

Preparation and characteristics of the In-doped ZnO thin films and the n-ZnO:In/p-Si heterojunctions for optoelectronic switch

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Received 10, February 2010

Abstract. n-ZnO:In/p-Si heterojunctions have been fabricated by sputter deposition of n-ZnO:In on p-Si substrates. The lowest resistivity n-ZnO:In film was obtained at a substrate temperature of 150°C using a ZnO target doped with 2 wt% In₂O₃. At substrate temperature above 300°C the resistivity of the film increases as the carrier concentration decreases. This implies a significant decrease in the donor impurity, which is ascribed to evaporation of the indium during film growth. The wavelength dependent properties of the photo-response for the heterojunction were investigated in detail by studying the effect of light illumination on current - voltage (I-V) characteristic, photocurrent spectra at room temperature. From the photocurrent spectra, it was observed that the visible photons are absorbed in the p-Si layer, while ultraviolet (UV) photons are absorbed in the depleted n-ZnO:In film under reverse bias conditions. The properties of ZnO:In films prepared by r.f. magnetron sputtering are good enough to be used in photoelectrical devices.

Keywords: n-ZnO:In/p-Si; Heterojunction, R.F. magnetron sputtering, Current-voltage characteristic, Photocurrent.

1. Introduction

Zinc oxide (ZnO) films have been extensively studied for practical application including bulk acoustic resonators [1], grating-coupled wave-guard filters [2], acoustic-electric devices [3], transparent electrode materials for various electronic devices such as solar cells, electroluminescence displays, etc. [4, 6]. Heterojunction solar cells consisting of a wide band gap transparent conductive oxide (TCO) on a crystal silicon (Si) wafer have a number of potential advantages such as an excellent blue response, simple processing steps, and low processing temperatures. One promising type of TCO/Si solar cells uses aluminum doped ZnO (ZnO:Al) or indium doped ZnO (ZnO:In) on p-type Si wafer, where the ZnO film is prepared by spray pyrolysis [5], sol-gel methods [4, 9], or r.f. magnetron sputtering [7, 8]. In this work a detailed investigation on the n-ZnO:In film properties and the I-V characteristic, photocurrent of the n-ZnO:In/p-Si heterojunction has been carried out and the results are discussed.

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2. Experimental

Indium doped Zinc Oxide (ZnO:In) thin films were deposited on silicon (Si) substrates by employing the R.F. magnetron sputtering technique. P-type ($10\ \Omega\text{cm}$) Si (100) wafers were used as substrates for the n-ZnO:In/p-Si heterojunction diodes. The Si (100) wafers were cut into pieces of $1.5\text{ cm} \times 1.5\text{ cm}$. Prior to the deposition, the wafers were dipped for 1 min into buffered oxide etchant ($\text{HF}/\text{H}_2\text{O} = 1:7$) to remove native oxides. Then the samples were ultrasonically cleaned with boiling acetone, ethanol and de-ionized water for 10 min. Finally the wafers were rinsed with de-ionized water and then blown dry with nitrogen gun. The ZnO:In films were deposited with a R.F. magnetron sputtering system using a 0.5 cm thick pressed ZnO:In target with 7.5 cm diameter. Five targets with a mixture of ZnO (99.9 % purity) and In_2O_3 (99.9% purity) were employed as source materials. The targets were prepared using conventional sintering process (Fig.1). The contents of In_2O_3 added to the five targets were 1%, 2%, 3%, 5% and 10% in weight, respectively. The substrate holder was placed 80 mm away from the target. The chamber was evacuated to a base pressure of 1×10^{-6} Torr before heating substrate .

