Ultraviolet sensing properties of polyvinyl alcohol-coated aluminium-doped zinc oxide nanorods

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Abstract. Undoped and aluminium (Al)-doped zinc oxide (ZnO) nanorods have been synthesized by electrochemical route. The synthesized materials have been characterized by X-ray diffraction, UV-visible spectrometer and scanning electron microscope. The Al-doped ZnO nanorods have been coated with polyvinyl alcohol. Current-voltage characteristics have been investigated in dark and under UV-light illumination. Aluminium doping in ZnO increase its electrical conductivity and further polyvinyl alcohol coating on Al-doped ZnO increase UV sensitivity of the material. Response and recovery time of Al-doped ZnO and PVA-coated Al-doped ZnO nanorods have been recorded. PVA-coated Al-doped ZnO nanorods shows very fast response and recovery time of 10 s in comparison to uncoated ZnO (20 min) nanorods.

Keywords. Electrochemical; aluminium-doped zinc oxide; PVA-coated; UV sensing.

1. Introduction

Metal oxide semiconductors have received considerable attention due to their excellent physical and chemical properties (Johnson *et al* 2001; Vayssieres *et al* 2001; Kolmakov and Moskovits 2004). Zinc oxide (ZnO), one of the most attractive semiconductor materials for the applications in photonic crystals (Seelig *et al* 2003), photo-detectors (Lin *et al* 2008), photodiodes (Chang *et al* 2012), light emitting diodes (Willander *et al* 2009), gas sensors (Gupta *et al* 2010) and solar cells (Beek *et al* 2004) is attracting enormous attention because of its novel optoelectronic and electrical properties (Chena *et al* 2009; Ardakani *et al* 2012). Out of the various applications of metal oxide semiconductors, UV-photodetectors are useful in space research, missile warning systems, high flame detection, air quality monitoring, gas sensing, accurate measurement of radiation for the treatment of UV-irradiated skin, etc. (Zhang *et al* 2009).

Metal oxides having good optical and structural properties also require good electrical properties to be used in electronic devices. ZnO exhibit *n*-type conductivity due to its native defect of zinc interstitials and oxygen vacancies (Kang *et al* 2008). Dopant atoms of higher valance elements such as aluminium (Al), indium (In) and gallium (Ga) are used to improve its electrical conductivity (Jin *et al* 1988). Doping of Al is preferable, due to its easy incorporation in ZnO structure, cheap, high abundance and non-toxic nature (Lee and Park 2003; Horwat and Billard 2007; Zhou *et al* 2007; Caglar *et al* 2008). Undoped and doped zinc oxide films have been usually grown by various deposition techniques, such as electrospinning (Lotus *et al* 2010), chemical spray technique

(Olvera *et al* 2010), pulsed laser deposition (Kang *et al* 2004), D.C. magnetron sputtering (Takeda and Fukawa 2004), RF magnetron sputtering (Zhu *et al* 2000), atomic layer deposition (Luka *et al* 2011), metal organic chemical vapour deposition (Kim and Kim 2003), molecular beam epitaxy (Sano *et al* 2004), metal organic vapour phase epitaxy (Ma *et al* 2004), reactive deposition (Zhenguo *et al* 2003), spray pyrolysis (Nunes *et al* 2002), filtered vacuum arc deposition (Gontijoa *et al* 2012), sol-gel (Armelaio *et al* 2001) and cathodic electrodeposition (Yoshida *et al* 2004; Postels *et al* 2008; Jehl *et al* 2010) on different substrates. In this paper, we have also reported the synthesis of pure and Al-doped ZnO nanorods by simple electrochemical route. The defects on the surface of nanostructure decrease its UV-sensitivity. Qin *et al* (2011) reported the improvement in ultraviolet radiation sensitivity of ZnO nanoparticles by coating with PVA. We report here, enhancement in electrical conductivity upon Al-doping in ZnO. Surface passivation of Al-doped ZnO nanorods has been carried out with PVA to improve its UV-radiation sensitivity.

