Structural, Electrical and Optical Studies of ZnO/TiO_2Thin Films Fabricated by RF Sputtering Process for UV application

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***Abstract*: ZnO based nanostructure composites are eye-catching for high-tech applications of energy conversion due to wide range in operating potential window. ZnO are regarded as one of the most capable candidates for UV photodetectors due to its wide band gap, strong radiation and high chemical stability. This study presents about fabrication of p-ZnO/n-TiO_2 thin layer via radio frequency (RF) sputtering. This article reports fabrication, structural, optical, electrical and microstructural characterization of nanostructured p-ZnO/n-TiO_2 thin films. Nanostructured Zinc Oxide (ZnO) thin film was deposited on Aluminum coated glass substrates using radio frequency (RF) sputtering process for fabricating p-ZnO/n-TiO_2thin films. After deposition, these films are annealed at 523 K. Structural properties, surface morphology and quality of thin film have been studied using XRD, AFM, FE-SEM and Energy Dispersive X-ray Spectroscope (EDX) measurements.The optical property of the deposited nanostructured p-ZnO and n-TiO2 thin films on the glass substrate were characterised on the ultraviolet spectroscopy (UV-Vis spectroscopy).XRD measurements revealed the formation of ZnO and TiO_2.XRD analysis confirms the formation of pure crystalline form. The average crystallite size of as deposited nanostructured ZnO and TiO2 thin film was found to be 29 nm and 20.7nm respectively.The junction properties of p-ZnO/n-TiO_2were investigated using current–voltage measurements.The current was analyzed by sweeping the voltage from -5V to +5V and the knee voltage was found to be around 1.58V.The abrupt absorption on ~328nm wavelength was seen for both of the deposited films**

Keyword: Thin films, Microstructural, RF Sputtering, ZnO/ TiO2, Photodetectors

1. INTRODUCTION

Wide band gap semiconductors are extensively used in ultraviolet (UV) detectors, particularly oxide semiconductors such as ZnO and TiO_2 which are environmentally friendly as well as chemically and thermally stable in harsh environment. UV photodetectors have been extensively used in a variety of commercial and military applications, such as flame sensing, secure space-to-space communications, pollution monitoring and early missile plume detection, *etc.* [1-3]. These applications require extremely sensitive devices with high response speed and high signal-to-noise ratio. Nowadays, a range of UV detectors are available, mainly Si-based photodetectors. However, Si-based photodetectors have considerable limitations, such as the need of filters to stop low energy photons (visible and IR light) and lower efficiency, to stay away from these disadvantages, UV detectors based on large bandgap semiconductors have received more and more concentration due to their intrinsic visible-blindness. Moreover, materials with large-band gap are chemically and thermally more stable compare with the material with narrow band gap, which make it capable for operating in harsh environments. A striking approach to improve efficiency and diminish costs of modern hybrid photovoltaic's is the application of nanostructured metal-oxides thin film such as TiO2 [4]. Crystalline structure of TiO2exists mainly in three forms such as anatase, rutile and brookite. Anatase form offers much advanced photoactivity than that of rutile. Amongst the different materials studied thus far, Titanium dioxide (TiO2), an n-type semiconductor (anatase 3.2 eV and rutile 3.0 eV) has an extremely wide range of application field due to the ease it can be used to fabricate various one-dimensional nanostructures. ZnO as well as their nanocomposite forms [5-7]. The n-type character in these semiconductors originates from the large density of oxygen vacancies generally detected on the surface of these nanostructured materials. In turn, these vacancies change the material's chemical reactivity and stability by providing electron trap-sites, causing electron–hole recombination during operation of the device. To overcome this limitation, nitrogen doping has been the preferred method, with various approaches employed, such as chemical doping during synthesis. It is well known that the donor like defect such as oxygen vacancy and Zn interstitial are easily formed in the ZnO, which leads to natural n-type doping. From an electronic point of analysis, TiO_2 and ZnO are the best semiconductor candidates. Indeed, the valence band and the conduction band of ZnO are constituted of *d* orbitals and *sp* hybrid orbitals respectively. TiO_2 is constituted of *p* orbitals hybridized with *d* orbitals in the valence band and of *d* orbitals only in the conduction band. These two configurations are in support of an efficient electron-hole pair promotion [8]. In some studies, ZnO has a lower rate of recombination compared to TiO_2 [9,10] Among many metal oxide semiconductors, the beneficial properties of zinc oxide