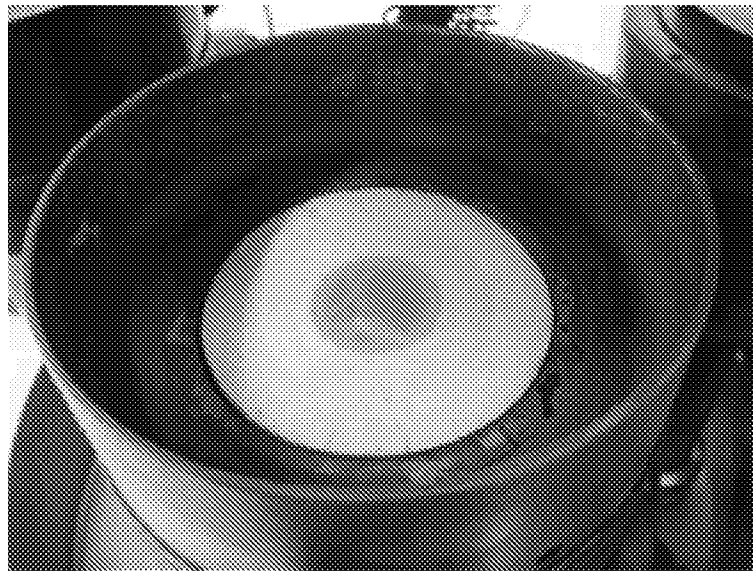


Fig. 1. Photograph of cathode surface of our ZnO:In target (2 wt% In_2O_3).

The ZnO:In films were deposited on Si substrates at different substrate temperatures of 50, 100, 150, 200, 250 and 400°C at a working pressure of 5.8×10^{-3} Torr argon atmosphere. The chosen R.F. power and the deposition period were 150 W and 1 h, respectively. After the ZnO:In film was deposited, for measuring the electrical properties, an In ohmic contact (0.5 mm diameter) was made onto the ZnO:In films being used as a top electrode and an In+Al ohmic contact was made onto the p-Si substrate being used as a bottom electrode, as shown in the inset of Fig. 8. The morphologies and structures of the products were investigated by SEM (JEOL-J8M5410 LV) and an atomic force microscopy (AFM) , X-ray diffractometer (Bruker-AXS D5005). A UV-2450PC UV-vis spectrophotometer was used to record the UV-visible absorption spectra. Electrical properties of the ZnO:In film were investigated using van der Pauw Hall measurements (Lake Shore 7600 series).

3. Results and discussion

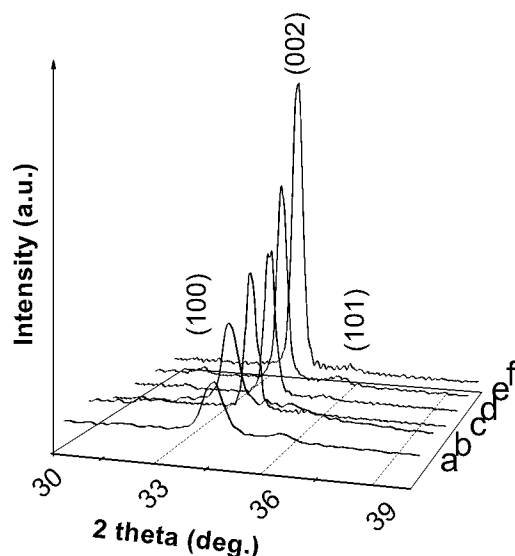


Fig. 2. X-ray diffraction spectra of the ZnO:In films deposited on p-Si at various temperatures. All the samples mainly show (002) diffraction peak, but the FWHM decreases with the deposition temperature (a- 50, b-100, c-150, d-200, e-250, f-300°C).

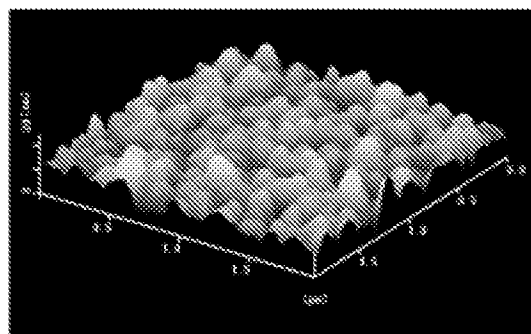


Fig. 3. AFM image of a ZnO:In film deposited on p-Si at a substrate temperature of 150°C.

Fig. 2 shows X-ray diffraction (XRD) spectra obtained from the ZnO:In films deposited in an Ar atmosphere. As the substrate temperature increases, the (002) diffraction peak in the polycrystal ZnO:In becomes sharper. According to the XRD spectra, The Full Width of Half Maximum (FWHM) of the (002) peak decreases with increasing the deposition temperature, that is, the grains of c-axis oriented texture increase in size with the temperature.

