PRAMANA
— journal of
physics

Vol. 65, No. 5
November 2005
pp. 809–814

Growth of zinc oxide nanostructures

K SREENIVAS, SANJEEV KUMAR, JAYA CHOUDHARY and VINAY GUPTA
Department of Physics and Astrophysics, University of Delhi, Delhi 110 007, India
E-mail: kondepudysreenivas@rediffmail.com

Abstract. Zinc oxide (ZnO) nanowhiskers have been prepared using a multilayer ZnO(50 nm)/Zn(20 nm)/ZnO(2 μm) structure on a polished stainless steel (SS) substrate by high rate magnetron sputtering. The formation of uniformly distributed ZnO nanowhiskers with about 20 nm dia. and 2 to 5 μm length was observed after a post-deposition annealing of the prepared structure at 300–400°C. An array of highly c-axis oriented ZnO columns (70–300 nm in dia. and up to 10 μm long) were grown on Si substrates by pulsed laser deposition (PLD) at a high pressure (1 Torr), and Raman studies showed the activation of surface phonon modes. The nanosized powder (15–20 nm) and nanoparticle ZnO films on glass substrate were also prepared by a chemical route. Nanowhiskers showed enhanced UV light detection characteristics, and the chemically prepared ZnO nanoparticle films exhibited good sensing properties for alcohol.

Keywords. Zinc oxide nanostructures; magnetron sputtering; pulsed laser deposition; sensors.

PACS Nos 81.15.Cd; 81.07.-b; 72.40.+w

1. Introduction

The rapid developments in the field of nanoscale science have stimulated intense research efforts to fabricate novel miniaturized devices for applications in nanoelectronics and photonics [1]. ZnO is a promising wide band-gap material. In recent years it has drawn considerable attention and finds immense applications for UV lasers, detectors and gas sensors. The sensitivity of ZnO for various sensor applications is enhanced with the development of nanostructures due to increased surface-to-volume ratio. Ultra-thin ZnO films having smaller grains are reported to exhibit improved UV photoresponse characteristics [2]. ZnO nanostructures have been synthesized by a variety of techniques [3] and efforts are focused on gas-phase condensation utilizing sputtering and pulsed laser deposition (PLD) techniques which are known to yield stoichiometric and porous structures easily. In the present work we describe the growth of ZnO nanostructures at a moderate temperature of 400°C by unbalanced magnetron sputtering and PLD techniques. Alternately a simple chemical route has also been explored for the preparation of nanocrystalline ZnO thin films and powders. A significant improvement in the

UV light sensing characteristics and chemical sensing of alcohols is shown with the prepared ZnO nanostructures.

2. Experimental

In this study, ZnO nanostructures were prepared using different techniques. For the growth of ZnO nanowhiskers, firstly a thin-film multilayered structure of ZnO(50 nm)/Zn(20 nm)/ZnO(2 μm) was prepared by magnetron sputtering on a stainless steel (SS) substrate using a 6″ dia. Zn target (99.99%) at a RF power level of 600 W. Magnetron configuration was altered to provide an unbalanced magnetic field to generate *in-situ* ionic bombardment during film growth to yield a porous microstructure [4]. In the multilayer stack, the bottom-most layer (2 μm-thick ZnO film) was deposited at 30 mTorr in an $O_2 : Ar$ (80 : 20) gas ambient, and the ultra-thin metallic Zn layer (20 nm) was deposited in 100% Ar. The top 50 nm thick ZnO layer was deposited at a high sputtering pressure of 50 mTorr to ensure the formation of a porous film. The multilayer structure when annealed in air at an optimum temperature of 400°C for 1 h showed the formation of nanowhiskers on the surface. Using the XrF excimer laser-based PLD system an array of *c*-axis oriented ZnO nanocolumns were fabricated directly on a polished silicon substrate at a high oxygen pressure (>500 mTorr) and small substrate-to-target distance (25 mm). Laser pulses with an energy density of 3 J/cm^2 and a pulse width of 10 ns and a pulse repetition rate of 10 Hz were used. The surface morphology and the crystallographic orientation were examined with a scanning electron microscope (JEOL JSM-840), and a Philips X-ray diffractometer (PW 1830) respectively. Raman spectra were excited using the polarized light from a coherent INNOVA 99 Ar^+ laser ($\lambda = 514.5$ nm) and analyzed using a Jobin Yvon T64000 spectrometer equipped with a charge coupled device in a back-scattering geometry. UV photoresponse was measured under an applied DC bias of 5 V between two planar electrodes (2 mm apart) on film surface, and a UV lamp (Black ray; model B-100AP, $\lambda = 365$ nm) was used for UV illumination. The photoresponse transients were recorded using a Keithley 150B microvolt ammeter, and a Tektronix digital storage oscilloscope (TDS 3032B). The sensitivity of nanocrystalline films for alcohol sensing, observed as a change in resistance, was recorded with a Keithley (2000) digital multimeter.