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(ZnO), such as high carrier charge mobility, and environmental robustness, have attracted significant interest for application in semiconductor devices [11].The broad band gap (3.37eV), better transparency, high charge mobility, high thermal stability and low synthesis cost are some of the key factors which make it suitable for fabrication of various optoelectronic devices and applications. In order to increase the efficiency of the sensor, different methods such as surface treatment and covering by other materials have been used by several groups [8-20].ZnO based nanostructures have a wide range of high-tech application e.g. photo detectors [12], light emitting diode [13], photo diodes [14], gas sensors [15] optical modulators wave guide [16], solar cells [17,18] and batteries [19].Such applications of nanomaterial's have been found to depend strongly on the crystalline structure, morphology, and grain size[20-25].Although TiO_2 and ZnO possess roughly similar value of energy band gap, the two semiconductors found their own application due to differences in their physical and chemical properties. The TiO_2 is better known for its chemical stability, high quantum yield and non-toxicity where as ZnO is better preferred in optoelectronic devices as light emitter/detector owing to semiconductor large exciton binding energy, high transparency in the visible range and low electrical resistivity. Researchers have paid more attention to the coupling of semiconductors, especially a heterojunction based on two kinds of semiconductors with different energy band structures to improve the sensitivity of photodetectors. ZnO and $TiO_2$are superior candidates to form a heterostructure junction with better properties than individual ones resulting from the coupling of different energy level structures. Therefore, in this study we have synthesized the nanostructured p-ZnO/n-TiO_2thin films using RF sputtering process for UV application. Various properties of thin films were analyzed by using X-ray diffraction (XRD) to obtain their structure and crystal phase, was obtained with the help of EDX. Electrical I-V measurements were carried out on SDA B1500A (Semiconductor Device Analyzer) from Agilent with probe station SPS2200 Microxact USA at room temperature. The atomic force microscopy (AFM) for thin film surface roughness, Field emission scanning electron microscopy (FESEM) for surface morphology,Semiconductor Device Analyzer (SDA B1500A) for current-voltage (I-V) characteristics and ultraviolet spectroscopy (UV-Vis) for optical characterization.

2. MATERIALS AND METHODS

By using RF sputtering process, nanostructured p-ZnO/n-TiO_2thin films have been deposited on glass substrates and on the p-type Si wafer**.** ZnO (A circular 2-inch diameter target) and TiO_2(A circular 2-inch diameter target) has been used as sputter targets for the development of ZnO and TiO2 thin films respectively.

Substrate has been cleaned properly prior to deposition of coating. Before deposition of p-ZnO thin film, we make aluminium metal contact on glass substrate using physical vapour deposition for making ohmic contact.

After making ohmic contact, development of nanostructured ZnO thin films has been carried out using RF/DC sputtering system from Advance Process Technologies, India. Coated specimens were annealed for 60 minutes at 523 K to improve the crystallinity of as deposited p-ZnO thin film. After proper annealing of ZnO thin films, nanostructured TiO_2 thin films has been deposited using RF/DC sputtering system. Technical details of thin film deposition for ZnO and TiO_2 have been shown in table1 and table2 respectively. The structural characterization of nanostructuredZnO and TiO2 thin film was carried out on PANalytical Powder-Xpert pro X-ray Diffractometer. Microstructural characterization with EDX (Energy Dispersive X-ray Spectroscope) was carried out on Nova Nano SEM 450 FESEM form FEI Netherland, AFM (Atomic Force Microscopy) for topographical study were carried out on Bruker Multimode 8in Scan Asyst mode. The compositional analysis of as deposited nanostructured thin films before and after annealing

optical property of the deposited nanostructured p-ZnO and n-TiO2 thin films on the glass substrate were characterised on the ultraviolet-visible spectroscopy (UV-Vis spectroscopy).

