Synthesis and characterization of ZnO nanostructures using modified chemical bath deposition method

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ZnO thin films were deposited using a simple, convenient and an inexpensive modified chemical bath method along with subsequent air annealing. The reaction mechanism for the growth of the ZnO nanostructure after the air annealing is also discussed. SEM observations reveal the formation of flowerlike nanostructures that are composed of leaf-like petals of thin nanosheets. The annealed ZnO nanostructures grow with the hexagonal crystal structure. The ZnO nanostructure exhibits a blue shift in its optical absorption spectrum. The room temperature photoluminescence study reveals UV emission peaks due to near band edge emissions along with defect related blue and green emission peaks.

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1. Introduction

The structural, electrical, optical, and mechanical properties of nanocrystalline semiconductors can be tuned with respect to size, shape, morphology, orientation, and defect states originated during the growth process \cite{1}. Hence control on morphology, size, orientations and defect states of nanomaterials continues to attract considerable attention, as these factors of nanomaterials have great influence on their above mentioned properties. It also opens a new window for the researchers to synthesize novel materials that behave uniquely with improved functionality \cite{2}. Amongst various other semiconducting materials, zinc oxide (ZnO) is widely studied because of its abundance in earth, environmental friendly nature, low cost, wide band gap, large exciton binding energy (60 meV) at room temperature, high transmittance in the visible region and excellent thermal and chemical stabilities \cite{3}. ZnO theoretically enables emissions of a full colour spectrum in a wide range, which covers red, blue, green and orange regions \cite{4}. Therefore, ZnO is a promising potential candidate for white light-emitting materials. Accordingly, designing ZnO with novel morphologies and nanostructures is of great importance for fundamental research as well as high-technological applications.

In the present work, we reported a cost effective modified chemical bath deposition (MCBD) route to deposit ZnO thin films with flowerlike nanostructure composed of leaf-like petals of thin nanosheets. The as-deposited thin films fabricated at lower temperatures usually were composed of hydroxide species, and other defects like voids, pinholes and grain boundary discontinuities. Annealing the as-deposited thin films reduces these defects, transforms hydroxide content into corresponding oxides and improves the crystallinity along with the recrystallization process. Hence, the as-deposited thin films were thermally annealed in air atmosphere at 300 °C for 2 h, and their structural, morphological and optical properties were investigated.

2. Experimental section

In a typical procedure, an appropriate amount of Zn(CH\textsubscript{3}COO\textsubscript{2} (0.2 M) was dissolved in 100 ml of deionized water (Milli Q 18 - 2 M\textOmega) in a beaker. An appropriate amount of aqueous ammonia was dripped into the solution and the precursor solution was heated to 60 °C prior to deposition. Then clean glass substrates were immersed in the resultant precursor solution for 40 s, for the
adsorption of [Zn(NH$_3$)$_4$]$^{2+}$ species on the substrate surface. In the second step, the zinc ammonia complex adsorbed substrate was immersed into a beaker containing deionized water maintained at the same temperature for 20 s, to convert the zinc ammonia complex into zinc hydroxide (Zn(OH)$_2$). After completion of five deposition cycles, the substrate was dried using a hair drier and used in further deposition processes. In the present work, 50 deposition cycles were conducted to complete the deposition process.

The pre-deposited substrates were annealed in air atmosphere at 300 °C for 2 h for the transformation of Zn(OH)$_2$ phase to ZnO. The crystal structure was determined using an X-ray diffractometer (Mac Science MXP18). The morphology of the ZnO product was observed using a scanning electron microscope (SEM) (JEOL, JSM-5600) equipped with an Oxford energy dispersive X-ray spectrometer (EDS). The optical absorption was recorded using a UV–visible spectrophotometer (Hitachi Model-330, Japan). Photoluminescence (PL) spectra of the products were analysed using a Hitachi F-4500 model.

3. Results and discussion

The reaction mechanism involved in the MCBD method, during the growth process, is as follows:

$$\text{Zn(CH}_3\text{COO)}_2 + 4\text{NH}_3 \rightarrow [\text{Zn(NH}_3\text{)}_4]\text{^{2+}} + [\text{CH}_3\text{COO)}_2]\text{^{2-}}$$

Above room temperature, the conversion of [Zn(NH$_3$)$_4$]$^{2+}$ into Zn(OH)$_2$ with the release of ammonia gas in the solution is possible. This can be illustrated as follows:

$$[\text{Zn(NH}_3\text{)}_4]\text{^{2+}} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 + 4\text{NH}_3\uparrow$$

The reaction that takes place during the conversion of Zn(OH)$_2$ into ZnO under thermal treatment in air at relatively higher temperatures proceeds as follows:

$$\text{Zn(OH)}_2 \rightarrow \text{Zn}^{2+} + 2\text{O}^2^- + 2\text{H}^+$$

$$\text{Zn}^{2+} + 2\text{O}^2^- + 2\text{H}^+ + \text{O}_2\uparrow \rightarrow [\text{Zn}^{2+} + \text{O}^2-] + \text{O}^2^- + 2\text{H}^+ + \text{O}_2\uparrow$$
(\text{Zn}^{2+} + \text{O}^{2-}) + \text{O}^{2-} + 2\text{H}^+ + \text{O}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O} + \text{O}_2$

