Available online at www.sciencedirect.com

ScienceDirect

Procedia Technology 23 (2016) 328 – 335

Procedia Technology

3rd International Conference on Innovations in Automation and Mechatronics Engineering, ICIAME 2016

"Examination of zinc oxide films prepared by magnetron sputtering"

Pranav Y. Dave[a#], Kartik H. Patel[a], Kamlesh V. Chauhan[a], Amit Kumar Chawla[b], Sushant K. Rawal[a*]

[a]CHAMOS Matrusanstha Department of Mechanical Engineering, Chandubhai S. Patel Institute of Technology (CSPIT),
Charotar University of Science and Technology (CHARUSAT), Changa- 388421, Gujarat, India
[b]Institute of Nanoscience and Nanotechnology, University of Petroleum and Energy Studies,
Energy Acres, Dehradun-248 007, Uttarakhand, India
[*]Corresponding Author: Sushant K. Rawal E-mail address: sushantrawal@outlook.com Tel.: +912697 265060

Abstract

Nano-structured zinc oxide thin films were deposited on corning glass substrate by magnetron sputtering process. Zinc oxide films were deposited at different gas ratio values of argon:oxygen kept at 2sccm:18sccm, 6sccm:14sccm, 10sccm:10sccm and 14sccm:6sccm. X-ray Diffraction (XRD) technique was used to characterize ZnO thin films. The XRD graphs indicate presence of (100) and (002) peaks for ZnO thin films. Contact angle and surface energy of nano-structured ZnO thin films were determined by contact angle goniometer. Zinc oxide films are hydrophobic by nature and their contact angle value varies from 98.3° to 102.1° with decrease in flow rate of oxygen gas and increase in argon gas flow rate. UV-Vis-NIR spectrophotometer was used to characterize optical properties of ZnO thin films.

Keywords: Zinc Oxide; Sputtering; Optical properties; Wettability

---

1. Introduction

Surface engineering is defined as modification of near-surface structure, chemistry or property of a substrate in order to achieve superior performance and durability. Wetting phenomenon which is identified with surface change or surface treatment procedure has gotten huge enthusiasm from both principal and application perspective. [1][2]. Zinc Oxide (ZnO) is a wide-band gap semiconductor of the II-VI semiconductor group that has several favourable properties, including good transparency, high electron mobility, wide band gap and strong room-temperature luminescence. Zinc compounds were probably used by early humans, in processed and unprocessed forms, as a

doi:10.1016/j.protcy.2016.03.034

paint or medicinal ointment [3]. Zinc oxide crystallizes in two main forms, hexagonal wurtzite and cubic zinc blende. The wurtzite structure is most stable at ambient conditions and thus most common. ZnO can also be obtained with a variety of particle structures, which determine its use in new materials and potential applications in a wide range and fields of technology. Therefore the development of a method of synthesizing crystalline zinc oxide which can be used on an industrial scale has become a subject of growing interest in science as well as industry [4][5][6][7].

As in many literatures it has been shown that the direct or indirect process is used to develop thin film of zinc oxide on substrates which has wide area of use in industries to make coated surfaces. Application of ZnO films is noteworthy and has aroused great interest due to their special electrical and optical properties. Zinc oxide has high refractive index, high thermal conductivity, binding, antibacterial and UV-protection properties. Many methods have been used to produce ZnO thin films on a solid substrate, such as self-assembly growth and electro-chemical deposition. Recently, there has been much interest in zinc oxide (ZnO) thin films for applications in sensors and transducers. One of the main purposes of developing ZnO coating is to make surface hydrophobic or super hydrophobic [8][9][10].

The objective of this paper is to examine wettability and optical properties of ZnO thin films prepared by magnetron sputtering technique. The aim is to convert hydrophilic behaviour of bare glass substrate into hydrophobic and reduce wettability of the substrate. The influence of argon:oxygen ratio on various properties of ZnO films is investigated in this paper.

