Optical and structural properties of ZnO nanostructure synthesized by thermal evaporation method

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ABSTRACT

Presently, ZnO nanostructures have found an intensive interest due to its wide applications in solar cells, UV lasers, nanogenerators, light emitting diodes, piezoelectronics, gas sensors and field emission devices. In this work, ZnO nanostructure is grown and characterized by field emission scanning electron microscope (FESEM), Energy Dispersive Miscrocope (EDS), X-ray diffraction (XRD) and photoluminescence (PL). Two emission peaks at wavelength 380 nm and 521 nm have been observed which corresponds to near band edge of bulk ZnO and green emission respectively. These peaks have been attributed to the excitonic transitions occurred from valence to conduction band and electronic transitions occurred between deep level defect states due to oxygen vacancies and interstitial of zinc. XRD measurement showed the hexagonal phase of synthesized ZnO nanostructure. FESEM analysis showed that the prepared ZnO nanostructure is composed of nanorods/nanowires in hexagonal shape with the diameter about 40 nm while EDS measurement has confirmed dense nanostructure with the compositional peaks of zinc and oxygen peaks.

Keywords: Thermal Evaporation, Photoluminescence, ZnO Nanostructure, Hexagonal Phase.

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INTRODUCTION

ZnO is a II–VI semiconductor material with wide band gap (3.37 eV), high piezoelectric constant and good physical and chemical stability and a large exciton binding energy of 60 meV which is responsible for excitonic ultraviolet emission at room temperature. Nanostructured materials have got great interest by the scientific community due to their amazing physical and chemical properties as comparison to bulk material. A wide band gap material has many benefits like high temperature and power operations, reduced electronic noise and raising breakdown voltages. ZnO has possible applications in gas sensors due to its large surface area which enhances the sensing properties of the sensors. Further, due to bio-safe characteristics of ZnO makes it suitable material for biomedical applications. Due to the presence of interstitial defects and vacancies ZnO nanowires are reported to have behave like a n-type semiconductor. A serious problem associated with ZnO is p-type doping which limits its application in electronics and photonics. In-fact, few publications have been reported on p-type doping (Ga and N co-doping method). However, successive p-type doping to ZnO can boost up its promising application in nanoscale devices where p-type and n-type ZnO nanowires can result as p-n junction diodes and LEDs further, field effect transistors based on such mechanism can be useful for the fabrication of complementary logic circuits. Excitonic emissions have been observed from ZnO nanorods however, the intensity of green emission increased with decreased diameter of nanowires which is as a result of larger surface-to-volume ratio of thin nanowires which favors a higher level of defects and surface recombination. Further, red luminescence band has been attributed to the doubly ionized oxygen vacancies however, quantum confinement yields blue shift in the near UV emission peak ZnO nanobelts.