A representative AFM image of the high-quality ZnO:In film is shown in Fig. 3. The mean square roughness for $1.5 \times 1.5 \mu\text{m}^2$ of the ZnO:In film is less than 4 nm, suggesting that the surface is flat and smooth. These results indicate that the sputtered ZnO:In thin films are appropriate for fabrication of solar cell.

A typical SEM photograph of a resultant n-ZnO:In film is shown in Fig. 4. The thickness of the film was typically 250 nm. Hall effect measurements show that the ZnO:In films are degenerately n-type semiconductor with resistivity in the range of 5.8×10^{-3} to $4.5 \times 10^{-4} \Omega\text{cm}$, with carrier density more than $3.2 \times 10^{20} \text{cm}^{-3}$ and Hall mobility between 6.02 and $15.13 \text{cm}^2/\text{Vs}$ for the films deposited on Si substrate.

Fig. 5 gives the substrate temperature (T_s) dependence of the resistivity for the films on Si substrates. These films were made at $P_{\text{Ar}} = 5.8 \times 10^{-3}$ Torr, sputtering power $P = 150$ W and the In_2O_3 content 2 wt % in the used target. At a substrate temperature of 150°C the film resistivity was a minimum and the carrier concentration was a maximum. It can be seen that as T_s increases from room temperature to 150°C, carrier concentration increases and the resistivity decreases from 5.8×10^{-3} to

4.5×10^{-4} cm. These variations originate from improved crystallinity, increased substitutional dopants and decreased interstitial dopants as T_s increased in the $T_s \leq 150^\circ\text{C}$ range. A remarkable increase in resistivity was observed from 150°C upwards. This suggests that the doped indium concentration in the film decreases with increasing substrate temperature.

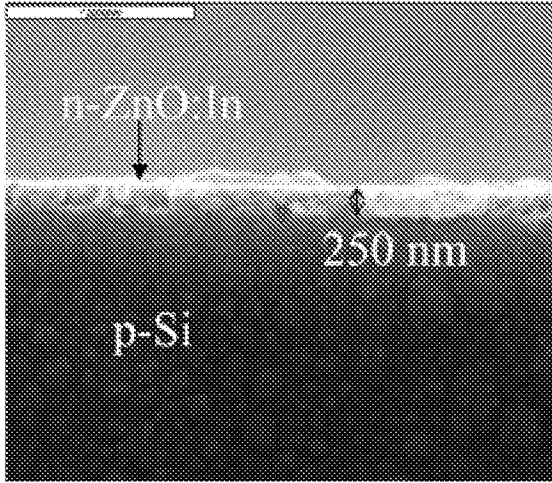


Fig. 4. SEM photograph of a ZnO:In thin film on Si substrate.)

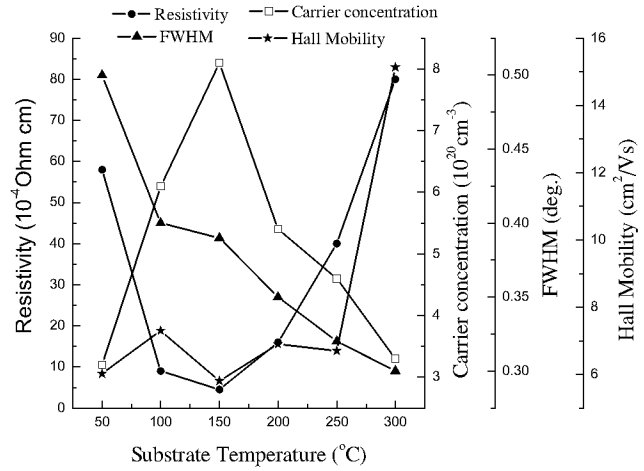


Fig. 5. The resistivity, Hall mobility and carrier concentration as a function of the substrate temperature T_s for the films on Si substrate.