Fig. 1(a) shows the XRD pattern of the ZnO thin film annealed at 300°C for 2 h. The comparison between the observed and standard diffraction peak positions and relative peak intensities conforms the hexagonal phase for the zinc oxide thin films (JCPD no. 36-1451). The well resolved XRD peaks of the diffraction pattern indicate that the ZnO thin film was well crystallized after the post-reaction annealing treatment. The average crystallite size of ZnO thin films was calculated using Scherrer’s formula [10] and is equal to 28 nm, that reveals the nanocrystalline nature of the ZnO thin film. The typical EDS pattern of the ZnO thin film is shown in Fig. 1(b). The strong peaks for Zn and O were detected in the EDS spectrum, and no impurity peaks were detected. The average atomic percentage ratio of Zn:O was 52:48, showing that the ZnO product was slightly rich in zinc species.

Fig. 2(a, b) shows the SEM images of the as-deposited ZnO thin film. It shows flowerlike nanostructure with an average size of about 10 μm, which are composed of thin nanosheet petals with thickness of about 50–75 nm and sheet width in the range of 3–4 μm. Fig. 2(c, d) shows the SEM images of the ZnO thin films annealed at 300°C for 2 h. No significant change was observed in the morphology of the as-deposited ZnO nanostructures, except slight rupture at the edges of the nanosheets. Fig. 2(e, f) shows the SEM images of the ZnO thin films annealed at 400°C for 2 h. It clearly reveals that the flowerlike nanostructures get ruptured and the film surface becomes somewhat smoother.

Fig. 3(a) shows the optical absorbance versus wavelength plot for the ZnO thin films annealed at 300°C. The absorption peak was centred at 363 nm, with a corresponding band gap of 3.432 eV that was slightly blue shifted with respect to the bulk band gap value of ZnO ($E_g = 3.3$ eV). It is due to the nanocrystalline nature of the ZnO nanostructures. It also shows small absorption peaks at longer wavelengths, implying that shallow and deep defect states emerged during the annealing process, which is consistent with the subsequent PL observation. The ZnO thin film contains numerous defects such as oxygen vacancies (V$_O$), zinc vacancies (V$_{Zn}$), interstitial zinc (Zn$_i$), interstitial oxygen (O$_i$) and antisite oxygen (O$_{2s}$). Thus the deep-level visible emission was caused by these intrinsic defects present in ZnO film [11]. In order to study PL properties, the room temperature PL spectra of the ZnO product with excitation wavelengths 300 and 325 nm were studied and are shown in Fig. 3(b). The figure depicts that the emission intensity decreases with increasing excitation wavelength. The results are consistent with our earlier report [12] as expected. It gives an emission peak centred at 394 nm, which is the near band edge emission, and a blue emission at around 460 nm with a small shoulder centred at 525 nm (green emission). The peak centred at 394 nm corresponds to the near band edge emission (NBE) and could be attributed to the recombination of the free excitation [13]. Zeng et al. [14] reported and experimentally validated that the blue emission (460 nm) of ZnO nanoparticles could originate from transitions involving Zn interstitial defect states, which is consistent with the elemental analysis presented in Fig. 2. The broad and weak green emission peak at 525 nm might originate from a singly charged oxygen vacancy that results from the recombination of a photo-generated hole with a charge state of the specific defects, such as oxygen vacancies, or that results from the surface deep traps or point defects [15]. It is also worth noting that the PL spectrum excited at 325 nm reveals a significant enhancement in the blue emission peak, indicating that the PL properties of semiconducting materials depend on the excitation wavelength. The ZnO nanostructure in thin film form exhibit significant PL emission in the visible range which revealed that there exist abundant crystal defects in deposited thin films, with more exposed surface areas and potentially good candidate for making new chemical sensors and solar cells [15]. It is inevitable to explore that the intensities of band edge emission and defects related PL emission significantly depends on the wavelength that was used for excitation. Also, if we dope the impurity materials such as Eu$^{3+}$ to enhance red light emission, then the present ZnO thin films can be used as intriguing candidates for white light emitting diodes.

4. Conclusion

A simple MCBD method was developed to synthesize interesting ZnO nanostructures. The growth mechanism of these ZnO nanostructures is mainly based on the formation of Zn(OH)$_2$ and
its subsequent decomposition to ZnO after air annealing. The annealed ZnO nanostructure exhibits a hexagonal wurtzite-type structure with a slight blue shift in the band gap because of its nanocrystalline nature and interesting morphological evolution. The room temperature PL spectrum shows UV and blue emission peaks along with a weak green emission. The PL emission covers a wide range in the visible region due to defects that originated during the crystal growth, giving new insights into their potential applications in chemical sensors, solar cells and light emitting diodes.

References