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Fabrication and optoelectronic characterisation of ZnO photonic structures

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Abstract

Zinc oxide (ZnO) is recognised as a potential II–VI photonic semiconductor and wavelength-scale ordered patterning of such material helps favourably in tailoring the photonic properties. Here we present two novel approaches for fabricating ZnO photonic structures, namely, via a synthetic route and via electrochemical deposition. We demonstrate fabrication of well-ordered mesa and microphotonic structures from self-assembly of template-assisted electrochemical deposition. We have explored various aspects of the fabrication techniques for achieving an optimized performance. Several optical, electrical and structural techniques are used to highlight the potential utility of these ZnO photonic structures. Our results suggest that these structures show promise in many novel photonic applications.

Keywords: Optical materials and properties; Microstructure; Semiconductors, ZnO nano and mesophotonic structure

1. Introduction

Zinc oxide (ZnO) is recognised as a potential II–VI photonic semiconductor materials owing to its wide band gap (~3.37 eV) and high exciton binding energy (~60 meV) [1]. It possesses considerable potential for applications in optoelectronic devices such as UV lasers, gas and bio sensors. Nanostructuring and/or wavelength-scale ordered patterning of ZnO should assist the tuning of optoelectronic properties even more usefully. The last few years have witnessed tremendous efforts on understanding the physical and optical properties of ZnO with particular attention on fabrication and device applications [2]. Many fabrication methodologies and top–down approaches have been applied to obtain high quality nano/microstructured ZnO thin films [3,4]. It is also well established that ZnO optoelectronic properties strongly vary depending on the fabrication and it is highly desirable to fabricate high quality devices at low cost. Recently, we explored an economical way of fabrication for high quality semiconductor photonic structures from self-assembly templating followed by electrochemical deposition [5].

In this paper, we demonstrate two important and economical ways of fabricating ZnO nanostructures: chemical synthesis and template-assisted electrochemical deposition. We optimise the growth parameters by measuring various optical, structural and electrical properties. With our studies, based on characterisation, we demonstrate the quality and further exploratory evidence for potential applications of these structures.

2. Experimental

Two separate ways of fabrication of ZnO were taken up to produce (1) nano to microsized ZnO spheres and (2) micro and nanoporous inverse opal ZnO structures. For the primary task, the ZnO nanoparticles were synthesised by the hydrolysis of Zinc Acetate dihydrate (ZnAc) with Diethylene Glycol (DEG) from two-step synthesis [6]. For electrochemical deposition we have used two kinds of electrolytes under potentiostatic configuration: (1) aqueous mixture of 5 mM $ZnCl_2$ and 0.1 M KCl and (2) 0.1 M of aqueous $Zn(NO_3)_2$, using ITO coated glass as a conductive substrate. For template-assisted growth,

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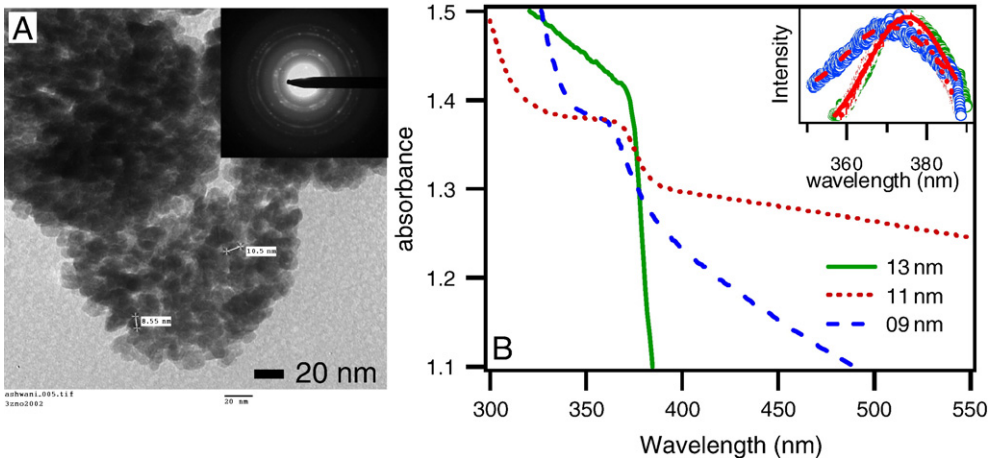

Fig. 1. (A) TEM picture of ZnO nanoparticles with inset of SAED pattern, (B) Absorption and emission (inset) of various sizes of nano-ZnO. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

self-assembled latex spheres were used as a template and Zinc Hydroxide has been electrodeposited into the interstitial spaces of polymer spheres [5]. Subsequently, the polymer spheres were removed using appropriate organic solvents, resulting in Zinc Hydroxide inverted voids as perfect replica of the spheres. Both bare and microstrutured Zinc Hydroxide samples were annealed at 400 °C for 12 h to obtain crystalline ZnO.