Various techniques are available for the synthesis of ZnO nanostrcutures such as thermal evaporation, laser ablation, template assisted growth, chemical vapor deposition (CVD)/oxidation, metal-organic vapor-phase epitaxy, metal-organic CVD, template-assisted growth, sol-gel method, chemical bath deposition etc. [1-9]. Among these methods the thermal evaporation is the most widely used as it is more simple, economic and tunable to its desired properties. A. Wisitsoraat et al. have demonstrated a new technique for the synthesis of ZnO nanostructure by using thermal evaporation of ZnO-CNTs mixture [10]. They synthesized ZnO polypods including tripods, tetrapods, mulitpods with triangular nanobelts/nanoneedles by thermal evaporation of ZnO-CNTs mixture. However, by thermal evaporation of ZnO and graphite powder under the same condition has produced ZnO particles and short rods. In addition, considerable carbon content in ZnO nanostructure is observed by EDX. The single crystal structure of ZnO polypods is confirmed by XRD and TEM whereas photoluminescence analysis showed flat green luminescent band between 480 and 530 nm. Aurangzeb Khan et al. have synthesized metallic Zinc nanowires by thermal evaporation and vapor transport methods at low substrate temperature (100–200 ^{0}C) with a mixture of ZnO and graphite powder of ratio 2:1 by weight is heated at nearly 1000 ^{0}C [11]. TEM and XRD analysis confirmed the crystalline nature of prepared ZnO nanowires. The characteristics of ZnO material is confirmed by cathodoluminescence and photoluminescence measurements, which showed a band edge ultra violet peak emission at 381 nm and a broad band centered at 495 nm. The proposed technique of nanowire synthesis is found to be useful for the preparation of nanostructure and nanodevices with low cost. Further, Y B Hahn et al. have reported the growth of perfectly hexagonal-shaped ZnO nanorods on nickel-coated Si(100) substrate via thermal evaporation using metallic zinc powder and oxygen [12]. The characterized samples showed that the synthesized nanorods were single crystalline with the wurtzite hexagonal phase and preferentially grown along the c-axis direction. The ZnO nanorods showed a strong band edge emission with very weak or no deep-level emission. A clear observation of free excitons at low temperatures (13–50 K) has found which indicates the high quality of as-grown ZnO nanorods. D. Yuvaraj et al. have grown the zinc film containing hexagonal plate stack and tower-like microstructures on Si substrates at high temperature by thermal evaporation [13]. They found that the ZnO nanoneedles selectively grown from the facets of the zinc microstructure at temperature above 300 ^{0}C in atmosphere however; TEM analysis showed that single crystalline and bicrystalline nanoneedles were formed in this oxidation process. Further, based on the structural and morphological analysis, a possible mechanism for the selective growth of ZnO nanoneedles during thermal oxidation was proposed. Y.B. Hahn et al. have presented the growth of ZnO nanowires on silicon (100) substrates by oxidation of metallic Zn powder at temperature 600 ^{0}C [14]. TEM analysis and SAED patterns showed that the as-grown nanostructures were highly crystalline in nature and grown along the [0 0 0 1] direction and the obtained result was found consistent with the XRD analysis. The obtained ZnO nanowires of diameter 30–60 nm and length 2–4 mm showed a reduced near band edge emission in the UV region at 380 nm alongwith a strong deep level emission observed in the visible region at 500–530 nm at room temperature. Zhong Lin Wang et al. have demonstrated an effective approach to grow large-area, hexagonally patterned and aligned ZnO nanorods. The synthesis was based on a catalyst template produced by a self-assembled monolayer of submicron spheres and guided vapor–liquid–solid (VLS) growth on a single crystal alumina substrate [15]. The obtained ZnO nanorods were observed uniform in shape and length with vertically aligned on the substrate and distributed according to the pattern defined by the catalyst template. The explored approach have possibility of creating patterned one-dimensional nanostructures for applications as sensor arrays, piezoelectric antenna arrays, optoelectronic devices, and interconnects. Q.X. Zhao et al. have reported the zinc oxide nanorods by vapor-liquid–solid (VLS) catalytic growth [16]. The obtained results showed the formation of ZnO nanostructure strongly influenced by the growth conditions and used substrates. It is notable that the oriented ZnO nanorods were grown on a substrate with a similar crystalline structure as ZnO. The diameter and length of oriented-ZnO nanorods grown on silicon substrate were found to be ~300 nm and 20-35 µm respectively; further using optical pumping lasing action is achieved at room temperature. Qian Liu et al. have reported the epitaxial growth of ZnO nanosheets and nanoneedles from a Zn/ZnO core/shell structure by thermal oxidation of Zn films made up of hexagonal nanodiscs or nanoprisms within an ultra-low temperature range from 250 to 400 ^{0}C [17]. They observed that the stability difference among different facets of hexagonal Zn crystal structures plays a key role in the formation of ZnO nanosheets, nanoneedles and the Zn/ZnO core/shell structure as well as ZnO hollow structures. Further, vapor–solid mechanism is suggested to explain the epitaxial growth process of the ZnO products. B. Postels et al. have reported the growth of high density vertical ZnO nanorods on silicon substrates coated with Au by using electrochemical technique [18]. They have observed the variations in nanorods diameter from 100-250 nm with corresponding lengths of 1-4 µm. They achieved the growth of ZnO nanorods between neighbouring strip conductors bridging the gap between them further photoconductivity was measured after annealing the sample at 300 ^{0}C. Tena-Zaera et al. have grown the ZnO nanowire arrays from the reduction of dissolved molecular oxygen in solutions containing different anions [19]. By changing the nature of anions in the solution, a significant variation in nanowires diameter from 65-110 nm with corresponding lengths of 1-3.4 µm was obtained. Nanowires exhibiting the lowest and highest aspect ratios were obtained in chloride and acetate solutions respectively. By X-ray diffraction measurement no spurious phases were observed hence, changing the chemical nature of the anions in solution allows for the dimensions and the deposition rate of electrodeposited ZnO nanowire arrays to be controlled.