The FWHM of the (002) X-ray diffraction peak as a function of substrate temperature is also indicated in Fig. 5. The FWHM decreased with increasing substrate temperature up to 300°C . The resistivity of the films also depends on the composition of the targets. Fig. 6 gives the film resistivity as a function of In_2O_3 contents in the targets. The films were produced at $P_{\text{Ar}} = 5.8 \times 10^{-3} \text{ Torr}$, $P = 150 \text{ W}$, and T_s equal to room temperature. No much difference is observed for the resistivity of the films when In_2O_3 contents in the targets are 1, 2 and 3 % (the resistivity is as low as $8 \times 10^{-4} \Omega\text{cm}$). But as the In_2O_3 contents increase, an obvious increase is observed for the resistivity. For the In-doped ZnO films, as shallow level n-type dopants, In atoms are incorporated in the samples substitutionally, creating more free electrons and making the samples become more conductive. However, when In contents are more than a limit (here it is 3% wt% for In_2O_3), the excess In atoms as interstitial atoms exist in the films, which, as scattering centers, reduce the mobility of the films and, subsequently, increase the resistivity.

The I-V characteristic between two of indium contacts on the ZnO film is linear as shown in Fig. 7. Ohmic contact of Al with the p-Si substrate can be formed easily because the aluminum is a typical acceptor impurity for Si. The photo I-V characteristics, which were measured under condition of illuminating the heterojunction by the 365 nm (UV) and 580 nm (visible) light, are shown in Fig. 8. It is observed that the heterojunction exhibits a rectifying behavior in the presence of light. From Fig. 8, it is found that under forward bias conditions, no significant change in the current takes place with illumination by either visible or UV light. While the current under reverse bias conditions is affected by both types of illuminations.

The mechanism responsible for this I-V characteristic can be explained on the basis of the n-p junction model [1]. To understand the model, first it is necessary to consider the optical property of the

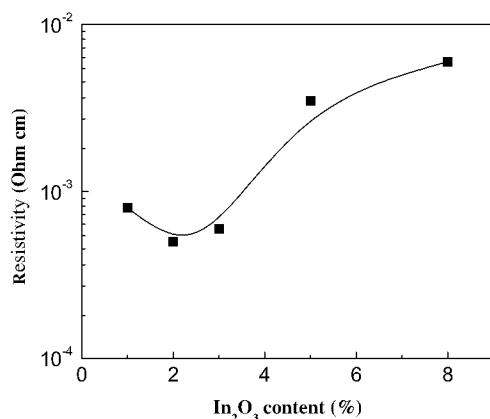


Fig. 6. The variation of resistivity with target In_2O_3 contents for ZnO:In films.

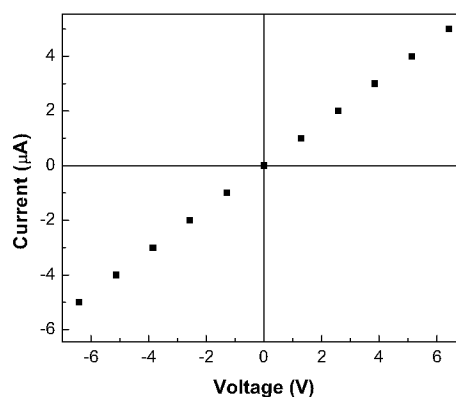


Fig. 7. I-V characteristic between indium contacts on an n-ZnO:In film.

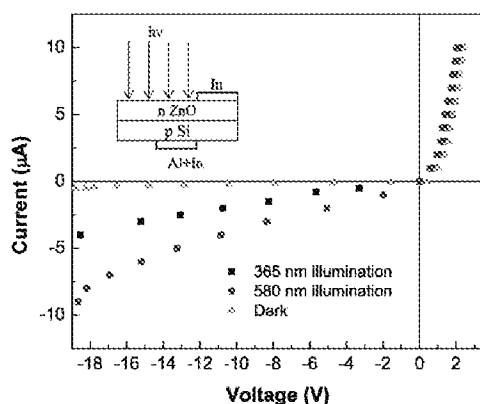


Fig. 8. I-V curves of n-ZnO:In/p-Si structure taken in the air under illumination by 365 nm and 580 nm light and in the dark.

