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Effect of Oxygen Annealing on the Surface Defects and Photoconductivity of Vertically Aligned ZnO Nanowire Array

Ajay Kushwaha, Hemen Kalita and M. Aslam

***Abstract*—**Post growth annealing of solution grown ZnO nanowire array is performed under controlled oxygen ambience. The role of annealing over surface defects and their consequence on dark/photo-conductivity and photosensitivity of nanowire array is investigated. Surface defect properties are explored using various measurement tools such as contact angle, photoluminescence, Raman spectroscopy and XPS measurements. The contact angle of the NW films reduces due to oxygen annealing and nanowire film surface changes from hydrophobic (96°) to hydrophilic (16°). Raman and XPS spectroscopy reveal that oxygen annealing improves the crystal quality of the nanowire films. The defect band emission intensity (relative to band edge emission, I_D/I_{UV}) reduces from 1.3 to 0.2 after annealing at 600 °C at 10 SCCM flow of oxygen. An order enhancement in dark conductivity is observed in O_2 annealed samples, while photoconductivity is found to be slightly reduced due to lower concentration of surface related oxygen defects.

***Keywords*—** Zinc Oxide, Surface defects, Photoluminescence, Photoconductivity, Photosensor and Nanowire thin film.

I. Introduction

ONE dimensional nanostructures are the most promising materials for variety of optoelectronic applications ranging from sensing devices, LEDs to solar cells [1]–[3]. The nanowire array films offer the most suitable design due to availability of high surface area which can effectively modulate the optical and electronic characteristics [4]. The defect states arise due to surface species/defects and ultimately modify the charge carrier mobility and concentration which results the alteration of electrical conductivity [4]. Photoluminescence spectra of ZnO, generally consists of two emission peaks, one is in UV range called as band-edge emission and second is a broad emission peak in visible region [5]. The unstructured broad peak in visible range is related to defect states emission, which convoluted by green, yellow and red emission peaks. The defect states and their related emission is a debatable topic and various hypotheses have been adopted to explain emission phenomenon [6], [7]. The origin of green emission is more controversial, numerous defects like Zn interstitial, oxygen vacancies, Zn vacancies, oxygen interstitial and impurities are considered to be cause [7], [8]. Oxygen vacancies are the widely accepted defects types responsible for green emission in solution grown nanowires [9]. The charged oxygen vacancies are higher in concentration at nanowire surface (singly and double charged oxygen vacancies) hence nanowire films shows intense defect emission peak [10]. Surface modifications via chemical process or post growth techniques were adopted to control the surface defects of ZnO nanowire [11], [12]. Post growth annealing treatment of ZnO film in oxygen atmosphere is also explored previously [11], [13]–[15]. However, controlled oxygen annealing of ZnO NW films and correlation of their optical and electrical properties with surface defects is not studied well. Therefore, in present report, we have investigated the oxygen annealing effect on ZnO nanowire surface properties and photoconductivity. Surface of ZnO nanowire is extensively modified after oxygen heat treatment and it changes from hydrophobic to hydrophilic. Oxygen annealing results a good control over the surface related defects (mainly oxygen vacancies) and reduces defect emission from 1.3 to 0.2 (UV emission v/s defect emission intensity). The dark conductivity of O_2 annealed NW film increases by an order of magnitude in comparison to as-grown NW films. Photosensitivity of nanowire film decrease due to reduction in defect states, but the photoresponse time is improved due to O_2 annealing.

II. Experimental Section

Solution grown nanowire films were annealed at different temperatures and different oxygen gas flow rates [16]. The flow rate of oxygen was controlled from 5- 50 SCCM (Standard Cubic Centimeters per Minute) using mass flow controller and the annealing temperature was varied from 200 to 600 °C with heating rate of 10 °C using a programmable tube furnace. The tube furnace with one inch quartz tube diameter was utilized which was part of the wall-mounted CVD set up. Morphological analysis of ZnO nanowire was done using JEOL-JSM 6390 scanning electron microscope.