Table 1: Technical details of thin film deposition (*p*-ZnO)

Substrate	***p*-Si <100>**	**Glass**
Film thickness	100nm	100nm
Ar flow rate	15 sccm	15 sccm
Nitrogen flow rate	15 sccm	15 sccm
RF power	75 watts	75 watts
Base pressure	$7x10^{-6}$ mbar	$7x10^{-6}$ mbar
Deposition pressure	$1\text{-}3x10^{-3}$ mbar	$1\text{-}3x10^{-3}$ mbar
Deposition rate	2 nm/ min	2 nm/min
Annealing temperature	523 K	523 K

Table 2: Technical details of thin film deposition (*n*- TiO_2)

Substrate	***p*-Si <100>**	**Glass**
Film thickness	100nm	100nm
Ar flow rate	15 sccm	15 sccm
RF power	75 watts	75 watts
Base pressure	$7x10^{-6}$ mbar	$7x10^{-6}$ mbar
Deposition pressure	$1\text{-}3x10^{-3}$ mbar	$1\text{-}3x10^{-3}$ mbar
Deposition rate	2 nm/ min	2 nm/min
Annealing temperature	523 K	523 K

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3. RESULTS AND DISCUSSION

3.1 XRD Analysis

The RF sputtered polycrystalline thin films were subjected to the XRD analyse is shown in Figure 1 which indicates the formation of TiO2 anatase phase. The intensity of thin films shows TiO2 major peaks around 2θ = 25.3, 48.1 and 53.9. XRD analysis also confirms the formation of ZnO with major peaks at 2θ = 31.581º, 34.207º, 35.9º and 56.202º asshown in the figure 1. The XRD spectrums show that the nanostructured ZnO thin films have polycrystalline hexagonal wurtzite structure with highly (002) preferred orientation. The XRD diffraction spectrum shows polycrystalline structure of ZnO and TiO2. The XRD pattern was taken in the presence of thin film geometry in powder XRD setup where the beta nickel filter was used to remove the Kα2 emission peak of the X-Ray generator. The crystallite size and the FWHM of the observed peak were analyzed by the deby-Scherrer formulae. The average grain size of as deposited nanostructured ZnO thin film was found to be 29 nm whereas 20.7 nm for nanostructured TiO_2 thin film

3.2 FESEM Analysis

The surface morphology of as deposited nanostructured Zinc Oxide thin film (figure 2), annealed nanostructured Zinc Oxide thin film (figure 3) and nanostructured TiO_2 thin film (figure 4) were analyzed using Field Emission Scanning Electron Microscope (FESEM). The deposited films were almost uniform, homogenous, intact and crack free as depicted in the figure 2 and figure 4. Surface morphology indicates slightly grain size increment in case of annealed ZnO thin films (Figure 3). Energy dispersive X-Ray spectroscopy confirms the presence of required elements in all cases with no impurities. It is clear from the FESEM images that the grains are unvaryingly distributed over the substrate with good adhesion.