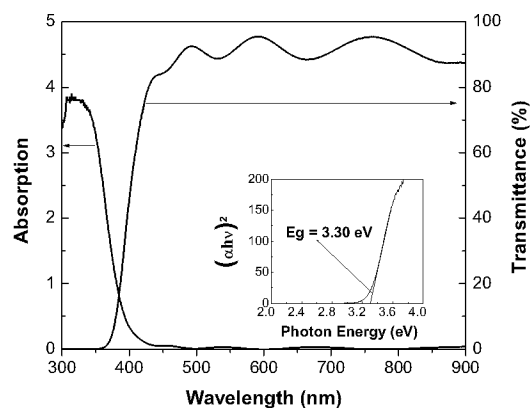


Fig. 9. Transmittance and absorption spectra of n-ZnO:In films on glass substrate.

ZnO:In layer. The band gap of ZnO:In ($E_g = 3.3$ eV) is larger than the energy value of visible photons ($\lambda \geq 400$ nm) and, therefore, it is transparent to the visible light. It is observed from the transmittance spectrum that the present ZnO:In films is highly transparent ($T \geq 90\%$) in the visible region (Fig. 9). Therefore, the visible light passes through the ZnO:In layer and is absorbed primarily in the underlying p-Si layer, generating electron-hole pairs responsible for the observed photocurrent under reverse bias conditions. However, due to a limited penetration depth of the light in the p-Si layer, the photocurrent becomes saturated even though the depletion layer width in p-Si increases.

For measurement of the photoresponse spectra, photocurrent was measured when the n-ZnO:In/p-Si diode was irradiated from the n-ZnO:In side by a light under a fixed bias voltage. Fig. 10 shows such photocurrent spectrum with bias voltage of -1 V. As discussed above, the incident visible light is absorbed primarily in the p-Si layer and the generated electrons and holes are drifted to the ZnO:In (positive) side and the Si (negative) side, respectively, then biased at -1 V. When the n-ZnO:In side was

irradiated by a 365 nm (3.4 eV) UV light, the UV photons are absorbed in the ZnO layer, generating electron-hole pairs responsible for the observed photocurrent.

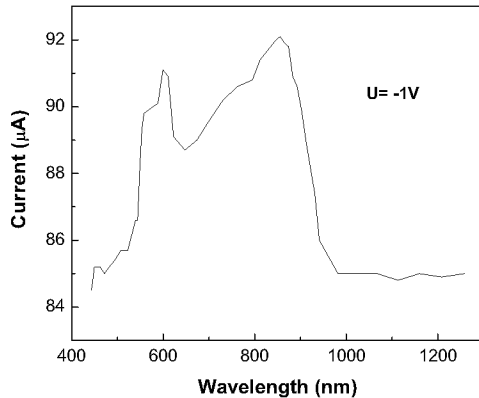


Fig. 10. Photocurrent spectrum of the n-ZnO:In/p-Si heterojunction at bias voltage -1V.

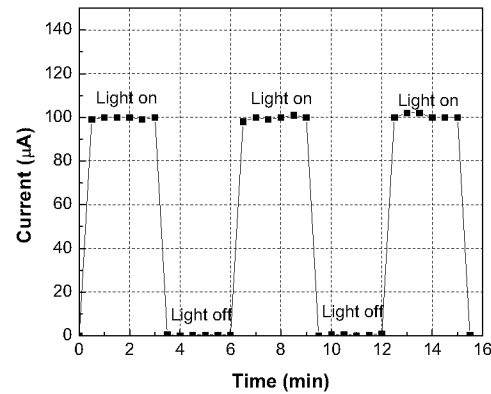


Fig. 11. Effect of irradiation on current generation in the n-ZnO:In/p-Si cell.

The photocurrent response to the irradiation with a xenon short-arc lamp is shown in Fig. 11. The photocurrent builds up to 100 μA upon irradiation by the light, and drops to zero when the light is interrupted. After studying the optical and electrical properties of n-ZnO:In/p-Si heterojunction, we used this heterojunction to make an optoelectronic switch. This device contains three main parts: the detector, the comparator and the executor. The schematic diagram of our device is shown in figure 12.

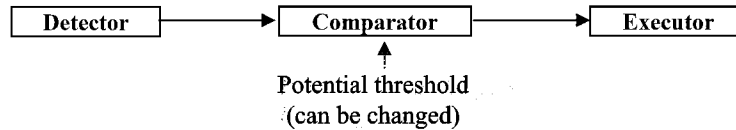


Fig. 12. The schematic diagram of auto-switch device for optoelectronic switch.