3. Results and discussion

3.1 *ZnO nanowhiskers*

The surface microstructure of ZnO(50 nm)/Zn(20 nm)/ZnO(2 μm)/SS structure showed no appreciable change with post-deposition annealing up to 200°C. Interestingly at 300°C, formation of a few nanowhiskers was observed on the surface, and their presence was more prominent after an annealing treatment at 400°C (figure 1a). It may be noted from figure 1a that nanowhiskers were observed on the entire surface with an average diameter of about 20 nm, and their length varied from 2 to 5 μm. Only peaks corresponding to the wurtzite phase of ZnO were observed and

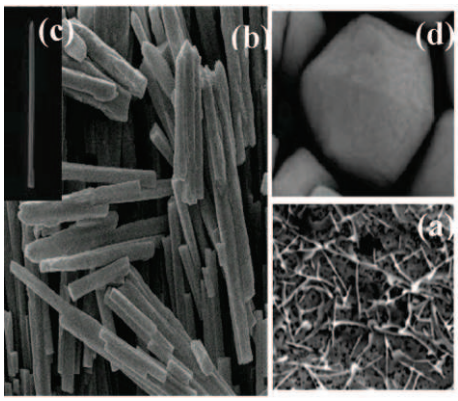

Figure 1. SEM images showing ZnO (**a**) nanowhiskers, (**b**) nanocolumns, (**c**) single column and (**d**) tip of the column.

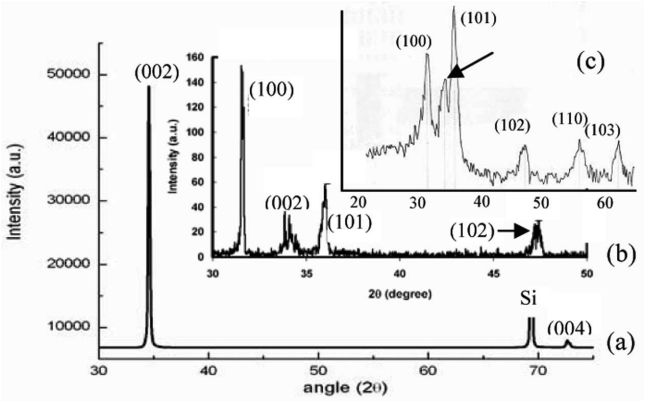

Figure 2. XRD profile of ZnO (**a**) nanocolumns, (**b**) nanowhiskers and (**c**) nanocrystalline film.

the X-ray diffractogram shown in figure 2b revealed a polycrystalline structure for the nanowhiskers.

The Zn layer (20 nm) and ZnO overlayer (50 nm) deposited at high pressure can be assumed to be distributed in the form of scattered islands, or nanoclusters. A post-annealing treatment at 400°C in air results in the conglomeration of the underlying Zn islands which have a high surface tension in the molten stage, and the ZnO overlayer nanoclusters could remain absorbed on them. These Zn droplets (or islands) serve as a nucleation center, and drive the growth of ZnO nanowhiskers in the horizontal direction. The ZnO nanoclusters are expected to coalesce together and recrystallize in the form of fine whiskers. The growth of nanowhiskers continued till the underneath molten Zn is completely consumed, or mixes with the ZnO nanoclusters after reacting with atmosphere oxygen in air at 400°C. Formation of nanowhiskers was not observed at higher annealing temperatures ($\geq$500°C), and could be due to the possible evaporation of Zn nanocluster without forming the