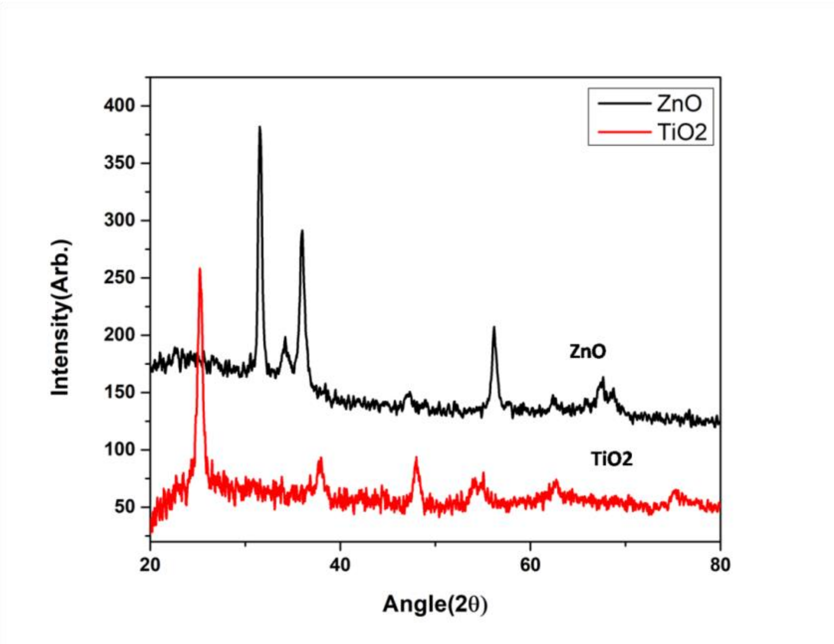

Figure 1. XRD pattern of nanostructured ZnO and TiO_2 thin films

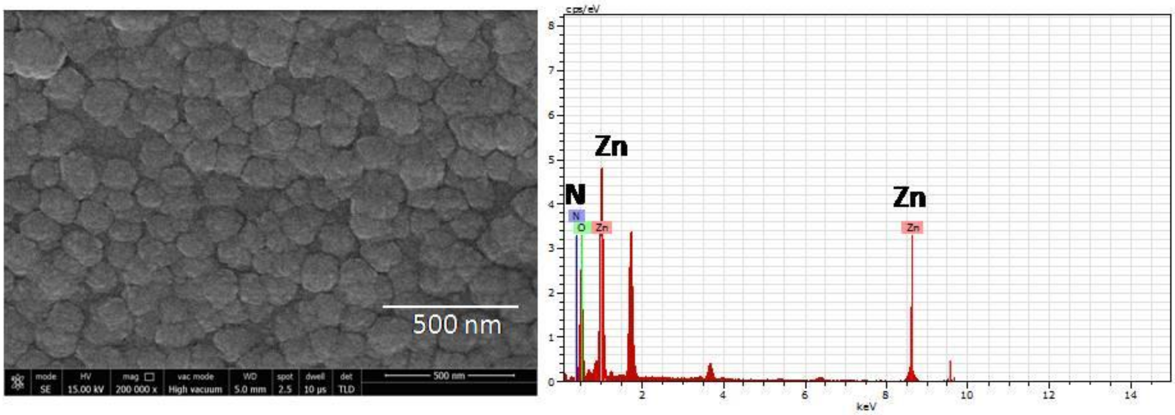

Figure2. Surface morphology of nanostructured Zinc Oxide thin film

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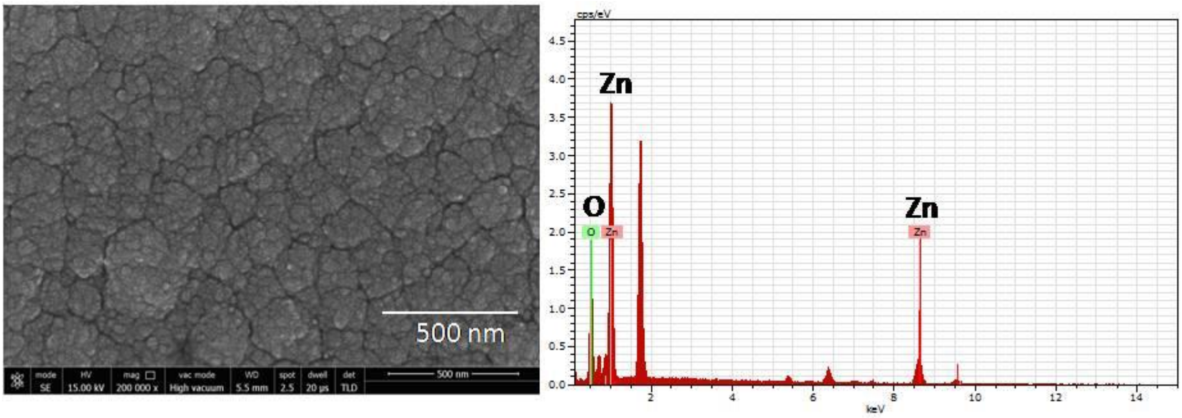