2. Experimental details

Zinc Oxide (ZnO) thin films were deposited by RF magnetron sputtering in a custom designed cylindrical chamber (Excel Instruments, India). A 2” diameter zinc target of 99.99% purity was used for sputtering. The RF power was kept constant at 150W, deposition temperature at 500ºC, sputtering pressure was kept at 1.0Pa and target to substrate distance was 50mm. The chamber was initially evacuated to around $5\text{x}10^{-4}$Pa by a turbo molecular pump backed by a rotary pump; thereafter argon and oxygen gas of high purity (99.999%) was injected into the chamber. ZnO films were deposited at different gas ratio values of argon:oxygen kept at 2sccm:18sccm, 6sccm:14sccm, 10sccm:10sccm and 14sccm:6sccm; the corresponding sample names are indicated by O18, O14, O10 and O6 respectively. The flow of gases was controlled by Mass Flow controller (MFC), (ALICAT instruments, USA). The structural properties of zinc oxide films were characterized by X-ray diffractometer (XRD) using Bruker D2 phaser, advance diffractometer with Cu-Kα radiation having wavelength 1.54Å. To determine whether the films are hydrophilic of hydrophobic by nature, contact angle meter (Rame-Hart model 290) was used to find the contact angle of water with the films. Optical transmission and absorption were measured in the 300-800 nm wavelength range using UV-Vis-NIR spectrophotometer (Shimadzu, model UV3600 plus).

3. Results and Discussion

Fig.1 shows the XRD pattern of zinc oxide thin films deposited on corning glass substrate at various gas flow ratio values of argon:oxygen at 2sccm:18sccm, 6sccm:14sccm, 10sccm:10sccm and 14sccm:6sccm indicating the proportion of argon as 10%, 30%, 50% and 70% respectively of the total gas inserted in the chamber. The XRD pattern shows presence of (100) and (002) peaks of ZnO.

The intensity of (002) peak increases with increase in the proportion of argon gas from 2sccm to 14sccm corresponding to 10% to 70% of the total gas flow rate but does not have any effect on evolution of (100) peak. This indicates that the evolution of various textures of ZnO depends on the proportion of various gases inserted in the chamber. Initially at argon:oxygen ratio of 2sccm:18sccm, the proportion of argon that is used as inert gas is low (10%) and oxygen that is used as a reactive gas is higher (90%). This hardly results in formations of various textures of ZnO; so very weak (100) and (002) peaks of ZnO are observed.

Oxygen is highly reactive, so when its proportion is very high (90%) it may have formed oxide layer leading to poisoning of metal zinc target. The evolution of (002) peak having significant intensity is observed only when the proportion of argon is increased from 10% to 30% and of oxygen is decreased from 90% to 70% of the total gas flow. A gradual rise of argon proportion to 70% and decline of oxygen proportion to 30% leads to formation of highly intense (002) peak of ZnO. Argon is an inert gas having higher atomic mass as compared to oxygen. So the increase in proportion of argon gas and subsequent decline in proportion of oxygen gas might have reduced the poisoning of metal zinc target. It is supported with the evolution of highly intense (002) peak, that may have formed only when higher amount of Zn atoms are ejected from zinc target by argon atoms thereby facilitating formation of ZnO films with (100) and (002) peaks as reported in literatures [11][12][13][14][15][16][17].

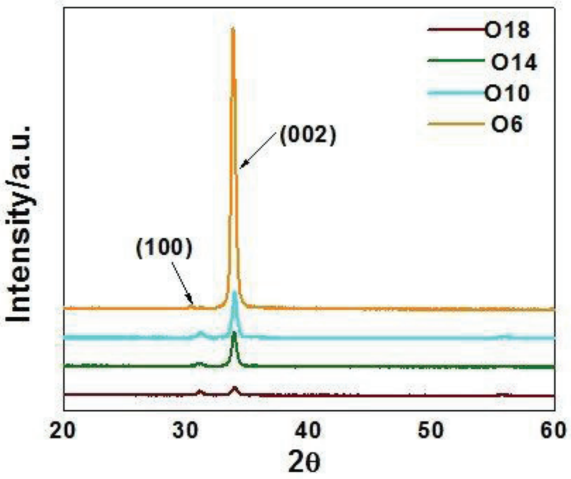

Fig.1: XRD graphs of zinc oxide films at different argon:oxygen ratio.