The mechanism of the device is based on the properties of the as-prepared heterojunction n-ZnO:In/p-Si: when light intensity is changed, the detector (in our devices, it is the heterojunction of n-ZnO:In/p-Si) will convert an optical signal into an electrical signal.

Operation of the device is follows: When the detector is illuminated, the signal obtained by detector is amplified by the first amplifying stage, then, this signal is compared to potential threshold. The comparator is designed as a trigger Smith, it has two thresholds to avoid jump of output when amplifier output voltage approximates to potential threshold. Assuming light intensity is strong enough, output of the first amplifying stage is at high voltage level, so output of the comparator is at low voltage level ($V_- \geq V_+$), led doesn't light. When light intensity is decreased, the output voltage of the amplifier is decrease. When $V_- \leq V_+$, the output of the comparator is inverted so the led lights (Fig. 13).

This is principle to control the automatic light system. To change lighted level, we change potential threshold by changing valuation of varistor VR_1 . To compare the opposite way, we just invert film poles. In order to reduce the influence of noisy signal of high frequency we used a capacitor C_3 as a filter (Fig. 14).

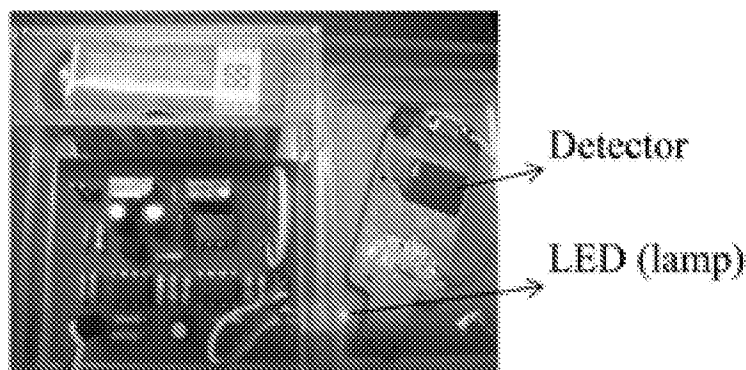


Fig. 13. Image of the devices.

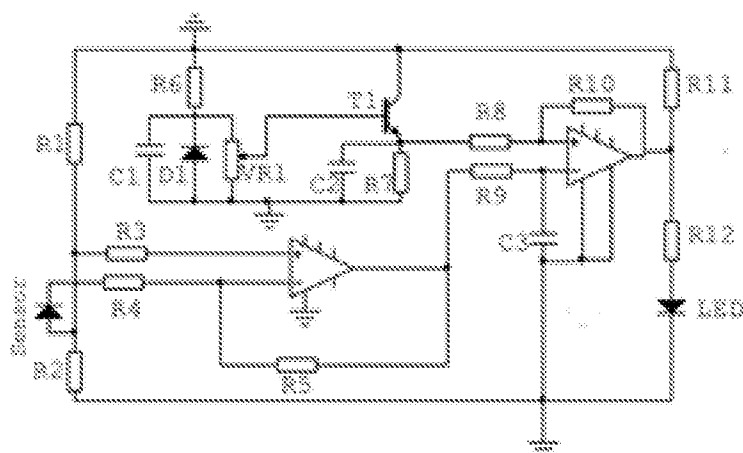


Fig. 14. The circuit diagram of the auto switch device for optoelectronic switch.

3. Conclusion

We have fabricated the n-ZnO:In/p-Si photodiodes using R.F. sputtering deposition at various temperatures. The resistivity of the ZnO films doped with 2 wt% indium was lowest and equal to $4.5 \times 10^{-4} \Omega\text{cm}$. All the diodes show rectifying behaviors both in irradiation by the light and in the dark. This means that the ZnO:In thin films prepared by the sputtering process are semiconductive thin films with a high quality and may be available to use in different photoelectrical devices.

Acknowledgments. This work is completed with financial support by the Vietnam National University, Hanoi (Key Project QG 09 05). Authors of this paper would like to thank the Center for Materials Science (CMS), Faculty of Physics, Hanoi University of Science, VNU for permission to use its equipments.

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