Figure 3. Surface morphology of nanostructured Zinc Oxide thin film annealed at 523K

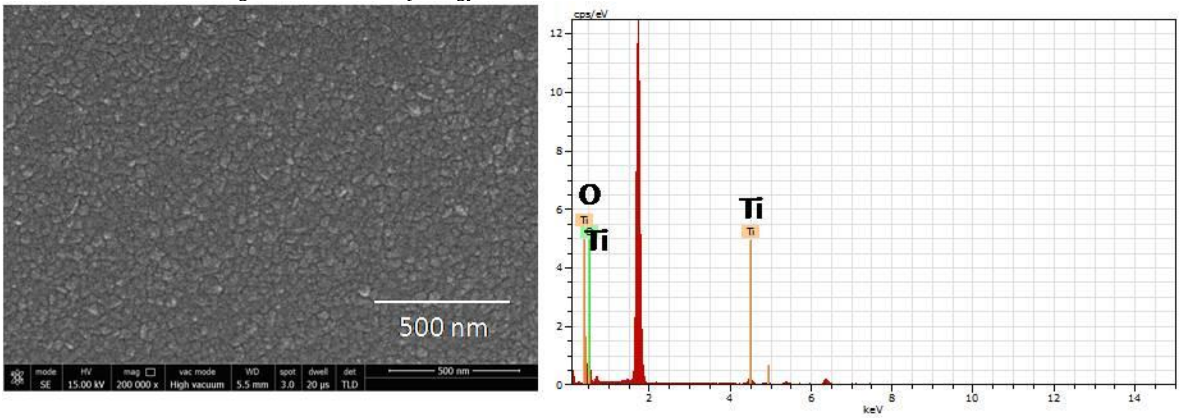

Figure 4. Surface morphology of nanostructured TiO_2 thin film

3.3 AFM Analysis

The AFM analysis were carried out for both RF sputtered nanostructured ZnO (figure 5) and TiO_2 (figure 6) thin film under the scan assist mode in the multi-mode AFM where nano meter scale tip of SiC was introduce to scan the sample in the window of 5 micron. Surface roughness, as a component of the surface texture, gives an indication about the quality of the surface. Results indicate that the root mean square roughness value is low for TiO2 thin films due. The root means square roughness for ZnO and TiO_2 thin films were found to be 12.2 nm and 2.46nm respectively. The results were made in the nano scope software and 2d and 3d image has been shown in figure 5 and figure 6for better perception of morphological study. It is evident from the images that the surface of the deposited film is approximately smooth, homogeneous and uniform.

3.4 UV-Vis characteristics

The ZnO and TiO2 were characterized on the UV-Vis spectroscopy for the study optical properties of the deposited nanostructured thin films on the glass substrate. The abrupt absorption on ~328nm wavelength was seen for both of the deposited films (figure 7). Although, showing the full transparency for throughout visible range in the given spectrum which infers that these films are good prospects for the UV sensing device application.