In this paper, thermal evaporation method is employed for the synthesis of ZnO nanostructure. In Section 2, the details of synthesis process have been presented. The structural and optical properties of prepared ZnO nanostructure are discussed in Section 3. Finally, Section 4 concludes the paper.

MATERIALS AND METHODS

We have used thermal evaporation method to synthesize ZnO nanostructure on p-type (100) silicon substrate. For synthesis, the source material i.e. mixture of as purchased ZnO and graphite powders of ratio 1:1 was kept in the centre of the quartz tube. While silicon substrate of 1.5 cm^2 was kept at the end of the tube towards downstream of N_2 gas with distance ~5-10 cm from the source material. Before placing the silicon substrate in the tube it was cleaned with a buffer solution to remove the native oxide layer and further washed with de-ionized water. The temperature of the furnace was ramped upto 1050 ^{0}C at a rate of 50 °C per minute under the constant flow of high purity N_2 as carrier gas (30-35 SCCM). The process was done for 30mins and further after the furnace cooled to room temperature the silicon substrate taken out from the tube for the characterization. The surface of silicon substrate was found whitish in color. The morphology and composition of the as prepared sample was examined by field emission scanning electron microscope (FESEM, Hitachi S-4800) scanning electron microscopy. The structural property of the as prepared sample was analyzed by X-ray diffraction (D8 Advance, Bruker AXS). Photoluminescence measurement was done at room temperature using xenon lamp as the source with excitation wavelength 325 nm (Photoluminescence Spectrometer, PerkinElmer-LS-55).

RESULTS AND DISCUSSION

The crystallinity and crystal phase of ZnO nanostructure synthesized on silicon substrate was examined by x-ray diffraction (XRD) which is shown in figure 1. XRD pattern shows the intense peaks at 2θ values corresponding to (100), (002), (100), (102), (110), (103), (112), (201) (004) and (202) planes of hexagonal phase of ZnO nanostructure.
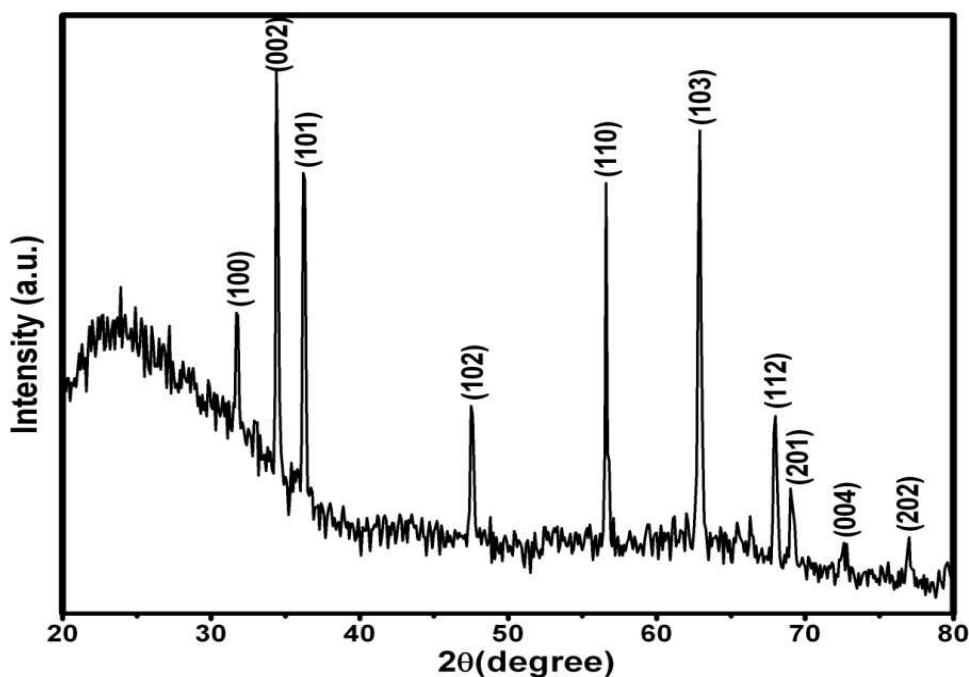

Figure 1. X-ray diffraction pattern of as prepared ZnO nanostructure

The obtained XRD pattern has got good matching with others reported works [10, 20] and standard JCPDS data (Card No.36-1451). The sharp peaks in the XRD spectra confirmed the high degree of crystallinity of prepared ZnO nanostructure.

