



Effects of the Molar Ratio on the Photo-Generated Charge Activities of ZnO-TiO₂ Composites

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In this study, optical properties of ZnO-TiO₂ nano composite materials grown on Si substrates by Sol-gel method were investigated. The optical properties of thin films obtained with different molar ratio of the two semiconductors were characterized using visible UV spectra. The energy band gap of the photodiodes was calculated as 3.32 eV, 3.19 eV and 3.16 eV for undoped TiO₂, 1:5 ZnO doped TiO₂ and 1:2 ZnO doped TiO₂ composites, respectively. Electrical properties of the ZnO: TiO₂ composites were assessed where capacitance – voltage and Current – voltage measurements were performed. It was determined that the band gap energy of TiO₂ photodiodes decreased and the diodes showed light sensitive properties with the improved ZnO doping.

Keywords: ZnO-TiO₂ composite, molar ratio, electrical properties.

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1. Introduction

Nanoparticles has mesmerizing structure, which was allocated with outstanding optical, electrical, optoelectronic, magnetic properties [1]. Therefore, nanostructures were deeply researched by researchers from different fields. It was previously reported that intrinsic properties of the nanoparticles can be altered depending on their size. Moreover, producing nanostructures in different chemical compositions and structures often alters their characteristics. For example, core shell structures were generally produced for multipurpose applications. Iron oxide based core gives magnetic characteristics to the nanoparticles. Besides, organic shells were often used to reduce cytotoxicity and increase cellular intake. Similarly, producing nanocomposites and Nano alloys can also be used to produce nanostructures with multiple purpose properties. For example, certain metallic nanocomposites addressed as multi modal and multi-purpose Nano drugs [2]. Producing alloys or composites with iron oxide based materials gives nanostructures a magnetic characteristic.

Transition metals have good electron affinity with outstanding electrical properties. Due to their phenomenal characteristics, transition metal oxides such as AgO, CuO, ZnO, and TiO₂ are vastly used in electric, catalytic, optoelectronic applications [3]. Among those materials, ZnO and TiO₂ nanostructures has an important role in optoelectronic applications ZnO and TiO₂ based materials were commonly researched and successful results were implied in photovoltaics and photodetector applications [4].

ZnO and TiO₂ has good electrical properties with tolerable reflectance and promising absorbance properties. Therefore, ZnO and TiO₂ were found to be two of the most promising photovoltaic device materials [5].

In our previous study, we investigated the photosensitivity and photo responsivity properties of our nanocomposite thin films. It was illustrated that our nanocomposite thin films were responsive to light where illumination intensity related photocurrent was observed. In this work electrical and electronical property of the ZnO: TiO₂ nanocomposite thin films were assessed.

2. Materials And Methods

The sol-gel nanoparticle production protocols were used in the production of ZnO doped TiO₂ photodetectors. 0.5M Titanium (IV) isopropoxide (Ti [OCH(CH₃)₂]₄) were dissolved in 10ml 2-methoxyethanol a beaker; and 0.5M zinc acetate dihydrate ((CH₃CO₂)₂Zn) were dissolved in 10ml 2-methoxyethanol in another beakers. Each beaker was stirred using a magnetic stirrer for 10 mins. 0.5ml ZnO solution was added 2.5ml TiO₂ and 1ml ZnO solution was added to 2ml TiO₂ solution where ZnO doped TiO₂ solution in 1:5 molar rates ZnO doped TiO₂ solutions in 1:2 molar rates were obtained. Si wafer then sonicated in ethanol for 5 mins and sonicated in deionized water. Lastly, HF: H₂O (1:10ml) were prepared and sonicated for 5 mins and washed using pure water. Samples were then dried using N₂ gas. 2 cm x 2 cm wafers were cut; 6 layers of film were then spin coated on substrates. Spin coating was applied at 3000 rpm for 30 secs for each layer. Each layer was dried on a hot plate for 2 mins the temperature of which is 100 °C. 6 layers of coating applied. At 420 °C, film coated substrates were annealed for 1h. When the coating procedure was finished, Al contact was applied using thermal evaporator. The coating was applied at 2 - 4 Å/s evaporation rate. Total 100 nm contact were coated that photodetectors in Al/p-Si/ZnO: TiO₂/Al photodetectors were formed. Result products were then annealed at 570 °C for 5 mins under N₂ gas.