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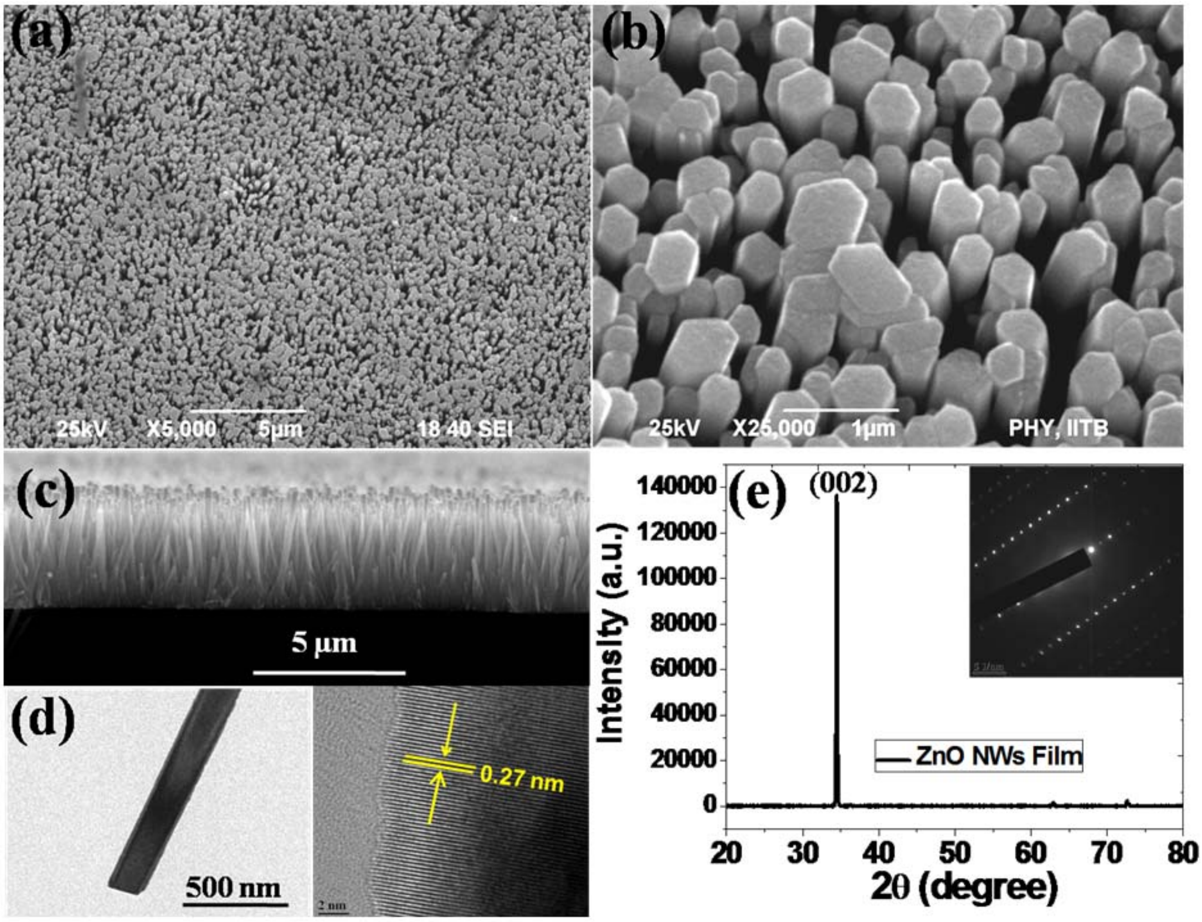

Fig.1 (a) Large area SEM image, (b) magnified SEM image and (c) cross-sectional view of ZnO nanowire film. (d) HRTEM image of single ZnO nanowire and lattice fringe. (e) XRD pattern of ZnO nanowire film (inset shows the selected area electron diffraction pattern of single NW)

Crystallographic measurements were performed on Xpert PANAlytic X-ray diffractometer using Cu Kα radiation (λ = 0.15404 nm) and scan step of 0.017 (2θ/sec). HRTEM (JEOL JEM 2100F, field emission gun transmission electron microscope (operated at an accelerating voltage of 200 kV) measurements were performed to confirm the structural and morphological characteristics of ZnO nanowires. The GBX Digidrop was used to measure the contact angle of a drop of water placed on ZnO NWs sample. The Keithley dual channel current-voltage source meter (model: 2602A) was utilized for four probe conductivity (I-V) measurements. The UV light (365 nm wavelength and 10 mW power) is typically illuminated normal to the nanowire film surface. PL measurement was performed using VARIAN CARY-eclipse fluorescence spectrophotometer under 290 nm excitation.