Scherrer formula [18] was used to calculate the average crystallite size (*d*) of the samples as shown in equation (1).

$$d = \frac{0.9\lambda}{\beta \cos\theta_B} \qquad (1)$$

Where λ,θ_B and β are the X-ray wavelength (1.54056 Å), Bragg diffraction angle and line width at half maximum of the most dominant peak, respectively. The average crystallite size of ZnO thin films is given in table.1. The average crystallite size increases from 18nm to 27nm with increase in argon gas flow rate and with decrease in oxygen gas flow rate. The (002) peak of ZnO films becomes narrow and intense with increase in argon gas flow rate which results in larger average crystallite size with decrease of the oxygen gas flow rate.

Table.1 Calculated parameters of zinc oxide thin films at different argon:oxygen ratio.

Sample Name	Argon:Oxygen ratio (sccm)	Avg. $d_{(XRD)}$ (nm)	Band Gap (eV)	Refractive Index (*n*)	Thickness from %T data (nm)	Wettability as per Contact Angle in (°)
O18	02:18	18	3.33	1.54	751	98.3
O14	06:14	21	3.37	1.55	934	99.4
O10	10:10	24	3.42	1.57	1268	100.8
O6	14:06	27	3.48	1.61	1476	102.1

Thickness of film and transparency are inversely proportional to each other, when thickness of film increases, its transparency decreases. Fig.2 shows the spectral transmittance of zinc oxide films at different gas flow rate of argon and oxygen. The thickness of the zinc oxide films was calculated from the transmission data as reported in literature [19] and is given in Table 1. It was observed that the thickness of zinc oxide films increases from 751nm to 1476nm with the increase in argon proportion in the gas flow ratio. The higher proportion of argon in gas ratio might have prompted removal of more zinc atoms from metal target, consequently reacting with oxygen atoms present in the chamber ultimately leading to formation of thicker zinc oxide films on the substrate.

The transmission data was used to obtain the reflective index of the film by using a model proposed by J.C. Manifacier *et al*. [20]. The calculated refractive index is given in table.1. The refractive indices of ZnO films have been reported to be in between 1 to 2, depending on the film thickness and its structure [11]. The refractive index of deposited zinc oxide films increases from 1.54 to 1.61 with increase in argon:oxygen gas flow ratio. The absorption spectra of zinc oxide were recorded as a function of the wavelength. S. Flickyngerova *et al*. [21] measured transmission of ZnO thin film and calculated the absorption co-efficient (α) by Tauc plot and measured optical band gap (E_g).

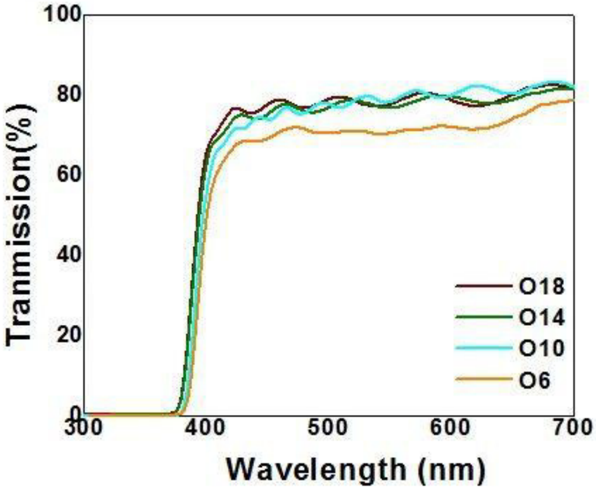

Fig.2: Optical transmission curves of zinc oxide films deposited at different argon:oxygen ratio.