3. Results and Discussion

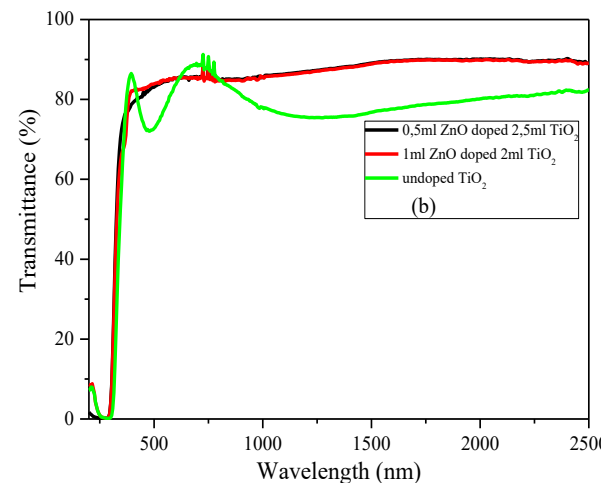
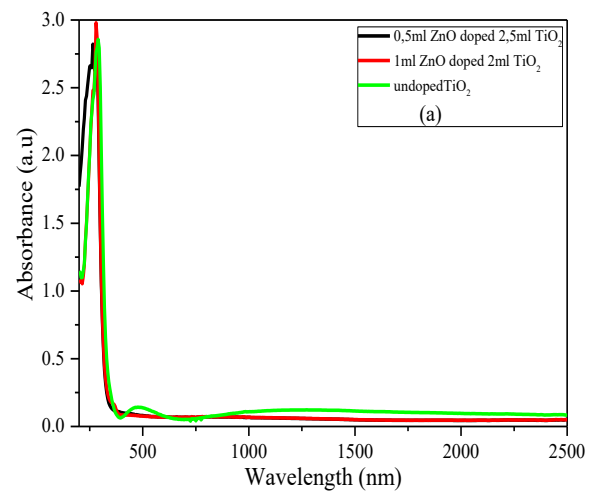
3.1 Optic Properties

Optic properties of the photodetectors illustrated in Figure 1 where Abs - wavelength (a), reflectance - wavelength (b), transmittance - wavelength (c) and Abs - hv (d) characteristics were presented. It was seen in Figure 1a and Figure 1b that TiO₂ and ZnO doped TiO₂ films show low absorbance and reflectance in visible range which illustrates that photodetectors can be used in solar applications. In Figure 1c, it was seen that and the transmittance values of the TiO₂ and ZnO doped TiO₂ films were high which is between 72% and 88%. Such a case also supports the case that thin films can be used in photodetector and solar detector applications. Using absorbance data, Eg (energy band gap) of the thin films were determined. Following formula was used in the calculations

$$\alpha h\nu = A(h\nu - E_g)^n \quad (1)$$

where $\alpha = F(R)/d$, A is a constant, d is the thickness of thin films, Eg is band gap energy, n is a constant which determines the optic transfer. Two different kinds of transfer may be observed: direct transfers (i) indirect transfers (ii). Indirect transfers were determined as $n=1/2, 3/2, 5/2\dots$ while direct transfers were determined as $n=1, 2, 3\dots$ [6-8]

$(\alpha h\nu)^2 - h\nu$ characteristics were illustrated in Figure 1d where Eg for undoped TiO₂, 1:5 ZnO doped TiO₂ and 1:2 ZnO doped TiO₂ were calculated as 3.32eV, 3.19 eV and 3.16 eV, respectively. It was illustrated that increased ZnO dopant rate decreases the bandgap energy.