III. Results And Discussion

A. Morphological and Structural Investigations

A large area SEM image of ZnO nanowire array film is given in Fig. 1a. The nanowires are uniformly distributed and well oriented on the ZnO quantum dot template glass substrate. Fig. 1b shows the magnified view of these array, the nanowires have 250 ± 60 nm diameter with hexagonal faceted shape. The cross-sectional image of the NW films clearly demonstrated that film is highly oriented and grown normal to the substrate surface with 4 µm long nanowire. HETEM image shows that the nanowire diameter is 250 nm as demonstrated in Fig.1d, the lattice spacing is observed using high resolution imaging and is approximately 0.27 nm. X-ray diffraction pattern of NWs film is presented in Fig.1e, the plot shows very strong orientation along (002) plane, which verifies the c-axis oriented growth. The XRD pattern matched with the bulk JCPDS [00-020-1437], this confirms the as-grown NWs are wurtzite in nature. The selected area electron diffraction pattern (inset of Fig. 1e) demonstrates single crystalline nature of ZnO NWs.

B. Surface Properties of ZnO Nanowire Films

The surface wettability test is useful to understand the suitability of NWs based electrodes in dye sensitized solar cell and other biomedical applications [17]-[18]. The surface properties of ZnO nanowire films are investigated by measuring the contact angle of distilled water. Fig. 2 shows the contact angle measurement of as-grown and oxygen annealed samples. The as-grown NWs film is hydrophobic in nature with 96° contact angle. The hydrophobic nature of NWs array is due to the available large voids among nanowires. The trapped air in these voids plays important role in surface wettability. It is previously shown that high trapped air between film and water leads to increase hydrophobic nature [19], [20]. The as-grown sample has higher tendency to adsorb oxygen at surface, hence as-grown array shows larger value of contact angle. When nanowire array is annealed in oxygen, the surface of nanowire is reconstructed and surface amorphous layer and $Zn(OH)_2$ layer gets converted in zinc oxide and the crystal quality of ZnO NWs is improved [21]. The surface trapped oxygen reduces after annealing and other surface impurities (carbon related) are removed from the surface [22].

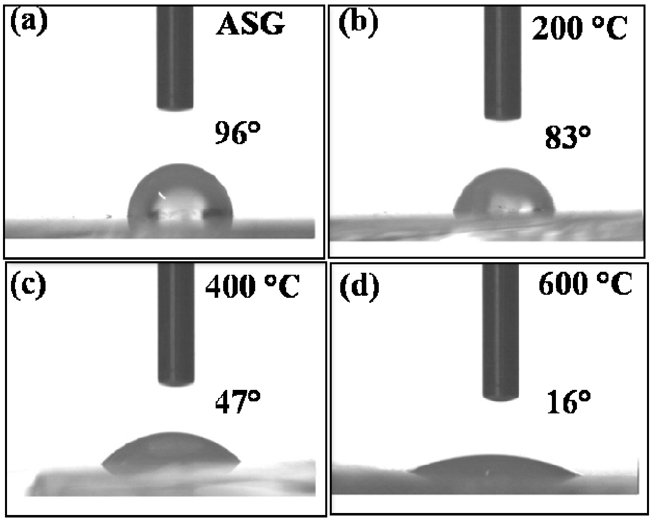

Fig. 2 Contact angle measurements of (a) as-grown (b) 200 °C (c) 400 °C and (d) 600 °C oxygen annealed ZnO nanowire films