Figure 2 shows FESEM images of ZnO nanostructure prepared at 1050 ^{o}C for 30mins. Figure 2(a) and (b) reveals that the prepared nanostructure consists of hexagonal shaped of ZnO nanorods and nanowires grown on silicon substrate. Figure 2(c) is the magnified image of figure 2(b) in which formation of nanowires can be visible and figure 2(d) depicts the high magnification image of ZnO nanowires with average diameter about 40 nm.
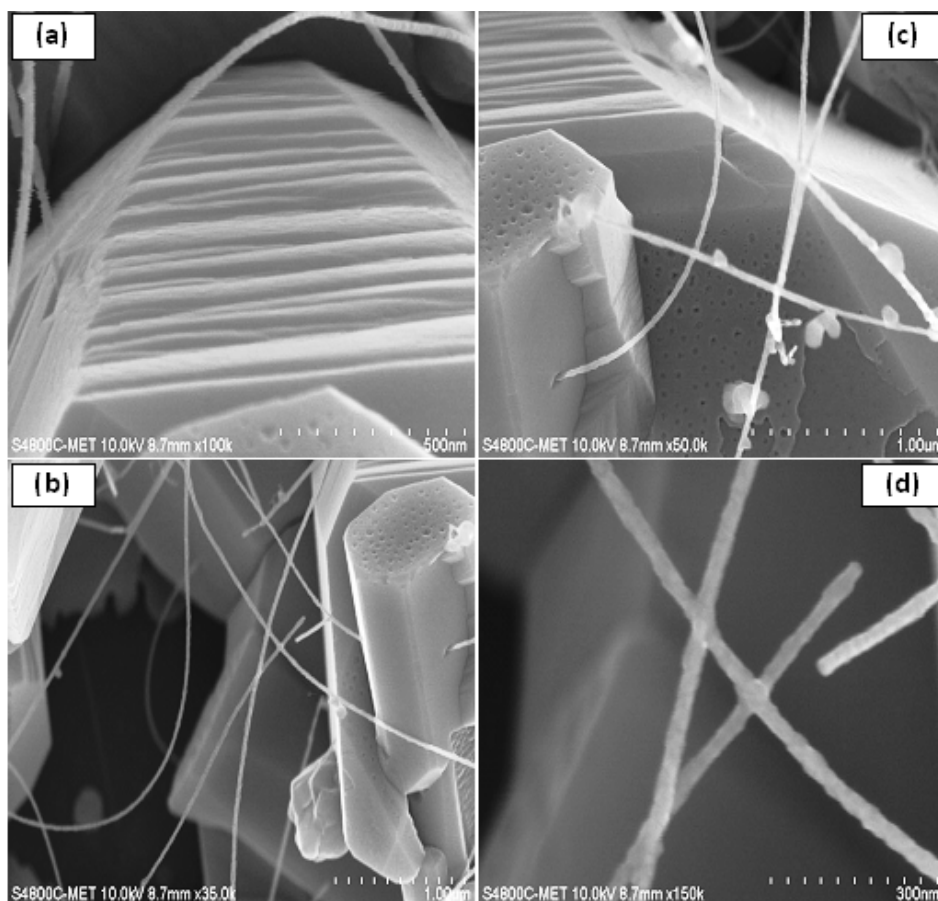
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Figure 2. FESEM images of ZnO nanostructure prepared on silicon substrate

The chemical composition of prepared ZnO nanostructure was observed by an energy dispersive scanning (EDS) spectroscope attached to FESEM. Figure 3 depicts EDX spectra of as prepared ZnO nanostructure by thermal evaporation on silicon substrate which confirms that the synthesized product is composed of zinc and oxygen. However, the presence of silicon peak in the spectrum is due to the used silicon substrate. Our result is good consistent with others reported works [12, 14].
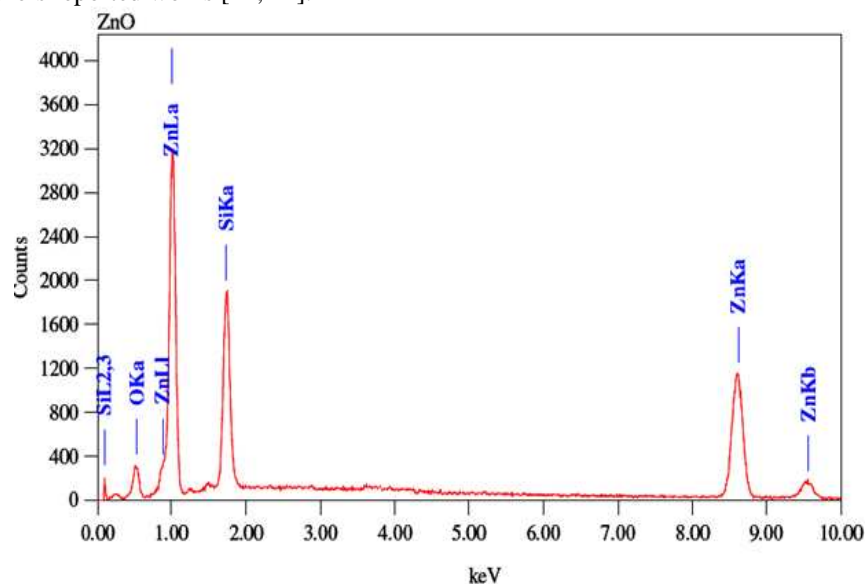

