light detection have not been studied so far as per our knowledge. Therefore, in this experimental work, we fabricated Pt/ZnO/Pt and Pt/Cr doped ZnO/Pt diodes and evaluated the Schottky parameters and photosensing properties of these fabricated diodes.

2. Experimental

ZnO film was deposited on Si (100) substrate by RF magnetron sputtering of ZnO (99.99%) target. Cr doped ZnO thin film was also deposited on Si (100) substrate by RF magnetron sputtering of ZnO target and DC magnetron sputtering of Cr (99.99%) target simultaneously. Pure Ar atmosphere at 2.7 Pa was maintained during deposition of ZnO and Cr doped ZnO films. Substrate surfaces were cleaned with 3:1 solution of H_2SO_4 and H_2O_2 to remove any organic matter on silicon surface. After that, the substrate was soaked in dilute HF solution to remove any oxide layer present on the substrate. Silicon substrate was then washed with water, alcohol and acetone respectively by using ultrasonic stirring. Targets surfaces were cleaned before deposition by presputtering process for 15 min. Distance between target and substrate was 12 cm. Temperature of substrate was monitored by thermocouple attached near substrate and controlled at 20 °C by substrate holder cooling system. RF power equal to 80 W was maintained with DC power off for the deposition of ZnO film. The DC power equal to 50 W and RF power equal to 80 W was used for the deposition of Cr doped ZnO film. The concentration of Cr was controlled by the DC power. Deposition rates for both films were measured by depositing films for different times and measuring the thickness using surface profiler. Using

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these measured deposition rates, thickness of both films was controlled. The thickness of both films was controlled ~120 nm. Platinum (Pt) electrodes with dimension 400 μm × 400 μm were sputtered on the films through a shadow mask by thermal evaporation. The distance between Pt electrodes was 100 μm.

Film thickness was measured with Surface Profiler (Alpha-step IQ, KLA Tencor). The Bruker D8 advance XRD was used for structural analysis of the films. Asylum research AFM was used for surface characterization of the films. The elemental analysis was performed by the Energy dispersive spectroscopy (EDX) attached to a scanning electron microscope (JEOL JSM-6360). Study of photodetection properties of deposited films was performed using precision semiconductor parameter analyzed Agilent 4156C. A commercial halogen lamp of 35 W was used as light source.

3. Results and discussions

The films structures were identified by XRD with JCPDS card number 01–079-0207 corresponding to hexagonal ZnO. No peak of Cr or other impurity phase was observed in the XRD patterns. Si peak was observed in Cr doped ZnO thin film which may be from the silicon substrate on which the film was deposited. Diffraction from (002) orientation peak was observed in XRD pattern of ZnO film. In Cr doped ZnO film, diffraction peaks corresponding to (100) and (101) orientations were also observed in addition to (002) orientation peak. Higher intensity of (002) orientation peak in Cr doped ZnO film than those of (100) and (101) orientation peaks indicate preferential growth of (002) oriented film. The preferential growth of these films may be attributed to the presence of net dipole moment along c axis [19]. By the substitution of smaller size Cr^{+3} (ionic radius 0.063 nm) ions in place of Zn^{+2} ions (ionic radius 0.074 nm) [15], a decrease in lattice parameters is expected. Due to the shrinkage in lattice parameters, XRD peaks of Cr doped ZnO shift towards higher 2θ values as can be seen in Fig. 1.

EDX analysis of ZnO and Cr doped ZnO film is shown in Fig. 2(a–b).

EDX analysis confirms the presence of Zn and O in ZnO film and Cr, Zn and O in the Cr doped ZnO film. Si peak observed in EDX may be from Si substrate. No other element was observed in EDX analysis. EDX analysis shows 1.5 atomic percent Cr in ZnO. Inset to the Fig. 2 shows the surface morphology of ZnO and Cr doped ZnO film. Average roughness equal to 3.3 nm and 4.1 nm was observed for ZnO and Cr doped ZnO films respectively over 1 μm^2 surface area.

Fig. 3(a–b) shows current-voltage (*IV*) characteristics of Pt/ZnO/Pt and Pt/Cr doped ZnO/Pt diodes with and without light shined on the diode.