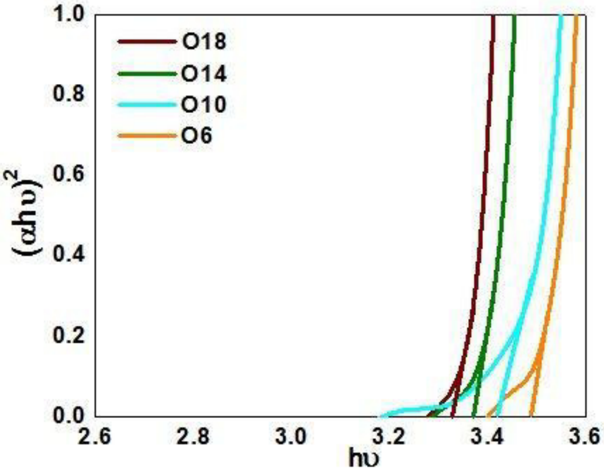

Fig.3: Optical absorption curve of zinc oxide films deposited at different argon:oxygen ratio.

Zinc oxide is a direct wide band gap and large exciton binding energy as reported in literatures [22][23][24]. The calculated band gap values of ZnO films at different argon:oxygen gas flow ratio is shown in Fig.3. The band gap value of ZnO thin films varies between 3.33eV-3.48eV for different argon:oxygen gas flow ratio as given in Table

1. ZnO films are getting thicker with larger average crystallize size as the proportion of argon increases and oxygen decreases in argon:oxygen gas flow ratio resulting in higher band gap values which are consistent with literatures [12][18][23][25]. The transmission of ZnO films also decreases with increase in argon:oxygen gas flow ratio as evident from Fig. 2 resulting in more absorption and greater band gap values.

The AFM micrographs of ZnO thin films for samples O18 and O6 are shown in Fig. 4. As the proportion of argon gas in the argon:oxygen ratio increases, the thickness of ZnO thin films increases giving higher surface roughness values. When the argon:oxygen ratio is varied from 2sccm:18sccm, 6sccm:14sccm, 10sccm:10sccm and 14sccm:6sccm, the surface roughness of ZnO films observed are 4.11nm, 9.52nm, 12.84nm and 16.32nm respectively.

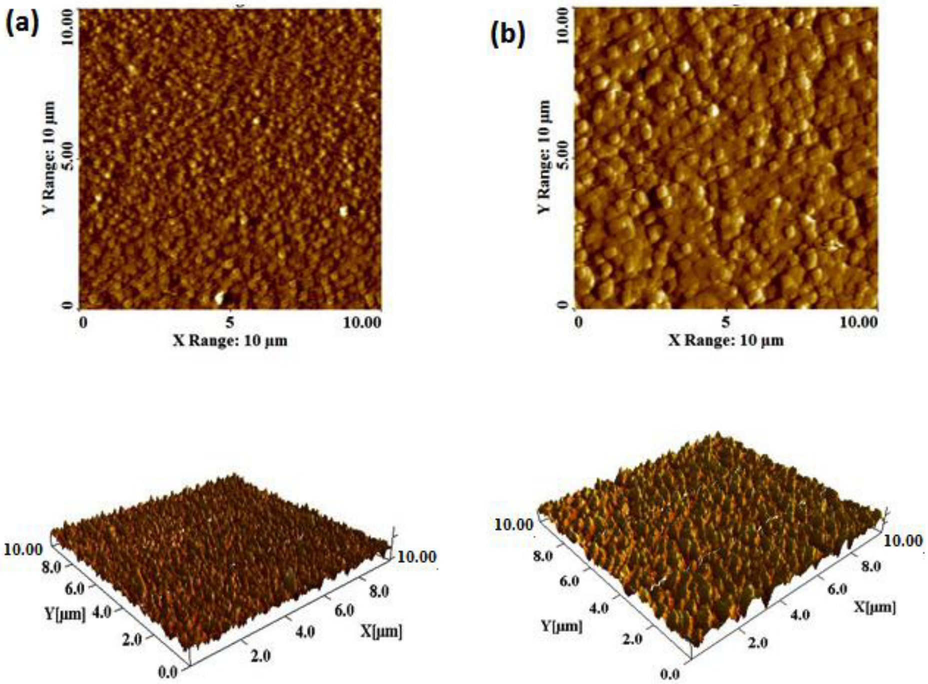

Fig.4: AFM images of ZnO thin film deposited at different argon:oxygen ratio of (a) 02:18sccm and (b) 14:06sccm.