2. Experimental

Nanorods of ZnO and Al-doped ZnO were grown from aqueous solution of zinc nitrate and hexamethylenetetramine (HMT). Aqueous solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and HMT was prepared using double-distilled water. The solution was stirred constantly. The temperature of the solution was maintained at 80 °C. The two electrodes were lowered in the solution to which a potential ranging from 0.8 to 1 V was applied by using a D.C. power supply. Indium tin oxide-coated glass plate was used as cathode. The distance between the electrode plates was kept at 10 mm. 1–2 wt% (Al to

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ZnO) aluminium doping in ZnO were obtained using aluminium nitrate. Pure ZnO nanorods were prepared by electrodeposition from aqueous solution. Aluminium-doped ZnO nanorods were also prepared using same technique. Prepared Al-doped ZnO nanorods were dip-coated with very dilute solution of polyvinyl alcohol (0.5% by weight in water) and dried in vacuum. Synthesized materials were structurally characterized by using a Bruker D8 X-ray diffractometer with a high-star 2-d detector. The diffraction pattern was recorded from 20 to 80°. Photoluminescence spectra of Al-doped ZnO and undoped ZnO films were also studied using Shimadzu spectrofluorometer RF-5301PC. All the measurements were performed at room temperature in ambient conditions. Size and morphology of the synthesized nanorods were characterized by using dual beam scanning electron microscope (SEM). UV-visible absorption spectra of the synthesized materials were also recorded by using Shimadzu 2401PC spectrophotometer. Electrodes were made by depositing two silver point contacts on top of the films. Current–voltage (I–V) characteristics of samples were measured using a Keithley-2400 source meter interfaced with computer under darkness and under illumination by a 340 nm UV LED with an intensity 45.58 mW/cm². The area of the photo detectors exposed to UV-light was kept constant (160 mm²) in all the measurements. Response and recovery of the photodetectors were recorded by computer-controlled Keithley-6514 electrometer.

3. Results and discussion

X-ray diffraction pattern of the synthesized ZnO and Al-doped ZnO nanorods are shown in figure 1. Curves A and B in the figure represent XRD of pure ZnO and Al-doped

ZnO nanorods, respectively, in the range of 20–80°. Curve A of figure 1 indicates that all the diffraction peaks correspond to crystalline ZnO with the hexagonal wurtzite structure (Olvera *et al* 2010). No characteristic peaks from other impurities are detected. The peak at 34.77 2 θ value is strongest, corresponding to (002) lattice plane in ZnO. Other lower intensity peaks at 2 θ values of 32.02, 36.63, 47.89, 56.02, 63.14, and 72.27 corresponds to (100), (101), (102), (110), (103) and (004) lattice planes, respectively. Curve B of figure 1 indicates that Al-doped ZnO also exhibited polycrystalline structure similar to ZnO hexagonal wurtzite type (JCPDS #36-1451). In Al-doped ZnO, the intensity of the peak at 34.77 2 θ value decreases in comparison to undoped ZnO. Peaks at 56.02 and 72.77 2 θ values which correspond to (110) and (004) planes are missing in Al-doped ZnO. These results indicate that doping of aluminum in ZnO structure decreases its crystallinity.

XRD spectra revealed that no peaks due to Al or any other impurity are observed. This reveals that Al replaced Zn from the lattice or Al segregated to the non-crystalline region in grain boundary (Lee and Park 2003). The formation of stress by the difference in ion size between Zn ($r_{\text{Zn}}^{2+} = 0.074$ nm) and Al ($r_{\text{Al}}^{3+} = 0.054$ nm) with doping is known to be responsible for aggravation in ZnO crystallinity (Zhou *et al* 2007). As compared to Zn²⁺, extrinsic Al³⁺ capture more oxygen due to larger nuclear charge of Al³⁺ decreases the crystalline and hexagonal structure of the thin films (Horwat and Billard 2007).

The SEM micrographs of undoped and Al-doped ZnO nanorods are represented in figure 2(a and b). The average diameter and length of the nanorods are about 100 nm and 1 μ m, respectively. The insets in figure 2(a and b) shows enlarged images of the nanorods. Some granular structure is observed on the surface of the nanorods in the case of

Figure 1. XRD patterns of pure (curve A) and Al-doped ZnO (curve B) nanorods.