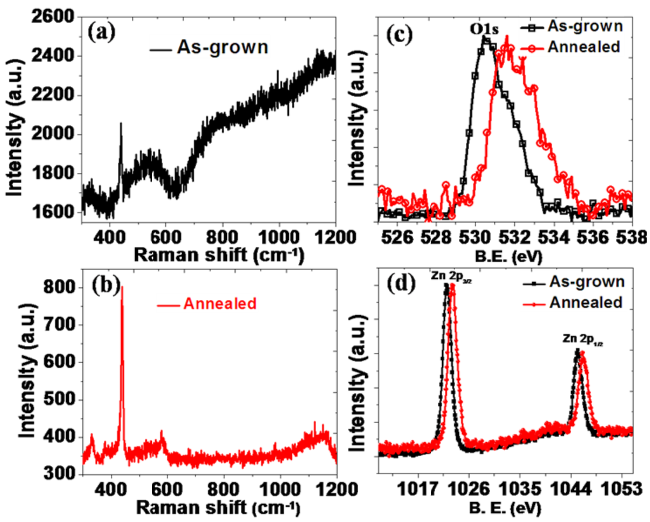

Fig. 3 Raman spectroscopy of (a) as-grown (b) oxygen annealed (400 °C) ZnO nanowire films. X-ray photoelectron spectroscopy plots (c) oxygen O1s peak and (d) Zn $2p_{3/2}$ and Zn$2p_{1/2}$ peaks of asgrown and oxygen annealed ZnO NWs films

The nanowire becomes more clean and crystalline with less trapped air in voids, which leads to a reduction in contact angle [20]. The sample annealed at 600 °C shows relatively higher hydrophilic nature with 16° contact angle. Fig.3a and Fig.3b show the Raman spectra of the as-grown and oxygen annealed (600 °C) ZnO NWs films. The sharp peak at 439 cm^{-1} corresponds to the non-polar E_2 (high) optical phonon mode, becomes more intense after oxygen annealing, which attributes an increase in the crystallinity of the films [23]. This enhancement in E_2 peak indicates the improvement of oxygen content or reduction of oxygen vacancies in ZnO NW system [23]. In contrast to the annealed NWs, the as-grown sample shows broader and intense peak at 540 cm^{-1} which indicates oxygen deficiency in as-grown NWs [24]. The higher intensity of 540 cm^{-1} peak also indicates the presence of higher impurity level and defects (oxygen vacancies/ zinc interstitials) in as-grown nanowires [25], [26] . We believe oxygen annealing of solution grown nanowire renders improvement in crystal quality of nanowires. Surface properties of ZnO nanowire films are further investigated using X-ray photoelectron spectroscopy. Oxygen 1s peak of annealed sample is found to be shifted to higher binding energy than as-grown sample. In as-grown sample oxygen are chemically adsorbed at the nanowire surface, while after annealing the concentration of surface defects and chemically adsorbed oxygen get reduced. The shift in binding energy of O_2 annealed ZnO NWs might be related to the unbounded and free surface oxygen [27]. Fig. 3d compares Zn $2p_{3/2}$ and $2p_{1/2}$ peak of XPS measurements. Zn $2p_{1/2}$ and Zn $2P_{3/2}$ peaks are shifted to higher binding energy as shown in the inset of Fig. 3d. The positive shift in Zn peaks is related to the enhancement in the carrier concentration and mobility of the nanowire films [27]-[29].

C. Surface Defects and Electrical Conductivity

Further the concentration of defect states is studied using room temperature PL measurements. The high surface area in nanowire films dominates in defect emission; hence surface modification of ZnO nanowire could leads to change its optical properties. The post growth annealing in oxygen mainly changes the concentration of oxygen vacancies at the surface of nanowires. Fig. 4a shows the PL spectra of as-grown and oxygen annealed NW films. Oxygen annealing at fix flow rate of 10 SCCM results good control over the defect emission intensity. Defect band emission is widely suppressed at 600 °C annealing temperature, however complete suppression is not observed. The band edge emission becomes week in this temperature, which is related to the excess oxygen or creation of oxygen interstitials at NWs surface. Dark current measurements of as-grown and oxygen annealed samples at 200, 400 and 600 °C are shown in Fig. 4b. The result shows dark conductivity improves with the increase of annealing temperature. Approximately an order increase in the device conductance has been noticed after 600 °C annealing than as-grown NW films. The enhanced electrical conductivity is result of reduced band bending at NWs surface and improved crystal quality.