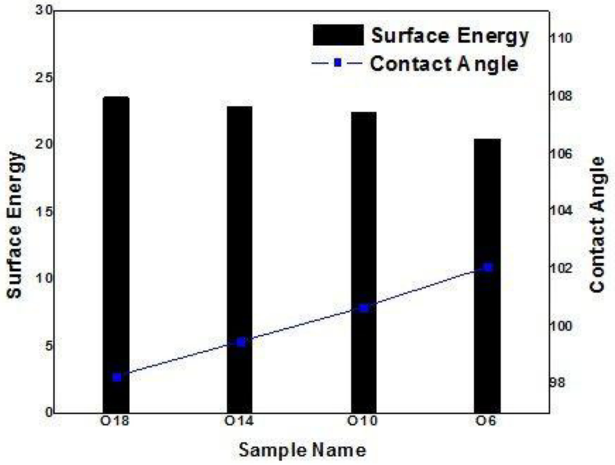

Fig5: Contact angle and surface energy of zinc oxide films deposited at different argon:oxygen ratio.

Surfaces with high thickness of film commonly show fewer mechanical properties than flat surfaces, and this is a crucial problem for the application of highly hydrophobic surfaces [26]. Surface energy and contact angle are inversely proportional to each other [25]. Wettability of solid surface is determined through contact angle. Young's equation defines the contact angle 'θ' by analyzing the forces acting on a fluid droplet resting on a solid surface. The contact angle 'θ' is the angle formed by a liquid at the three phase boundary where the liquid, gas and solid intersect. So, the equilibrium of forces among the surface tensions at 3-phase boundary is described by the Young's equation:

$$\gamma_{SG=}\gamma_{SL} + \gamma_{LG}\cos\theta \qquad (2)$$

where γ_{SG}, γ_{SL} and γ_{LG} are surface tension of the solid-gas, solid-liquid and liquid-gas interfaces respectively and θ is the equilibrium contact angle asgiven in equation (1) [3]. Fig.5 shows the contact angle and surface energy values of ZnO thin films deposited at different argon:oxygen ratio.

The contact angle of ZnO films increases while its surface energy decreases with increases the concentration of argon gas. When the argon:oxygen ratio is 2sccm:18sccm, the contact angle was found to be 98.3°. The maximum contact angle for ZnO film is observed at argon:oxygen ratio of 14sccm:6sccm which is 102.1°. At high flow rate of argon, highly intense (002) peak of zinc oxide films is found with larger crystallize size that might have imparted higher contact angle values and lower surface energy.

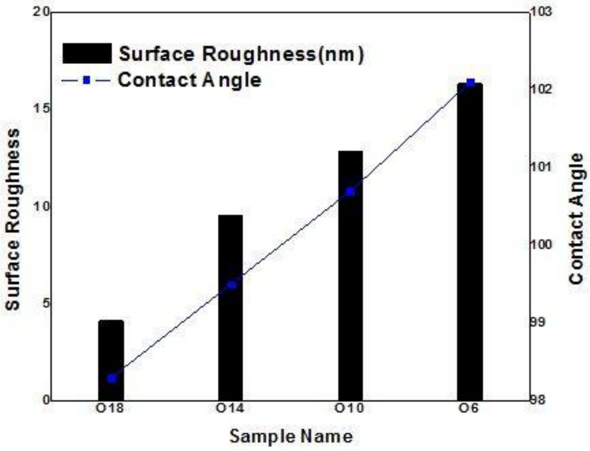

Fig.6: Contact angle and surface roughness of zinc oxide films deposited at different argon:oxygen ratio.

Surface roughness and contact angle are directly proportional to each other. The relation between contact angle and surface roughness of ZnO films is shown in Fig.6. It is observed that the contact angle of ZnO films increases with increase in surface roughness which is consistent with literatures [15][27].