(a)

(b)

Figure 2. SEM images of pure and Al-doped ZnO nanorods synthesized by electrochemical method: (a) SEM micrograph of ZnO nanorods and (b) SEM micrograph of Al-doped ZnO nanorods.

aluminium doping as can be seen from figure 2(b). The optical absorption spectra of undoped and Al-doped ZnO nanorods are shown in figure 3. It is noted that pure ZnO nanorods have lower absorbance in visible range of spectrum. The absorbance in visible region of electromagnetic spectrum increases after doping with aluminium in ZnO structure. This behaviour may be due to the introduction of aluminium defect states within the forbidden bands, which may lead to absorption of incident photon in visible region. The absorption edge of Al-doped ZnO nanorods shows bathochromic shift with respect to the undoped ZnO. Similar behaviour has also been reported in case of Mn-doped ZnO films by Shinde *et al* (2006).

Figure 4(a) shows the photoluminescence (PL) spectra of undoped ZnO nanorods at different excitation wavelengths. The UV emission with a sharp peak at 387 nm is originated from excitonic recombination dominating the near band edge emission (Liu *et al* 2004). The other peaks at 415 nm and broader peak in the visible region at 550 nm is associated

Figure 3. UV-visible absorption spectra of pure ZnO nanorods (curve A) and Al-doped ZnO nanorods (curve B).

Figure 4. (a) Photoluminescence (PL) spectra of undoped ZnO films at different excitation wavelengths. (b) Comparison of PL spectra of undoped and Al-doped ZnO films.

with the deep level emission due to recombination of photo-generated hole with the electron that belongs to a singly ionized oxygen vacancy and structural defects such as interstitial zinc or oxygen (Liu *et al* 2004). The peak at 415 nm (0.298 eV) is more pronounced at higher excitation energies 3.64 eV (340 nm). From the calculated defect levels in ZnO films, the defect due to zinc interstitials corresponds to 2.9 eV (Willander *et al* 2010). The PL peak at 415 nm is quite close to the calculated defect level due to zinc interstitial. PL spectra of Al-doped and undoped ZnO at 340 nm excitation wavelength is depicted in figure 4(b). Introduction of Al in the synthesis of ZnO thin films results in the depression of the PL from the defect levels particularly, due to interstitial zinc in Al-doped ZnO films.

Figure 5(a and b) shows I–V characteristics of undoped, Al-doped and PVA-coated Al-doped ZnO nanorods under dark and in UV illumination at room temperature in the

voltage range of 0–20 V. Silver contacts were made as electrodes take the current–voltage characteristics. Figure 5(a) and its inset shows I–V curve of Al-doped ZnO and undoped ZnO nanorods in dark and under UV-illumination. I–V curves show ohmic behaviour for both the samples. Similar type of ohmic characteristics has also been obtained with gold contacts on pure and Al-doped ZnO films by Mamat *et al* (2010). The electrical conductivity of ZnO nanorods increases upon doping with aluminium. Aluminium doping increases carrier concentration in ZnO nano structure because aluminium has one more valance e^- than zinc. Hence aluminium doping in ZnO nanostructure effectively improve its electrical properties. I–V characteristic shows that the current intensity for both the samples increase under UV-light illumination with respect to its dark value. The increase in photocurrent can be explained by photoexcitation of electrons from valance band to the conduction band of the material.