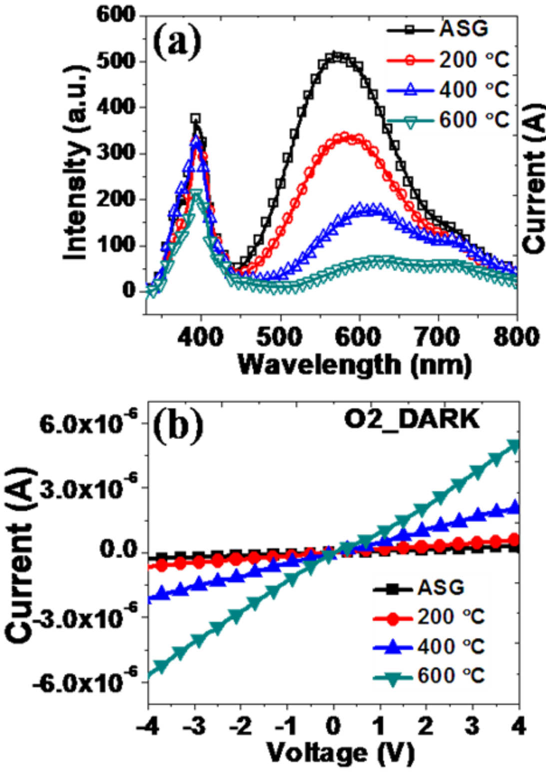

Fig. 4 (a) Room temperature PL spectra, (b) current-voltage profile of dark conductivity measurement and (c) photoconductivity measurement of as-grown and oxygen annealed NWs films (at various temperatures). (d) Dark and photo-conductance as-grown and annealed NWs films

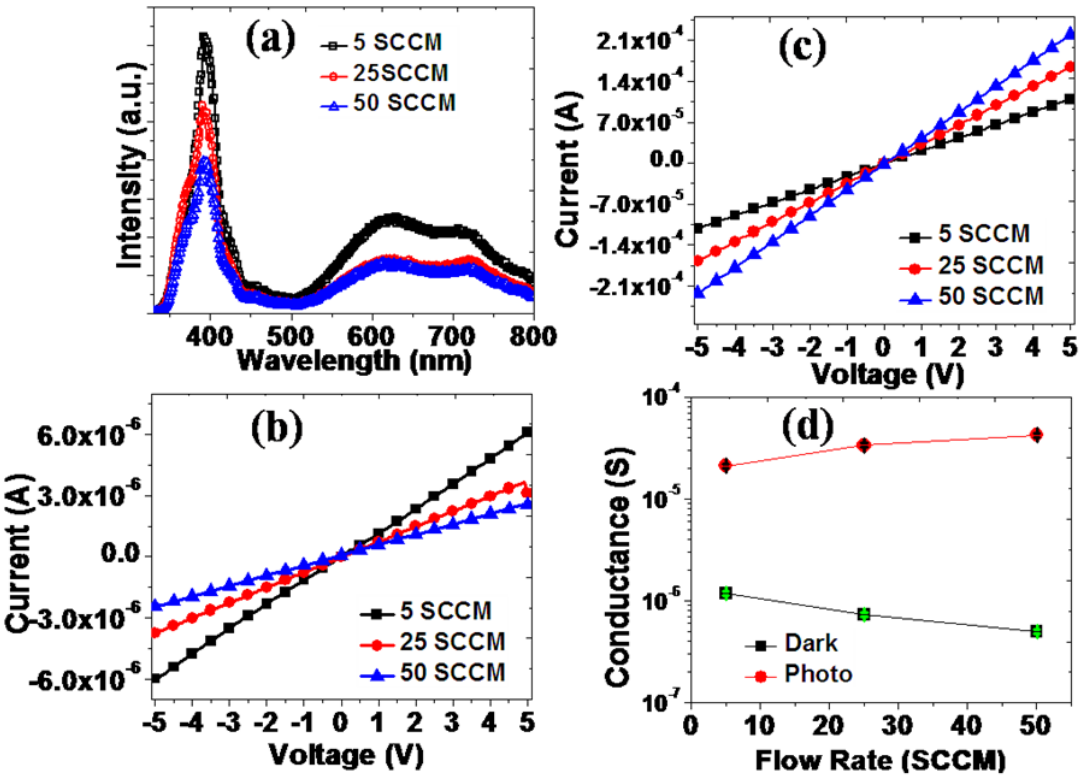

Fig. 5 (a) Photoluminescence measurement of ZnO nanowire films annealed at various flow rate of oxygen, (b) current-voltage profile of dark conductivity measurement and (c) photoconductivity measurement of as-grown and oxygen annealed NWs films (at various flow rate of oxygen). (d) Dark and photo-conductance as-grown and annealed NWs films