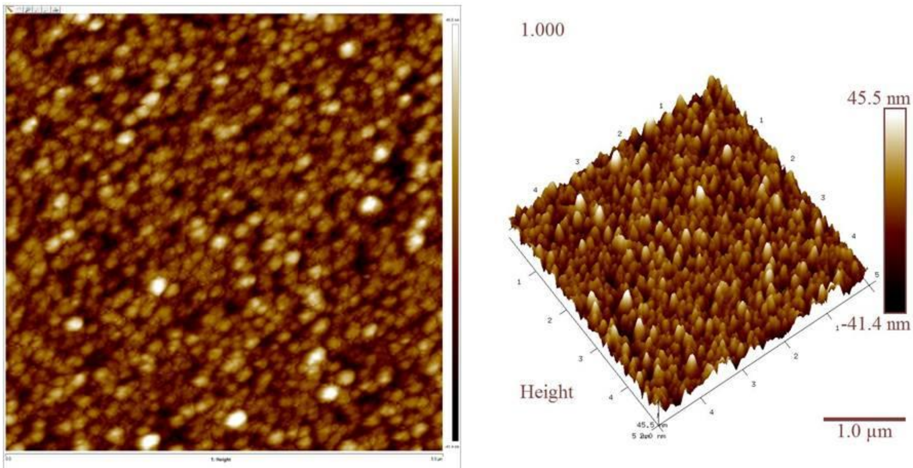

Figure 5. 2-D and 3-DAFM image of nanostructured ZnO thin film

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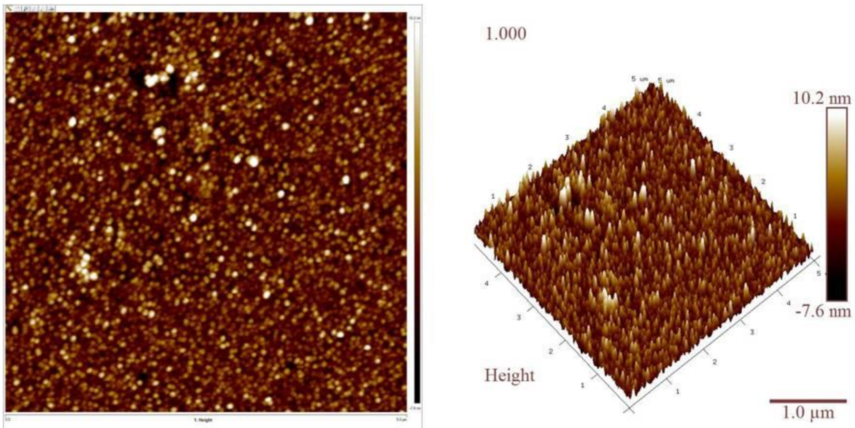