Qin *et al* (2011) reported that most of the UV-generated carriers in the ZnO are trapped by defects during transportation to the terminals. To overcome this effect, Al-doped ZnO are dip-coated with dilute solution of polyvinyl alcohol to reduce the surface defects. The I–V characteristics of PVA coated Al-doped ZnO in dark and under UV-illumination is shown in figure 5(b). Enhancement in photo-response is observed in PVA-coated Al-doped ZnO nanorods. This indicates that PVA acts as effective surface passivation material to improve the photo-sensitivity of Al-doped ZnO. Hence, PVA-coated Al-doped ZnO nanorods act as good UV sensing materials. Further, the UV response of Al-doped ZnO and PVA-coated Al-doped ZnO films are studied. The response and recovery times for PVA-coated Al-doped ZnO nanorods films were studied for three Al doping concentrations (1, 1.5 and 2 wt%). Figure 6(a–d) shows the response and recovery time of Al-doped ZnO and PVA-coated Al-doped ZnO films to 365 nm UV light. The response and recovery times are relatively fast for PVA-coated Al-doped ZnO nanorods (figure 6(b–d)) as compared to simply Al-doped ZnO (figure 6a). When both the photodetectors are illuminated by 365 nm UV light, the electrical resistance decreases sharply. On turning off UV light resistance returns to its initial value with a very fast recovery time of almost 10 s in case of PVA-coated Al-doped ZnO nanorods, whereas recovery, in case of uncoated Al-doped ZnO nanorods is very slow. Multiple experiments were performed and similar results were obtained with an accuracy of 7–10% for time constants. There was not much difference in the response times (~ 25 –30 s) however, the recovery times were found to be much larger in the case of 1 and 2 wt% Al doping as compared to 1.5 wt% Al doping concentration as depicted in figure 6(b–d). The on/off ratio in the case of 1, 1.5 and 2 wt% Al-doped ZnO films were found to be approximately 6, 4 and 1 Ω , respectively, which indicates that the sensitivity of 1 wt% Al-doped ZnO film is more than that for higher concentrations of Al doping. On the other hand, the recovery from the on to off state of 1 and 2 wt% Al-doped ZnO films were found to be slower as compared to 1.5 wt% Al-doped

Figure 5. (a) I–V curves of Al-doped ZnO in dark (curve A) and UV-light illuminated (curve B); inset: I–V curves of pure ZnO in dark (curve A) and UV-light illuminated (curve B). (b) I–V curves of PVA-coated Al-doped ZnO in dark (curve A) and UV-light illuminated (curve B).

Figure 6. UV-response and recovery for Al-doped ZnO nanorods based UV photo-detector (a) and PVA-coated Al-doped ZnO nanorods based UV photo-detector at 20 s on/off time scale for (b) 1 (c) 1.5 and (d) 2 wt% Al doping, respectively.

ZnO. ZnO films prepared with higher Al doping concentrations (> 2 wt%) were found to be non-uniform and showed irregular response to UV light. So, the optimum Al doping concentration was found to be 1.5 wt%. The effect on photoresponse of the thickness of the PVA coating on Al-doped ZnO film was also studied. When the thickness of the PVA coating on Al-doped ZnO was increased by increasing the concentration of PVA in water (> 0.5 wt%) that is used for dip coating, the sheet resistance of the films increased and photo-conducting effect was suppressed.

Photodetection mechanism is as follows. Initially, oxygen molecules adsorbed on the surface of ZnO nanorods decrease the carriers density by trapping free electrons, $O_2(g) + e^- \rightarrow O_2^-(ad) + e^- \rightarrow O_2^-(ad)$. This leads to

the formation of a depletion region near the surface, which significantly decreases the conductance. The UV response time is governed by adsorption and desorption of O_2 molecules on the surface (Chai *et al* 2009; Lupan *et al* 2009). After the photosensor is illuminated by UV light, the electron-hole ($e^- - h^+$) pairs are generated, ($h\nu \rightarrow e^- - h^+$). The holes (h^+) migrate to the surface to discharge the chemisorbed oxygen ions and lowering the depletion layer near the surface ($O_2^-(ad) + h^+ \rightarrow O_2^-(ad) + h^+ \rightarrow O_2(g)$). The remaining unpaired electrons contribute to the current. After UV light is turned off, the holes concentration is lower than that of electrons in Al-doped ZnO nanorods. However, h^+ recombines with e^- , simultaneously oxygen molecules readsorb on the surface and capture free electrons. This results in a decrease

in the conductance value. This fast response and recovery in case of PVA-coated Al-doped ZnO nanorods may be because of the surface passivation effect of PVA. Hence, PVA-coated Al-doped ZnO can be used as good UV sensing material.

4. Conclusions

Zinc oxide nanorods (undoped and aluminium-doped) have been synthesized by fast and easy electrochemical method. Coating of aluminum-doped ZnO nanorods with PVA shows enhanced UV sensitivity. PVA-coated Al-doped ZnO nanorods have fast response and recovery time in comparison to uncoated Al-doped ZnO nanorods. These results indicate that PVA-coated Al-doped ZnO nanorods can be used to fabricate low cost and sensitive UV sensor.

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