Plots show that the metal-semiconductor contact between Pt/ZnO and Pt/Cr doped ZnO are Schottky type in both cases, which is inconsistent with previous studies [20,21]. ZnO has a wide and direct band gap of 3.3 eV [9] and the electron affinity of 4.3–4.6 eV [22]. While the work function of Pt is 5.1 eV [21]. Since the work function of Pt is higher than the electron affinity of ZnO, therefore a Schottky type metal-semiconductor contact is formed between them. The *IV* measurements were carried out on Five (05) different devices and similar results were obtained. Schottky contact parameters such as the ideality factor and barrier height were extracted for both Pt/ZnO/Pt and Pt/Cr doped ZnO/Pt diodes using the thermionic emission model. According to the thermionic emission model ideality factor can be expressed as $\eta = (\frac{q}{kT})\{\frac{dV}{d(\ln I)}\}$. Here q is the elementary charge, k is the Boltzman constant and T is temperature. The values of $\frac{dV}{d(\ln I)}$ were calculated from the slope of the graph between $\ln(I)$ and V before transition point [23]. Effective barrier height ($\Phi_{B\ eff}$) at zero bias was calculated using equation $\Phi_{B\ eff} = (\frac{kT}{q})\ \ln(\frac{AA^*T^2}{I_o})$ [23]. Here A is the contact area, A^* is the effective Richardson constant of ZnO (32 $Acm^{-2}\ K^{-2}$) [23]. The Schottky contact parameters for Pt/ZnO/Pt and Pt/Cr doped ZnO/Pt diodes as extracted using this model are summarized in Table 1.

The Φ_{eff} decreases from 0.88 eV for ZnO film to 0.26 eV for Cr doped ZnO film as can be seen from Table 1. Wei et al. [24] has shown experimentally and from first principles calculations that Al doping reduces the value of work function of (002) ZnO film. Therefore, in our case the reduction in Schottky barrier upon Cr doping was expected as the reduction in work function of our (002) ZnO film was expected upon Cr doping as well.

For the study of photodetection properties of ZnO and Cr doped ZnO films, a commercial light source (λ = 390–455 nm, optical power = 1.7 μWcm^{-2}) was used. It can be seen from Fig. 3(a) that there is no appreciable increase in current when ZnO thin film was illuminated. However, an increase in current in the presence of light was observed in Cr doped ZnO thin film as can be seen from Fig. 3(b). It has been suggested that the adsorption and desorption of oxygen in the dark and light respectively is the main process behind the photodetection of Cr doped ZnO thin films. In the dark oxygen is adsorbed on the surface by consuming an electron from the conduction band according to the Eq. (1):

$$O_{2\ (gas)} + e^- \rightarrow O^-_{2(ad)} \quad (1)$$

When incident light of energy greater than the band gap of semiconductor film ($h\upsilon > E_g$) shines on its surface, an electron hole pair is generated. This generated hole combines with an oxygen molecule as per Eq. (2):

$$O_{2(ad)} + h^+ \rightarrow O_{2(gas)} \quad (2)$$

Consequently, oxygen molecules are desorbed from the film surface, resulting in an increase in the carrier concentration and increase in the current as compared to dark conditions [25]. Pictorial explanation of the photodetection mechanism is represented in Fig. 4.

Previous studies show that the band gap of pure ZnO thin films ranges from 3.25–3.3 eV [9, 26]. The maximum energy of incident visible light is in the range from 2.72–3.17 eV (λ = 390–455 nm). Since the energy of incident light is lower than the band gap of ZnO thin film, therefore, it does not give response to incident visible light. However, it has been observed that the band gap of ZnO decreases by the addition of Cr [16,17]. This narrowing in the band gap of ZnO by the incorporation of Cr has been attributed to sp-d spin exchange interaction between conduction band electrons and the d electrons of Cr ions [27]. Because of this interaction, shrinkage in conduction band edge and increase in valence band edge occurs which results in narrowing of band gap [28]. Due to this narrowing in band gap, Cr doped ZnO film show response to visible light.

Time dependent photocurrent measurements of Cr doped ZnO thin films were carried out between on and off states of visible light. The observed time dependent photo response for Cr doped ZnO film at 5 V is represented in Fig. 5.

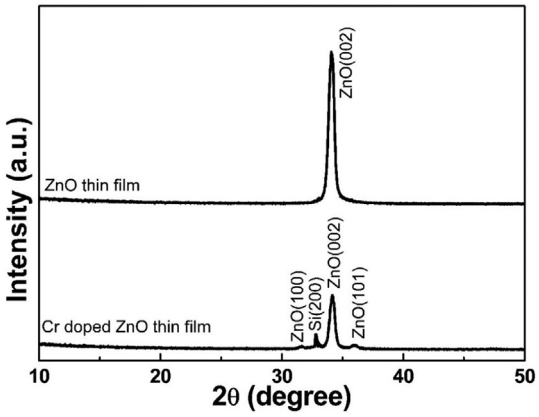

Fig. 1. X-Ray diffraction pattern of ZnO and Cr doped ZnO film.