Electron flow becomes easier due to reduction of barrier height between inter-nanowire junctions. The photosensitivity of annealed sample decreases due to reduction of surface trap levels [30]. Further, role of oxygen flow rate on the defect states and electrical conductivity is studied. Three different oxygen flow rate are selected for annealing experiments (5, 25 and 50 SCCM). Fig. 5a compares the PL measurements, the high flow rate annealed sample results decrease in band edge emission and green emission both. However, red emission intensity is relatively high which results due to creation of excess oxygen and oxygen interstitial defects. I-V measurements of above samples are given in Fig. 5b. Increase flow rate of oxygen reduces the dark conductivity of the film from 1.19µS to 0.5µS (flow rate changes from 5 to 50 SCCM). Photoconductivity slightly enhanced at higher flow rate annealing, Fig. 1d compares the dark and photo-conductance of oxygen annealed sample of different flow rates annealing. The UV light sensitivity increases in very small amount in high flow rate annealed samples.

D. Time Dependent UV Photoresponse

Time resolved photoresponse provides important information about surface properties of the NW films.

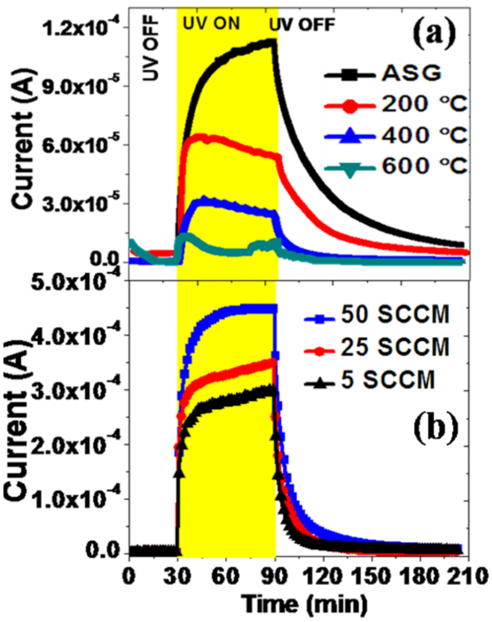

Fig.6 Time resolved UV light photoresponse of as-grown and oxygen annealed ZnO nanowire array films (a) at various temperatures and (b) at various gas flow rate

Nanowire surface properties play an important role to control the photoresponsivity due to availability of high UV light active area in NWs [30]. The surfaces oxygen desorption and re-adsorption mainly governs the current rise and decay profile. Fig. 6a represents the UV light ON/OFF response of as-grown and annealed ZnO nanowire films. The high annealing temperature renders lesser response time constant (exponential fitting results 70 sec for 600 °C annealed sample and 554 sec for asgrown), however, the change in magnitude of the photocurrent is high in as-grown case. The fast photoresponse in annealed samples is observed due to lesser involvement of surface processes and reduced surface traps [30]. The recovery of dark current (UV excitation OFF) is slow in as-grown NWs as shown in Fig. 6a. High oxygen vacancy defects at the as-grown nanowire surface creates high surface potential barrier to prevent recombination of electron and surface trapped holes. The slow recombination process causes persistency in photocurrent of ZnO nanowire films [30]. Annealing reduces the photocurrent persistency and higher temperature annealing shows high reduction in the value of PPC. Flow controlled annealing shows that high flow rate annealed samples have lesser change in photocurrent. Fig. 6b show that persistency in photocurrent is higher in high flow rate annealed sample due to relatively high defects states.