The average crystalline size for zinc oxide films increases from 18-27nm with increase in proportion of argon in argon:oxygen ratio and the average transmittance of ZnO films is over 60%. The deposited zinc oxide films are able to retain good transparency and are hydrophobic by nature having contact angle values of more than 98º for all values of argon:oxygen ratio.

4. Conclusion

ZnO thin films displays (100) and (002) peaks, the intensity of (002) peak increases with increase in the proportion of argon gas flow rate. The average crystallite size of ZnO thin films increases from 18nm to 27nm and its thickness increases from 751nm to 1476nm with increase in argon:oxygen ratio. The increase in thickness of ZnO films leads to higher surface roughness values. The surface roughness increases from 4.11nm to 16.32nm resulting in increase of contact from 98.3° to 102.1°.The band gap of zinc oxide films is observed within the range of 3.33eV-3.48eV.

5. Acknowledgement

This work has been supported by AICTE grant number 20/AICTE/RIFD/RPS (POLICY-III) 24/2012-13 sanctioned under Research Promotion Scheme (RPS). We are thankful to President and Provost of CHARUSAT for supporting this research work. We are thankful to Dr. T. K. Chaudhuri, Professor and Head, Dr. K. C. Patel Research and Development Centre (KRADLE) affiliated to Charotar University of Science and Technology (CHARUSAT), India for granting permission to use various equipment's available in their characterization laboratory.

6. References

[1] D. Kennedy and E. Mihaylova, Current and Future Applications of Surface Engineering Current and Future Applications of Surface, (2005), pp. 0–13.

[2] B. and Gupta, Surface Engineer and Wear, (2000), pp. 1–14.

[3] A. W. Momber, Surface Quality Aspects, Hydroblasting Coat. Steel Struct. - Chapter 5, (2003).

[4] J. Zhou, S. Yang, X. Y. Zeng, and J. H. Wu, Superhydrophobic ZnO for EWOD Digital Microfluidic Device for Application in Micro Total Analysis System (μ-TAS), J. Adhes. Sci. Technol., 26 (May 2013), (2012), pp. 2087–2098.

[5] W. Xu, J. Li, S. Lu, Y. Duan, C. Ma, X. Shi, Y. Chen, and Y. Yang, Preparation of superhydrophobic ZnO films on zinc substrate by chemical solution method., Chem. Res. Chinese Univ., 28 (3), (2012), pp. 529–533.

[6] S. Subhash Latthe, Recent Progress in Preparation of Superhydrophobic Surfaces: A Review, J. Surf. Eng. Mater. Adv. Technol., 02 (02), (2012), pp. 76–94.

[7] A. Kołodziejczak-Radzimska and T. Jesionowski, Zinc Oxide—From Synthesis to Application: A Review, Materials (Basel)., 7 (4), (2014), pp. 2833–2881.

[8] S. K. Ghosh, Functional Coatings and Microencapsulation: A General Perspective, Funct. Coatings By Polym. Microencapsul., (2006), pp. 1–28.

[9] Z. C. Jin, I. Hamberg, and C. G. Granqvist, Optical properties of sputter-deposited ZnO:Al thin films, J. Appl. Phys., 64 (10), (1988), pp. 5117–5131.

[10] S. M. Dae-Sik Lee, Jikui Luo, Yongqing Fu, William I Milne, Nae-Man Park, Sang Hyeob Kim, Mun Yeon Jung, Nanocrystalline ZnO Film Layer on Silicon and its Application to Surface AcousticWave-Based Streaming, J. Nanosci. Nanotechnol., 8 (4), (2008), pp. 1951–1958.

[11] N. Ekem, S. Korkmaz, S. Pat, M. Z. Balbag, E. N. Cetin, and M. Ozmumcu, Some physical properties of ZnO thin films prepared by RF sputtering technique, Int. J. Hydrogen Energy, 34 (12), (2009), pp. 5218–5222.