Various characterization techniques, namely, TEM, SEM, X-ray Diffraction (XRD), absorption, photoluminescence and nonlinear optical properties were employed for evaluating their performance. Photoluminescence (PL) measurements are carried out using a 1 kHz pulsed Nitrogen laser (337 nm) as an excitation source. Nonlinear optical properties studied using the *Z*-scan technique with a 532 nm Nd-YAG laser (6 ns, 10 Hz, with 4 mm input beam diameter) and a lens of 60 mm focal length. All the characterizations were performed at room temperature.

3. Results and discussion

Transmission electron microscope (TEM), reveals that the ZnO nanospheres obtained from the two-step synthesis are ranging between 5 to 13 nm mean radius (Fig. 1A). Selective area electron diffraction (SAED) and XRD of these ZnO nanospheres confirm high quality wurtzite crystalline structure (inset Figs. 1A and 2A). However, these structures are prone to agglomerate quickly (80–200 nm clusters) and no further capping has been utilised to avoid such agglomeration. Optical absorption and emission spectra of these ZnO nanospheres clearly show excitonic related absorption/emission peak, shifting towards the blue region as the size decreases (Fig. 1B). Though the size of the synthesised ZnO nanospheres is larger than the bulk exciton radius (~2.3 nm) [7], both absorption spectra and emission shows a distinct blue shift with decrease in size. Theoretical modelling based on the effective mass approximation, assuming ZnO nanoparticles as spherical, demonstrate weakly confined quantum effects and are in agreement with other reports.

Another inexpensive approach we investigated was template-assisted electrochemical deposition to fabricate periodic and quasi-periodic nano/microstructured ZnO. We have demonstrated that the pore sizes could be reduced down to 50 nm and as large as several microns. Prior to template-assisted growth, we modify various electrochemical deposition conditions and parameters, including the electrolyte recipe, with a view to improve the surface quality, optical properties and electrical conduction processes. Both from nitrate and chloride electrolyte solutions we observe relatively smooth ZnO thin film deposition, in contrary to earlier findings where ZnO growth was reported as irregular and uncontrollable [8,9]. We also observe strong

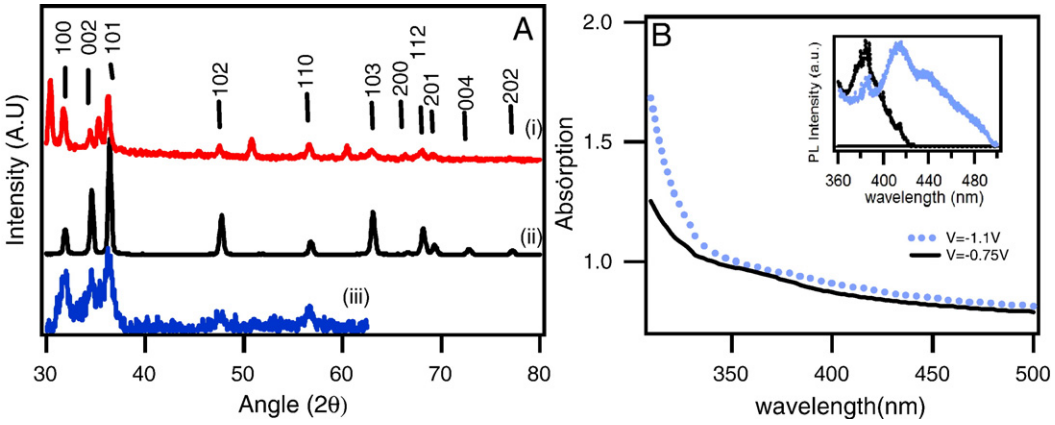

Fig. 2. (A) X-ray Diffraction of ZnO ((i) and (ii) are for electrodeposited thinfilm deposited at −0.75 and −1.1 V deposition potentials respectively and (iii) for synthesized nanoparticles; (B) Optical absorption spectra of electrodeposited thinfilm deposited at −0.75 and −1.1 V respectively. Inset is the photoluminescence of respective samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