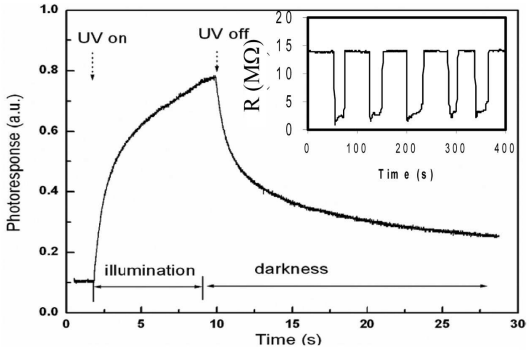

Figure 3. UV photoresponse of nanowhiskers. Inset: ZnO film alcohol sensor response.

intermediate molten phase (nucleating centers). The thickness of the intermediate Zn layer was very critical and nanowhiskers did not form when the thicknesses was more than 20 nm. Furthermore, the high sputtering pressure (50 mTorr) optimized for the deposition of ultra-thin ZnO overlayer (50 nm) was very important, and film deposition at lower pressures did not yield nanowhiskers at any annealing temperature.

The photoresponse of the ZnO nanowhiskers to UV light (λ = 365 nm, intensity = 1 mW/cm^2) is shown in figure 3. Upon illumination the photoconductivity transient in ZnO nanowhiskers increased rapidly in the initial stage, and then became relatively slower (figure 3). Upon switching off the UV light, the decay in the photoresponse was initially very sharp and then became slow. The initial fast rise in the photocurrent can be attributed to the electronic process which involves the generation of photogenerated carriers under UV light from the oxygen defects embedded at the grain boundaries. The growth of nanowhiskers at higher oxygen pressure (50 mTorr) and subsequently annealing at 400°C in air may incorporate oxygen at the grain boundaries.

3.2 *ZnO nanocolumns*

ZnO nanocolumns were fabricated directly on a Si substrate by PLD at a substrate temperature of 450°C. For the structure prepared at a substrate temperature >400°C, X-ray diffraction studies showed only (0 0 2) and (0 0 4) reflections of ZnO, indicating the growth of a preferred *c*-axis oriented column (figure 2a). The formation of isolated ZnO nanocolumns having hexagonal cross-section was observed (figure 1b) in the oxygen pressure range of 1–5 Torr. The average dia. of the columns at the optimum substrate temperature (450°C) was found to be 120–200 nm and the columns were vertically aligned on Si. The well-isolated columns coalesce at a higher substrate temperature of ∼800°C and get converted into a continuous film with large grains, and at lower substrate temperatures (<450°C) there was no evidence of isolated nanocolumns and a polycrystalline film with a rough and porous microstructure was formed. The key to the formation of well-aligned

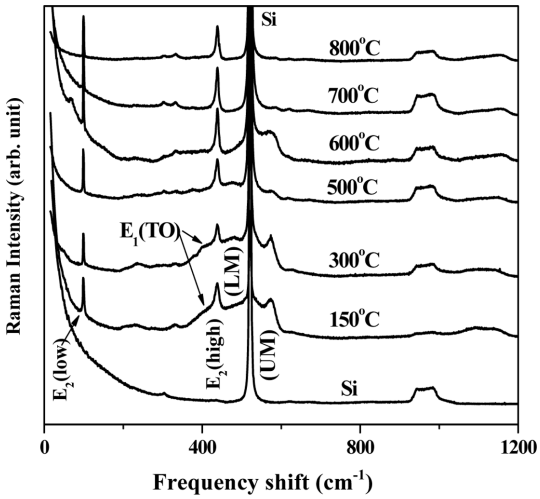

Figure 4. Raman spectra of ZnO nanostructures grown on Si by PLD at different substrate temperatures.

nanocolumns is the optimum growth temperature (400–650°C), essentially required to allow the settling of the ZnO nanoparticles one over the other. The diameter (70–250 nm) and length (up to 12 μm) of the columns were found to increase with increasing deposition time (2–20 min). The tip of the nanocolumn (5 μm long) is sharp (figure 1c) due to the self-nucleation of ZnO nanoparticles on Si along the c-axis growth direction.