IV. Conclusion

Oxygen annealing has shown modified surface properties of ZnO nanowire films. Solution grown nanowire NWs are found oxygen deficient and O_2 annealing improves the oxygen content in the films. Highly crystalline and good quality NWs film is produced after annealing in oxygen atmosphere. Defect emission intensity has been reduced but is not fully suppressed. Electrical conductivity of NWs films is also improved due to less scattering of charge carriers at NWs boundaries (grains) and reduction of surface depletion barrier.

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References

[1] J. Bao, M. Zimmler, F. Capasso, X. Wang, and Z. F. Ren, "Broadband ZnO single-nanowire light-emitting diode.," *Nano letters*, vol. 6, no. 8, pp. 1719, 2006.

[2] A. I. Hochbaum and P. Yang, "Semiconductor nanowires for energy conversion," *Chemical reviews*, vol. 110, no. 1, pp. 527, 2010.

[3] Q. Wan, Q. H. Li, Y. J. Chen, T. H. Wang, X. L. He, J. P. Li, and C. L. Lin, "Fabrication and ethanol sensing characteristics of ZnO nanowire gas sensors," *Applied Physics Letters*, vol. 84, no. 18, p. 3654, 2004.

[4] V. S. Sundaram and A. Mizel, "Surface effects on nanowire transport: a numerical investigation using the Boltzmann equation," *Journal of Physics: Condensed Matter*, vol. 16, no. 26, pp. 4697, 2004.

[5] U. Ozgur, Y. I. Alivov, C. Liu, M. Reshchikov, S. Dogan, V. Avrutin, S.-J. Cho, and H. Morkoc, "A comprehensive review of ZnO materials and devices," *Journal of Applied Physics*, vol. 98, no. 4, p. 041301, 2005.

[6] A. B. Djurisić and Y. H. Leung, "Optical properties of ZnO nanostructures.," *Small*, vol. 2, no. 8–9, pp. 944, 2006.

[7] K. Vanheusden, W. L. Warren, C. H. Seager, D. R. Tallant, J. a. Voigt, and B. E. Gnade, "Mechanisms behind green photoluminescence in ZnO phosphor powders," *Journal of Applied Physics*, vol. 79, no. 10, p. 7983, 1996.

[8] S. A. Studenikin "Fabrication of green and orange photoluminescent, undoped ZnO films using spray pyrolysis" *Journal of Applied Physics*, Vol. 84, No. 4, pp. 2287, 1998.

[9] F. H. Leiter, H. R. Alves, A. Hofstaetter, D. M. Hofmann, B. K. Meyer, and I. P. Institut, "The Oxygen Vacancy as the Origin of a Green

Emission in Undoped ZnO," *phys. stat. sol. (b)* 226, No. 1, R4–R5, 2001.

[10] B. Panigrahy, M. Aslam, D. S. Misra, M. Ghosh, and D. Bahadur, "Defect-Related Emissions and Magnetization Properties of ZnO Nanorods," *Advanced Functional Materials*, vol. 20, no. 7, pp. 1161, 2010.

[11] Y. Sato, H. Kusumi, H. Yamaguchi, T. Komiyama, and T. Aoyama, "Photoconductive properties of ZnO crystals with post-growth annealing," *Physica B: Condensed Matter*, vol. 376, no. 377, pp. 719, 2006.

[12] M. Rusop, "Post-growth annealing of zinc oxide thin films pulsed laser deposited under enhanced oxygen pressure on quartz and silicon substrates" *Materials Science and Engineering: B*, vol. 127, pp. 150, 2006.

[13] Q. Zhao, X. Y. Xu, X. F. Song, X. Z. Zhang, D. P. Yu, C. P. Li, and L. Guo, "Enhanced field emission from ZnO nanorods via thermal annealing in oxygen," *Applied Physics Letters*, vol. 88, no. 3, p. 033102, 2006.

[14] H. S. Kang, "Annealing effect on the property of ultraviolet and green emissions of ZnO thin films," *Journal of Applied Physics*, vol. 95, no. 3, p. 1246, 2004.

[15] Q. Xu, R. Hong, H. Huang, Z. Zhang, M. Zhang, X. Chen, and Z. .Wu, "Laser annealing effect on optical and electrical properties of Al doped ZnO films," *Optics & Laser Technology*, vol. 45, pp. 513, 2013.