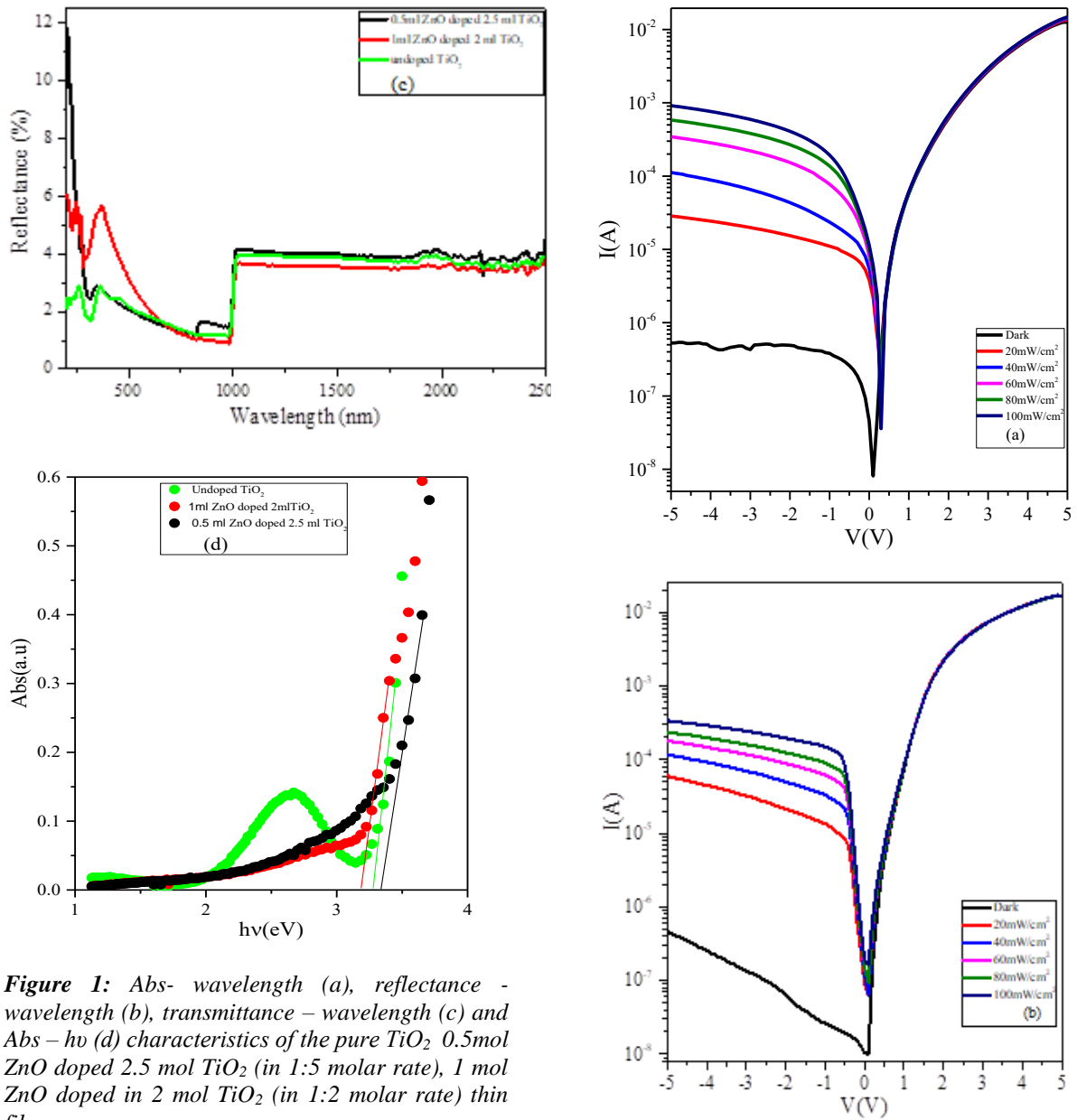


Figure 1: Abs- wavelength (a), reflectance - wavelength (b), transmittance – wavelength (c) and Abs – $h\nu$ (d) characteristics of the pure TiO_2 , 0.5mol ZnO doped 2.5 mol TiO_2 (in 1:5 molar rate), 1 mol ZnO doped in 2 mol TiO_2 (in 1:2 molar rate) thin films.

3.2 Photoresponsive Properties

I - V characteristics of the pure TiO_2 , 0.5 mol ZnO doped 2.5 TiO_2 (1:5 molar rate) and 1 mol ZnO doped 2 mol TiO_2 (1:2 molar rate) photodiodes were assessed between -5V and 5V. I – V characteristics were presented in Figure 2. The increased photocurrent was seen for increased illumination intensity. Increased photocurrents confirm that photodiodes exhibit photoresponsive and photovoltaic characteristics.

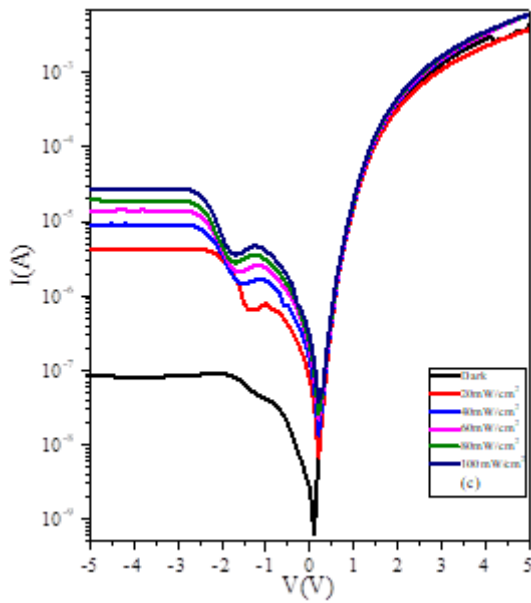


Figure 2: *I - V* characteristics of the pure TiO_2 (a), 0.5 mol ZnO doped 2.5 TiO_2 (1:5 molar rate) (b) and 1 mol ZnO doped 2 mol TiO_2 (1:2 molar rate) (c).

Capacitance – Voltage ($C - V$) characteristics of the pure TiO_2 and ZnO doped TiO_2 photodiodes were investigated in Figure 3. $C - V$ behaviours of the nanocomposite thin films were assessed between -5 V and 5 V in varying frequencies between 10 kHz and 1 MHz were used in the assessments. A prominent peak was seen in each graph. The tip of the peak was measured around -2 V, -1 V and 0.8 V for pure TiO_2 photodiodes, 1:5 and 1:2 ZnO doped TiO_2 photodiodes, respectively. The position of the peaks shifts towards positive region with increased ZnO dopant rate. The peaks illustrate the frequency dependence of the diodes where augmented capacitance was observed in low AC signal frequencies.