Figure 6. 2-D and 3-D AFM image of nanostructured TiO_2 thin film

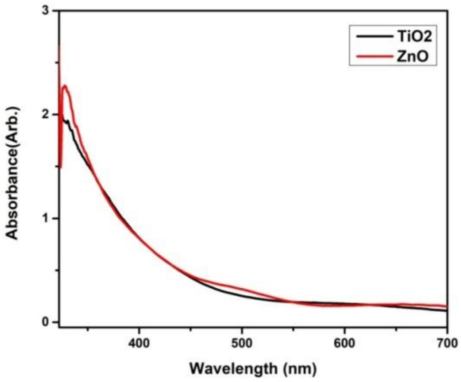

Figure 7. UV–visible absorption spectra of p-ZnO and n- TiO_2thin film

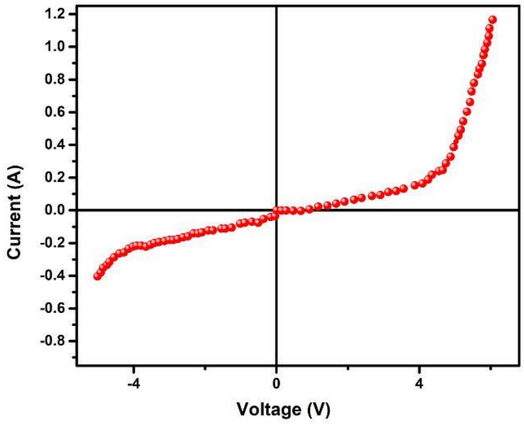

Figure 8. I-V characteristics of p-ZnO/n- TiO_2 thin film

3.5 Electrical Characterization

The electrical characterization plays a very important role for the hetrojunction diode. In this study the current Vs voltage characteristics were analyzed to see the behavior of p-ZnO/n- TiO_2thin films analyzed by the semiconductor device analyzer by two probe measurement. The ohmic contacts were confirmed by *I*–*V* measurements. The *I*–*V* plot of a fabricated p-ZnO/n- TiO_2thin films in forward and reverse bias conditions is shown in Fig. 8. The current was analyzed by sweeping the voltage from -5V to +5Vand and the knee voltage was found to be around 1.58V which also compliance with the wide band gap semiconductor material as ZnO based diode. The current transport mechanism of fabricated structure could be defined with the help of various regions as cutoff, linear and exponential. The different region can be explained in the curve such as the current is almost negligible till the ~1.58V around that would be defined as the cut off region. Further, a slight increment (almost linear) in the current can be seen up to the ~4V afterwards the current increases exponentially. On further increasing the voltage leads to the exponential growth in the current probably due to the charge carrier injection on the higher potential.

4. CONCLUSION

In summary, nanostructured p-ZnO/n- TiO_2 thin films have been deposited on glass substrate by RF sputtering process. XRD pattern confirmed the formation of ZnO and TiO_2.Crystallite size was in the nm range which is same as observed from the FESEM micrograph. AFM result is also in compliance with the FESEM result in order to study its root mean square roughness. All the structural studies have found a good prospect to use the nanostructured thin film for UV application. It can be concluded that the nanostructured p-ZnO/n- TiO_2 thin film showing a quite interesting results which insight a very prominent application in the field of UV photodetectorsand other opto-device application as well.AFM, FESEM and EDX results confirm that the deposited films were almost uniform, homogenous and crack free.

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REFERENCE

[1] Monroy, E.; Calle, F.; Pau, J.L.; Munoz, E.; Omnes, F.; Beaumont, B.; Gibart, P. AlGaN-Based UV Photodetectors. *J. Cryst. Growth* **2001**, *230*, 537-543.

[2] Sabpreet bhatti, Sujas Bhardwaj, Sachin Surve andV. N. Shukla, Optical properties of chromium & cobalt doped zinc oxide powder prepared by sol - gel combustion method with assistance of microwave radiations, International Journal of advanced technology in engineering and science, 3 (8) (2016) 123-128.

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ISSN: 2278-0181
Vol. 9 Issue 04, April-2020

[3] Sabpreet bhatti, Sachin Surve andV. N. Shukla, Structure and Magnetic characterization of Co & Cr doped nanoparticles synthesized by using Microwave method, Procedia Engineering, Materials Today: Proceedings 4 (2017) 3825–3831.

[4] G.K. Mor, S. Kim, M. Paulose, O.K. Varghese, K. Shankar, J. Basham, C.A. Grimes, Visible to near-infrared light harvesting in TiO2 nanotube array-P3HT based heterojunction solar cells, Nano Lett. 9 (2009) 4250–4257

[5] Sunandan Baruah, Chanchana Thanachayanont, Joydeep Dutta, Growth of ZnO nanowires on nonwoven polyethylene fibers, Sci. Technol. Adv. Mater. 9 (2008) 1-8.

[6] J.B. Varley, A. Janotti, C.G. Van de Walle, Mechanism of visible-light photocatalysis in nitrogen-doped TiO2, Adv. Mater. 23 (2011) 2343–2347.

[7] X. Yang, A. Wolcott, G. Wang, A. Sobo, R.C. Fitzmorris, F. Qian, J.Z. Zhang, Y. Li, Nitrogen-doped ZnO nanowire arrays for photoelectrochemical water splitting, Nano Lett. 6 (2009) 2331–2336.

[8] Geraldine L.-M. L´eonard, Carlos A. Paez, Alfonso E. Ramırez, Julien G. Mahy, Benoıt Heinrichs, Interactions between Zn2+ or ZnO with TiO2 to produce an efficient photocatalytic, superhydrophilic and aesthetic glass, Journal of Photochemistry and Photobiology A Chemistry,350, (2018) 32-43.