[16] A. Kushwaha and M. Aslam, "Controlled growth of highly oriented ZnO nanorod array on amorphous glass substrate and their optical and electrical properties," *International Journal of Nanoscience*, vol. 10, no. 4–5, p. 635, 2011.

[17] S. Wang, Y. Song, and L. Jiang, "Photoresponsive surfaces with controllable wettability," *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, vol. 8, no. 1, pp. 18, 2007.

[18] N. Verplanck, Y. Coffinier, V. Thomy, and R. Boukherroub, "Wettability Switching Techniques on Superhydrophobic Surfaces," *Nanoscale Research Letters*, vol. 2, no. 12, pp. 577, 2007.

[19] S. Patra, S. Sarkar, S. K. Bera, G. K. Paul, and R. Ghosh, "Influence of surface topography and chemical structure on wettability of electrodeposited ZnO thin films," *Journal of Applied Physics*, vol. 108, no. 8, p. 083507, 2010.

[20] M. Sun, Y. Du, W. Hao, H. Xu, Y. Yu, and T. Wang, "Fabrication and Wettability of ZnO Nanorod Array," J. Mater. Sci. Technol vol. 25, no. 1, pp. 53, 2009.

[21] V. R. Shinde, C. D. Lokhande, R. S. Mane, and S.-H. Han, "Hydrophobic and textured ZnO films deposited by chemical bath deposition: annealing effect," *Applied Surface Science*, vol. 245, no. 1–4, pp. 407, 2005.

[22] R. Sun, A. Nakajima, A. Fujishima, T. Watanabe, and K. Hashimoto, "Photoinduced Surface Wettability Conversion of ZnO and TiO 2 Thin Films," *J Phys. Chem. B*, vol. 105, no. 4, pp. 1984, 2001.

[23] A. C. Gandhi, H.-J. Hung, P.-H. Shih, C.-L. Cheng, Y.-R. Ma, and S. Wu, "In Situ Confocal Raman Mapping Study of a Single Ti-Assisted ZnO Nanowire.," *Nanoscale research letters*, vol. 5, no. 3, pp. 581, 2009.

[24] K. Alim, V. Fonoberov, M. Shamsa, and A. Balandin, "Micro-Raman investigation of optical phonons in ZnO nanocrystals," *Journal of Applied Physics*, vol. 97, no. 12, p. 124313, 2005.

[25] G. W. Cong, H. Y. Wei, P. F. Zhang, W. Q. Peng, J. J. Wu, X. L. Liu, C. M. Jiao, W. G. Hu, Q. S. Zhu, and Z. G. Wang, "One-step growth of ZnO from film to vertically well-aligned nanorods and the morphology-dependent Raman scattering," *Applied Physics Letters*, vol. 87, no. 23, p. 231903, 2005.

[26] G. Xiong, U. Pal, and J. G. Serrano, "Correlations among size, defects, and photoluminescence in ZnO nanoparticles," *Journal of Applied Physics*, vol. 101, no. 2, p. 024317, 2007.

[27] K.-W. Chae, Q. Zhang, J. S. Kim, Y.-H. Jeong, and G. Cao, "Low-temperature solution growth of ZnO nanotube arrays.," *Beilstein journal of nanotechnology*, vol. 1, no. 001, pp. 128, 2010.

[28] B. Panigrahy, M. Aslam, and D. Bahadur, "Controlled optical and magnetic properties of ZnO nanorods by Ar ion irradiation," *Applied Physics Letters*, vol. 98, no. 18, p. 183109, 2011.

[29] M. Haupt, Ladenburger, R. Sauer, K. Thonke, R. Glass, W. Roos, J. P. Spatz, H. Rauscher, S. Riethmuller, and M. Moller, "Ultraviolet-emitting ZnO nanowhiskers prepared by a vapor transport process on prestructured surfaces with self-assembled polymers," *Journal of Applied Physics*, vol. 93, no. 10, p. 6252, 2003.

[30] A. Kushwaha and M. Aslam, "Defect induced high photocurrent in solution grown vertically aligned ZnO nanowire array films," *Journal of Applied Physics*, vol. 112, no. 5, p. 054316, 2012.