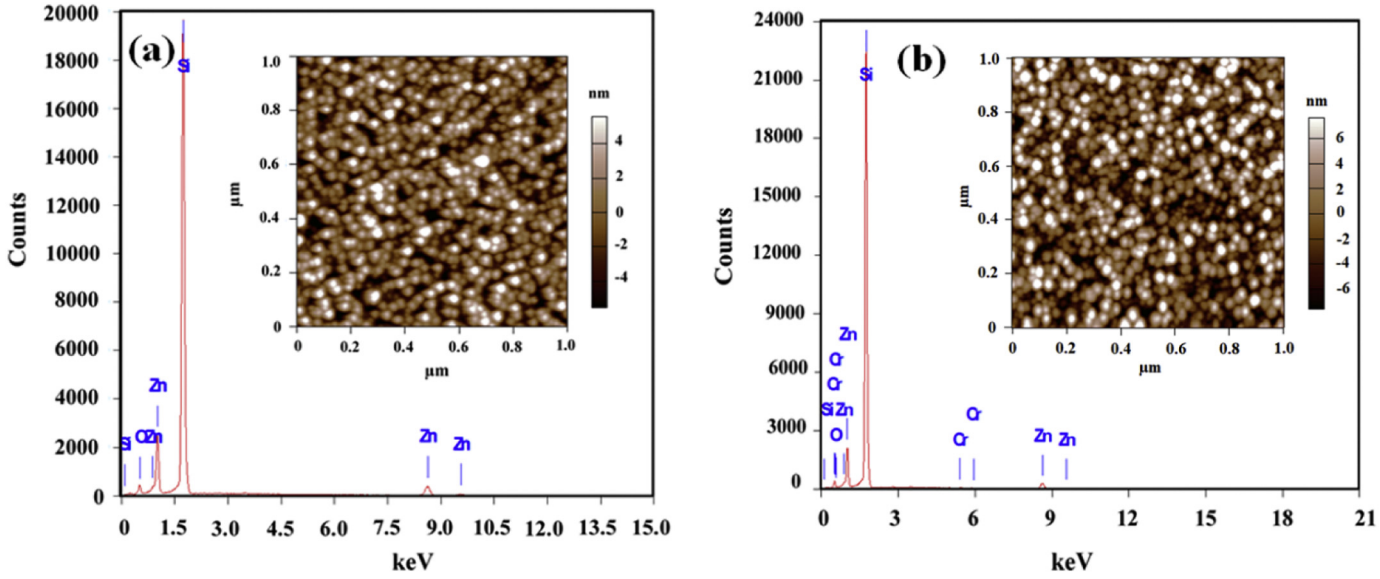

Fig. 2. (a) EDX spectra of ZnO film (b) EDx spectra of Cr doped ZnO film. Inset of figures show AFM images.

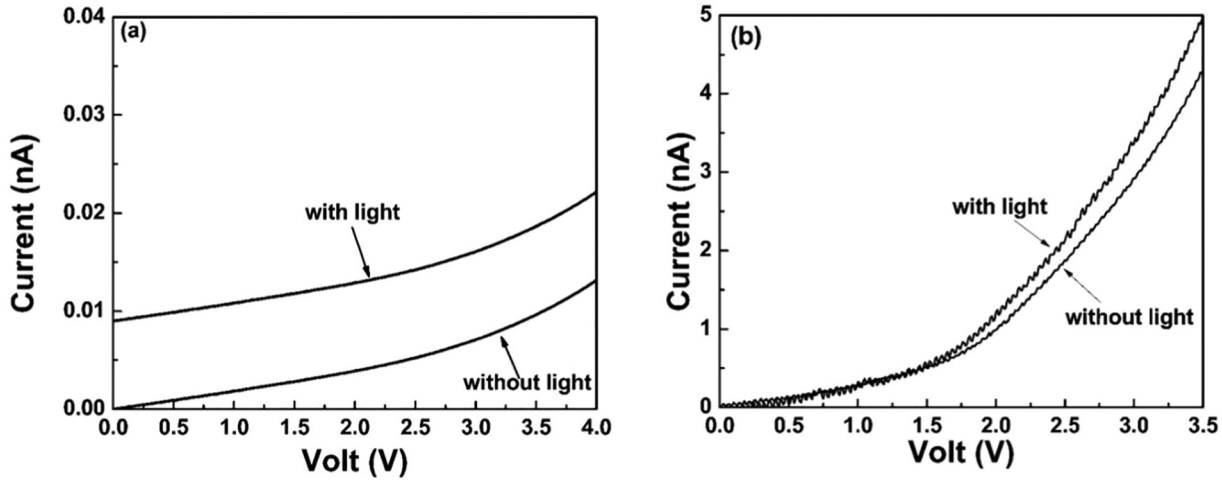

Fig. 3. Experimental *IV* characteristics of (a) Pt/ZnO/Pt diode. The *IV* curve of Pt/ZnO/Pt under light has been offset by 0.0025 nA for clarity. (b) Pt/Cr doped ZnO/Pt devices.