[12] G. Ferblantier, M. Al Kalfioui, A. Boyer, and A. Foucaran, Properties of RF magnetron sputtered zinc oxide thin films, 255, (2003), pp. 130–135.

[13] T. Yamada, K. Ikeda, S. Kishimoto, H. Makino, and T. Yamamoto, Effects of oxygen partial pressure on doping properties of Ga-doped ZnO films prepared by ion-plating with traveling substrate, 201, (2006), pp. 4004–4007.

[14] Y. Igasaki and H. Kanma, Argon gas pressure dependence of the properties of transparent conducting ZnO : Al ® lms deposited on glass substrates, 170, (2001), pp. 508–511.

[15] K. Khojier, H. Savaloni, E. Shokrai, Z. Dehghani, and N. Z. Dehnavi, Influence of argon gas flow on mechanical and electrical properties of sputtered titanium nitride thin films, 7 (1), (2013), p. 1.

[16] D. Horwat and A. Billard, Effects of substrate position and oxygen gas flow rate on the properties of ZnO : Al films prepared by reactive co-sputtering, 515, (2007), pp. 5444–5448.

[17] J. H. Kim, M. Lee, T. Y. Lim, J. H. Hwang, E. Kim, and S. H. Kim, Fabrication of transparent superhydrophobic ZnO thin films by a wet process, J. Ceram. Process. Res., 11 (2), (2010), pp. 259–262.

[18] A. M. Rosa, E. P. da Silva, E. Amorim, M. Chaves, a C. Catto, P. N. Lisboa-Filho, and J. R. R. Bortoleto, Growth evolution of ZnO thin films deposited by RF magnetron sputtering, J. Phys. Conf. Ser., 370, (2012), p. 012020.

[19] K. R. Wu, J. J. Wang, W. C. Liu, Z. S. Chen, and J. K. Wu, Deposition of graded TiO2 films featured both hydrophobic and photo-induced hydrophilic properties, Appl. Surf. Sci., 252 (16), (2006), pp. 5829–5838.

[20] W. R. W. P. Mag, E. G. Worden, R. G. Gutmacher, and C. J. G. Appl, Simple Method for the Determination of the Optical Constants, 9, (1976), pp. 1002–1004.

[21] S. Flickyngerova, K. Shtereva, V. Stenova, D. Hasko, and I. Novotny, Structural and optical properties of sputtered ZnO thin films, 254, (2008), pp. 3643–3647.

[22] E. S. Ates and H. E. Unalan, Zinc oxide nanowire enhanced multifunctional coatings for cotton fabrics, Thin Solid Films, 520 (14), (2012), pp. 4658–4661.

[23] P. Atienzar, T. Ishwara, B. N. Illy, M. P. Ryan, B. C. O'Regan, J. R. Durrant, and J. Nelson, Control of photocurrent generation in polymer/ZnO nanorod solar cells by using a solution-processed TiO2 overlayer, J. Phys. Chem. Lett., 1 (4), (2010), pp. 708–713.

[24] S. Lin, J. Huang, and D. Lii, The effects of r . f . power and substrate temperature on the properties of ZnO films, 176, (2004), pp. 173–181.

[25] W. J. Khudhayer, R. Sharma, and T. Karabacak, Hydrophobic metallic nanorods with Teflon nanopatches., Nanotechnology, 20 (27), (2009), p. 275302.

[26] V. Khranovskyy, J. Eriksson, A. Lloyd-spetz, R. Yakimova, and L. Hultman, Effect of oxygen exposure on the electrical conductivity and gas sensitivity of nanostructured ZnO films, Thin Solid Films, 517 (6), (2009), pp. 2073–2078.

[27] B.-B. Wang, J.-T. Feng, Y.-P. Zhao, and T. X. Yu, Fabrication of Novel Superhydrophobic Surfaces and Water Droplet Bouncing Behavior — Part 1: Stable ZnO–PDMS Superhydrophobic Surface with Low Hysteresis Constructed Using ZnO Nanoparticles, J. Adhes. Sci. Technol., 24 (15)–(16), (2010), pp. 2693–2705.