dependence of optical and optoelectronic properties on deposition parameters. Fig. 2A shows the wurtzite crystalline nature of ZnO, prepared from various deposition conditions. Fig. 2B shows the optical absorption features of two samples deposited at two different potentials, −0.75 V and −1.1 V, from $Zn(NO_3)_2$ solutions. Both the spectra shows a distinct absorption peak related to the exciton at about λ=360 nm and inset of Fig. 2B shows corresponding PL spectra of ZnO samples. Though the X-ray diffraction and optical absorption did not show any difference, PL spectra show marked differences with one UV emission centered at ~380 nm and other a broad blue–green (~420 nm) emission. While the former UV emission can be attributed to excitonic transitions, the latter could be due to deep level defects, which are associated with oxygen vacancy defects and interstitial Zn ions. It is possible to conclude from these results that the slow growth rate (lower potential deposition) would result in more defect-free ZnO. Therefore, appropriate choice of deposition parameters is crucial to suppress or enhance defect-related emission of ZnO.

Having developed ZnO growth which can be smooth and controlled, we use it to template ZnO nanostructures. We have fabricated nano/microvoids by template-assisted electrochemical growth, with various potentials ranging from −0.75 V to −1.12 V. For all the conditions we are able to obtain uniform filling of interstitial spaces with relatively smooth films (Fig. 3A and B) and thickness more than two spheres height. However, for bigger diameter (3 μm) sphere templates, structures grown above half sphere height and below full sphere are unusually flexible and collapse on their own (Fig. 3B).

The photoconductivity response of electrochemically-deposited samples were measured using a setup containing a UV–VIS lamp, monochromator, potentiostat, chopper (at 80 Hz) and a lock-in amplifier (Fig. 4A and B). The photocurrent response obtained was a broad symmetric band with a clear maximum at the exitonic band position (~360 nm). It also shows a marked shift to the UV with a decrease of the deposition potential. Unlike the PL response, we have not observed any photocurrent contribution from defect-related energy states, which are in the region of λ=400–500 nm. When changing the bias voltage from −0.1 V to +0.1 V, the photocurrent response increases with a sightly red-shifted peak maximum centred at ~360 nm. The increase of UV-driven photocurrent under various bias conditions indicates significant light absorption and photo-carrier generation in ZnO, which is a favourable result for electro-photonic devices.

As exemplary evidence, we have also performed third-order nonlinear optical response for one of the electrochemically-deposited ZnO film (deposited at −0.9 V potential with 1.3 μm thickness), to quantify the nonlinear refractive index and nonlinear absorption. *Z*-scan was performed for various input intensity levels. Details of the standard experimental setup can be found elsewhere [10]. Closed aperture *Z*-scan reveals distinct peak-valley configuration suggesting negative nonlinear effects (not shown here). Open aperture *Z*-scan data revealed an inverted bell-shaped transmittance curve centred at the focus (Z=0). Using relevant equations we fitted the experimental curves of both scans for extracting nonlinear refraction (γ) and nonlinear absorption (β) coefficients respectively. We repeated the