Raman spectra of ZnO nanocolumns grown at various substrate temperatures (T_s) (RT to 800°C) are shown in figure 4. E_2 modes at 108 cm^{-1} and 438 cm^{-1} for the wurtzite phase were clearly observed. A broad E_1(TO) mode at 410 cm^{-1} is found due to the polycrystalline structure obtained at $T_s < 400$°C [5]. Absence of E_1(TO) mode at substrate temperatures >400°C indicates the growth of aligned c-axis oriented columns. A well-defined broad peak was seen in samples at ∼574 cm^{-1} that disappeared at higher temperatures ($T_s > 600$°C). Both E_1(LO) and A_1(LO) modes are reported to be very weak in ZnO as compared to TO modes [5]. Therefore this mode may be due to surface phonon scattering, which is expected when crystallites are much smaller than incident λ. Also this mode is present between the LO and TO frequencies where surface phonon modes are expected. Therefore, modes at 574 cm^{-1} and 477 cm^{-1} are assigned to upper (UM) and lower (LM) surface phonon mode respectively that are activated due to interaction of light with the surface of the nanocolumns, and are absent in samples grown at higher substrate temperatures ($T_s > 600$°C).

3.3 *Nanopowder and nanoparticle film*

An attempt was made to synthesize the ZnO nanopowder and nanoparticle film by the chemical route. 0.1 M Zinc acetate dissolved in ethanol solution was refluxed

at 70°C. 0.14 M Lithium hydroxide was dissolved in ethanol at room temperature in ultrasonic bath. The prepared solution was added slowly to zinc acetate solution under vigorous stirring until a clear solution was obtained [6]. The prepared clear solution showed an emission of light green colour when exposed to UV light and slowly shifted to yellow with aging. On the addition of n-heptane, a white precipitate was obtained. The supernatant was removed using centrifugation and the obtained white precipitate was washed with ethanol. ZnO nanopowder of about 15 nm particle size was obtained after heating the product at 200°C for 2 h. Ethanol was once again added to the washed precipitate for redispersion of ZnO particles and the solution was used to deposit a film by spin coating on a glass substrate. The deposited film was annealed at 400°C for 2 h. The XRD spectra showed that the films are polycrystalline in nature corresponding to the wurtzite phase of ZnO (figure 2c). The films showed a good response for ethanol sensing, and consecutive back to back runs (inset of figure 3) did not show any drift in the observed response characteristics.

4. Conclusion

ZnO nanowhiskers have been synthesized by annealing a multilayered structure of ZnO(50 nm)/Zn(20 nm)/ZnO(2 μm)/SS at 300 to 400°C. The thin Zn layer acts as a self-catalytic agent to nucleate ZnO nanowhiskers and showed enhanced sensitivity to UV light. The vertically aligned and highly *c*-axis oriented ZnO nanocolumns were fabricated directly on Si at 450°C and at a high pressure 1–5 Torr. The activation of two surface phonon modes was observed in the Raman spectra of isolated nanocolumns. Nanoparticle ZnO films exhibited stable and fast response characteristics for sensing ethanol.

Acknowledgements

Authors thank the Department of Science and Technology (DST), Government of India for the financial support, and the two authors (SK and JC) thank the CSIR for research fellowship.

References

[1] M S Gudiksen, L J Lauhon, J Wang, D C Smith and C M Lieber, *Nature (London)* **415**, 617 (2002)
[2] Y Takahashi, M Kanamori, A Kondoh, H Minoura and Y Ohya, *Jpn. J. Appl. Phys.* **33**, 6611 (1994)
[3] *The chemistry of nanomaterials* edited by C N R Rao, A Muller and A K Cheethan (Wiley-VCG Verlag GmbH & Co. KGaA.Weinheim, 2004)
[4] Sanjeev Kumar, Vinay Gupta and K Sreenivas, *Nanotechnology* **16**, 1167 (2005)
[5] C A Arguello, D L Rousseau and S P Porto, *Phys. Rev.* **181**, 1351 (1969)
[6] E A Meulenkamp, *J. Phys. Chem.* **B102**, 5566 (1998)