It is evident that the current starts increasing immediately after the illumination and reaches to 22 nA. When the light is switched off the current decreases to initial value. The response time of a photodetector is the time required to increase the photo current from 10% to 90% of its maximum value. The recovery time is the time required to decrease the photo current from 90% to 10% of its maximum value. The response and recovery times of the Cr doped ZnO films were 5 s. The slight drift seen in the dark current in Fig. 5 may be due to persistent photoconductivity [29].

Response of a photodetector is defined as:

$$R = \frac{I_{ph} - I_{dark}}{P_{opt}}$$

where I_{ph} is the photo current, I_{dark} is the current in dark and P_{opt} is the incident light power [30]. Responsivity of Cr doped ZnO film was found out to be 1.3×10^{-3} A/W for visible light. Cr doped ZnO showed higher responsivity than that of observed for ZnO nanowires i.e. 1×10^{-4} A/W for 390–455 nm wavelength [31].

4. Conclusions

Approximately 120 nm thin ZnO and Cr doped ZnO films were deposited with RF magnetron sputtering with (002) preferred orientation. Pt contacts were then deposited onto the sputtered films by using thermal evaporation technique. Pt contacts formed Schottky type metal-semiconductor contacts with ZnO and Cr doped ZnO films. Calculated effective barrier height of Pt/Cr doped ZnO/Pt (0.26 V) was lower as compared to that of Pt/ZnO/Pt (0.88 V). Photosensing properties of Pt/ZnO/Pt and Pt/Cr doped ZnO/Pt diodes were studied under the illumination of visible light. Pt/ZnO/Pt diode did not show response for visible light. Pt/Cr doped ZnO/Pt diode responded to visible light with responsivity = 1.3×10^{-3} A/W. The both response and recovery

Table 1
Schottky parameters calculated using thermionic emission model.

	η	Φ_{eff} (V)	I_o (A)
ZnO film	2.80	0.88	4.39×10^{-12}
Cr doped ZnO film	1.55	0.26	2.94×10^{-10}

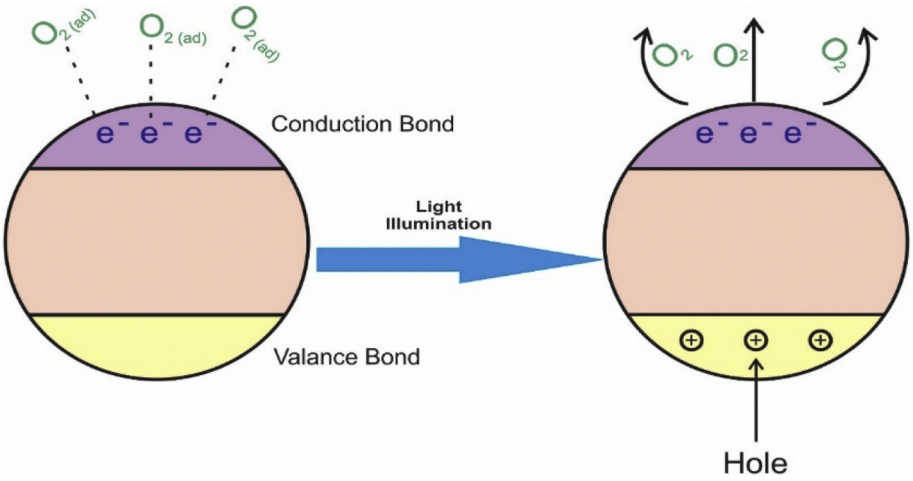

Fig. 4. photo sensing mechanism in ZnO based materials.

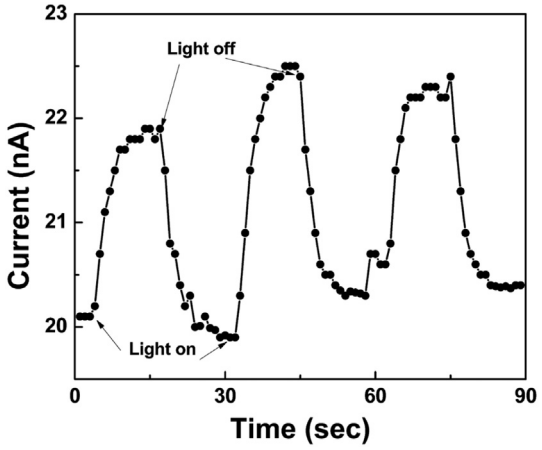

Fig. 5. Photo response and recovery characteristics of Pt/Cr doped ZnO/Pt device.

times of the Pt/Cr doped ZnO/Pt diode were 5 s. Photosensing results illustrates the decrease in band gap of ZnO film by Cr doping.

Conflict of interest

The author declare that they have no competing interest.

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