[9] R. Jose, V. Thavasi, S. Ramakrishna, Metal Oxides for Dye-Sensitized Solar Cells, Journal of the American Ceramic Society 92 (2009) 289-301.

[10] A. Solbrand, K. Keis, S. Södergren, H. Lindström, S.-E. Lindquist, A. Hagfeldt, Charge transport properties in the nanostructured ZnO thin film electrode – electrolyte system studied with time resolved photocurrents, Solar Energy Materials and Solar Cells 60 (2000) 181-193.

[11] Umesh Soni, Amit Pandey, V. N. Shukla, Influence of pH on ZnO and TiO2 Nanomaterials Synthesized by Sol Gel Method, International Journal for Research in Applied Science & Engineering Technology, 8 (3) 2020, 1227-1231, ISSN: 2321-9653.

[12] S. Liang, H. Sheng, Y. Liu, Z. Hio, Y. Lu, H. Chen, ZnO Schottky ultraviolet photodetectors, J. Cryst. Growth 225 (2001) 110-113.

[13] Noriko Saito, Hajime Haneda, Takashi Sekiguchi, Naoki Ohashi, Isao Sakaguchi, Kunihito Koumoto, Low temperature fabrication of light-emitting zinc oxide micropatterns using self-assembled monolayers, Adv. Mater. 14 (2002) 418-421.

[14] J.Y. Lee, Y.S. Choi, J.H. Kim, M.O. Park, S. Im, Optimizing n-ZnO@p-Si heterojunctions for photodiode applications, Thin Solid Films 403 (2002) 553-557.

[15] P. Mitra, A.P. Chatterjee, H.S. Maiti, ZnO thin film sensor, Mater. Lett. 35 (1998) 33-38.

[16] M.H. Koch, P.Y. Timbrell, R.N. Lamb, The influence of film crystallinity on the coupling efficiency of ZnO optical modulator waveguides, Semicond. Sci. Technol. 10 (1995) 1523-1527.

[17] M. Gratzel, Dye-Sensitized solid-state heterojunction solar cells, MRS Bull. 30(2005) 23-27.

[18] J.B. Baxter, A.M. Walker, K. van Ommering, E.S. Aydil, Synthesis and characterization of ZnO nanowires and their integration into dye-sensitized solar cells, Nanotechnology 17 (2006) 304-312.

[19] Prabal Sapkota, Honggon Kim, Zinceair fuel cell, a potential candidate for alternative energy, J. Ind. Eng. Chem. 15 (2009) 445-450.

[20] Ramesh Chandra Prajapati, Shubham Gautam, Sachin Surve and V N Shukla, "Structural, magnetic, electrical and optical studies of Cr doped nanostructured ZnO thin films for spintronics application" Mater. Res. Express, 6, (2019) 106412.

[21] P. Sharma, K. Sreenivas and K. V. Rao, Analysis of ultraviolet photoconductivity in ZnO films prepared by unbalanced magnetron sputtering, Journal of Applied Physics, Vol. 93, No. 7, 2003. pp. 3963-3970

[22] C. X. Shan, et al, Ultraviolet photodetector fabricated from atomic-layer-deposited ZnO films, J. Vaccum Science Technology B, Vol. 27, No. 3, 2009, pp. 1765-1768

[23] A. Goktas, High-quality solution-based Co and Cu co-doped ZnO nanocrystalline thin films: comparison of the effects of air and argon annealing environments, J. Alloys Compd. 735 (2018) 2038–2045.

[24] A. Agrawal, T.A. Dar, P. Sen, Structural and optical studies of magnesium doped zinc oxide thin films, J. Nano Electron. Phys. 5 (2013) 02025–02027.

[25] F. Yakuphanoglu, Y. Caglar, M. Caglar, S. Ilican, ZnO/p-Si heterojunction photodiode by sol–gel deposition of nanostructure n-ZnO film on p-Si substrate, Mater.Sci. Semicond. Process. 13 (2010) 137–140.