Figure 3. EDS pattern of ZnO nanostructure showing elemental composition

The room temperature PL spectrum of ZnO nanostructure prepared by thermal evaporation is shown in Figure 3. In PL spectrum two emission peaks can be clearly observed at 380 nm and at 521 nm. The emission peak at ~380 nm is corresponding to the near band edge of ZnO whereas a peak at ~521 nm indicates green emission.
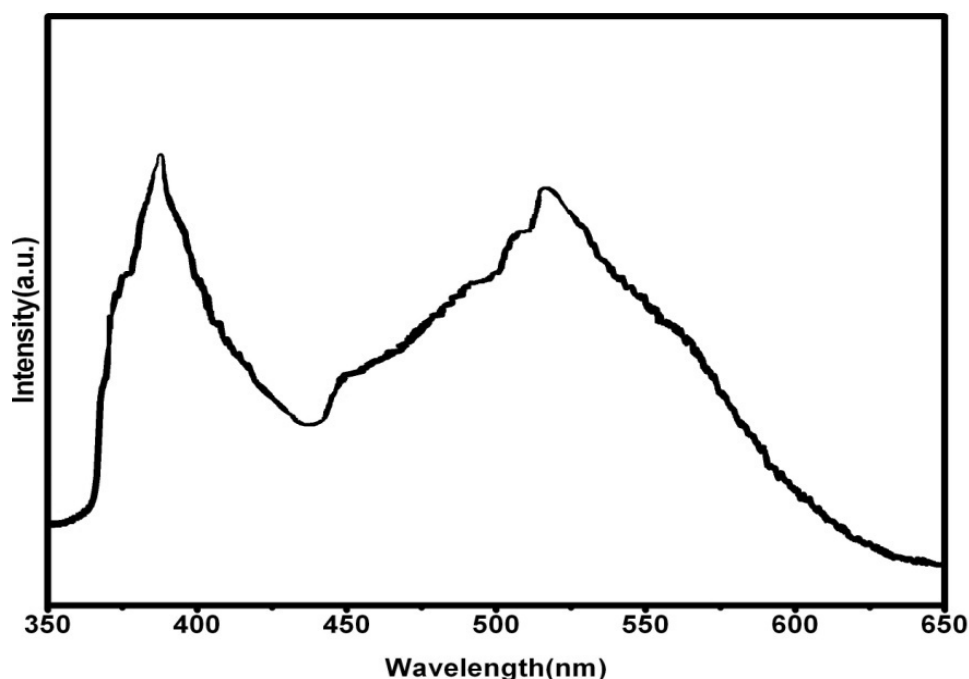
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Figure 4. Photoluminescence of as prepared ZnO nanostructure prepared by thermal evaporation

The near band edge emission is attributed to the excitonic transitions occurred from valence to conduction band however, green emission is attributed to the electronic transitions occurred between deep level defect states due to oxygen vacancies and interstitial of zinc. [10-12, 14, 21].

CONCLUSION

We have used thermal evaporation method to synthesize ZnO nanostructure on p-type (100) silicon substrate. The crystallinity and crystal phase of ZnO nanostructure were examined by XRD and confirmed hexagonal phase of ZnO nanorods/nanowires. The nanostructure composed of nanorods/nanowires was observed by FESEM with the diameter about 40 nm. EDS analysis shown that synthesized product is composed of zinc and oxygen whereas silicon peak is of silicon substrate used. By room temperature PL measurement two emission peaks were observed at 380 nm (near band edge) and at 521 nm due to green emission. The near band edge emission is attributed to the excitonic transitions occurred from valence to conduction band however, green emission is attributed to the electronic transitions occurred between deep level defect states due to oxygen vacancies and interstitial of zinc.

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