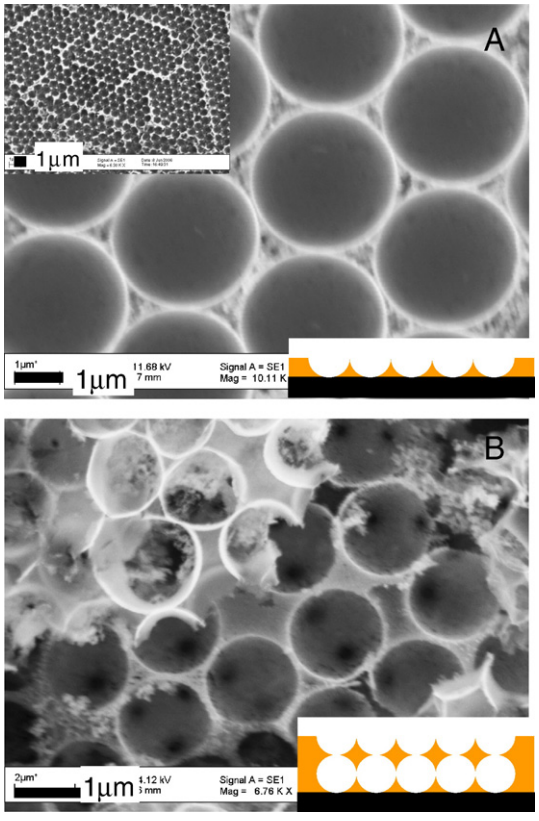

Fig. 3. SEM picture of microporous ZnO (inset of (A) is for 700 nm mesoporous ZnO). (A) and (B) are grown (as represented in the schematic figures) up to 0.5*d* and >1.5*d* respectively, where *d* is the diameter of the templated spheres (d=3 μm).

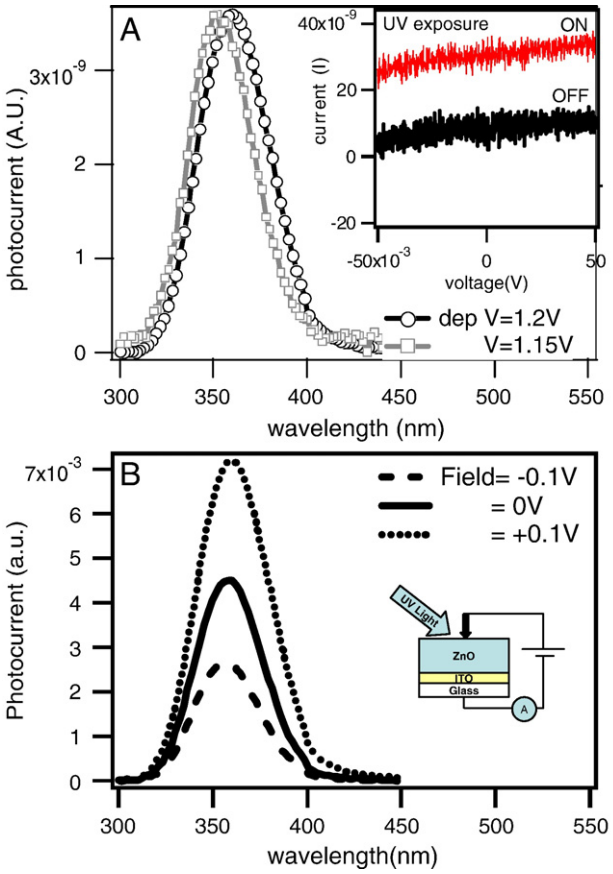

Fig. 4. (A) Photocurrent vs incident light wavelength (bias voltage=−0.1 V) for ZnO thin films, fabricated from different deposition potentials 1.2 V and 1.15 V. (Inset is forward I–V characteristics for UV light ON and OFF); (B) Photocurrent vs incident light wavelength for ZnO thin film (deposited at −1.2 V) under various bias voltages.

experiments several times and for various intensities to ensure consistent measurements. The third-order nonlinear coefficients thus obtained were $\gamma = 4.7 \times 10^{-11}$ cm^2/W and $\beta = 3.2 \times 10^{-6}$ cm/W. Open aperture data reveals positive nonlinear absorption (β) suggesting that the origin is predominantly due to two-photon absorption (TPA). The laser energy (hν) also meets the criteria for TPA, $E_g < 2h\nu < 2E_g$ where E_g is the band gap. Since we have not observed any features related to saturation of absorption at the energy of laser, our findings further suggest that the influence of defect states is weaker and dominated by electronic bands and exciton [11]. Further optoelectronic studies on the nano and microphotonic architectures are under progress.

4. Conclusions

In conclusion, we have demonstrated two novel inexpensive and simple approaches, synthetic route and electrochemical deposition, to fabricate ZnO photonic architectures. Several optical, electrical and structural techniques were employed to highlight the electro-photonic performance of these ZnO nanostructures. Also we have demonstrated the potential ability to produce well-characterised nano and microphotonic structures, which could further tailor the optoelectronic properties.

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