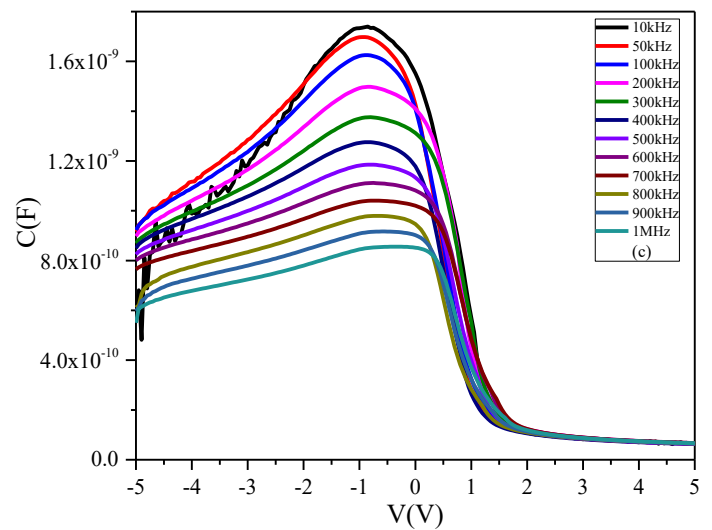
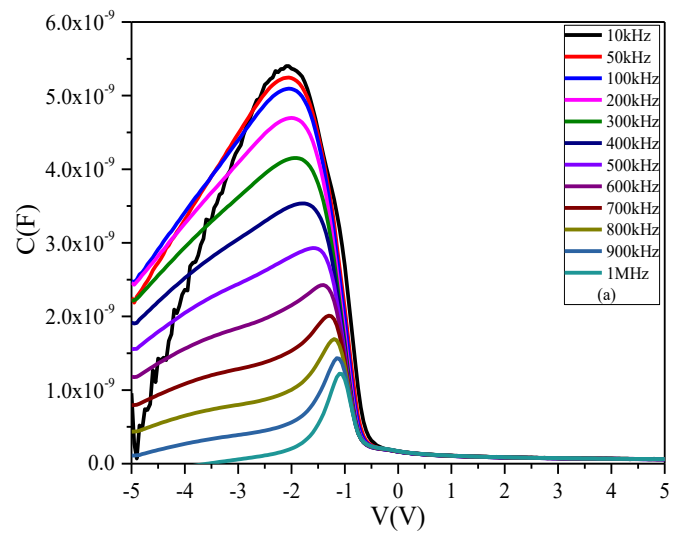
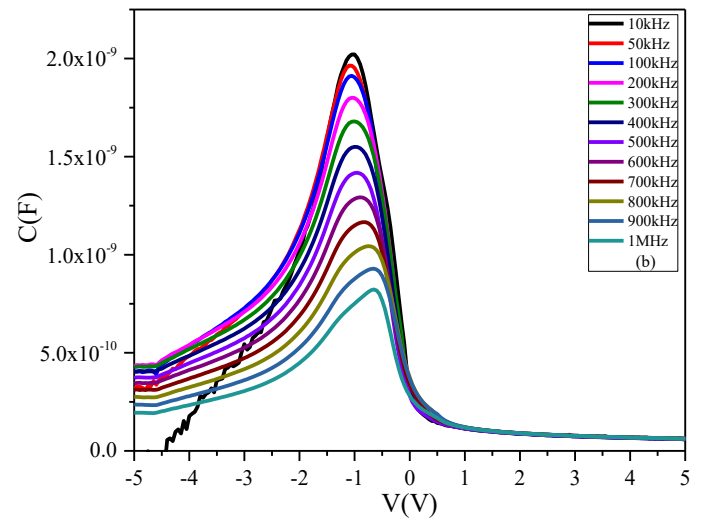


Figure 3: *C–V characteristics of pure TiO₂ (a), 0.5 mol ZnO doped 2.5 TiO₂ (1:5 molar rate) (b), and 1 mol ZnO doped 2 mol TiO₂ (1:2 molar rate) (c) photodiodes.*

4. Conclusion

In the study, TiO₂ and ZnO doped TiO₂ photodiodes were produced using sol gel method. Optic properties were checked, it was seen that photodiodes show good high transmittance with low reflectance. Using UV-vis data bandgap energies of the photodiodes were calculated. ZnO doping decreases the bandgap energies of the photodiodes. Photovoltaic properties of the photodiodes confirmed that photodiodes are responsive to the light where increased photocurrent and photocapacitance were observed for increased illumination intensity. Such a case was confirmed that photodiodes have the potential to be used in solar tracking applications.

Acknowledgements

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