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Synthesis and characterization of Mn-doped ZnO nanorods grown in an ordered periodic honeycomb pattern using nanosphere lithography

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Abstract

We report a study of the structural, optical and magnetic properties of undoped and Mn-doped ZnO nanorods grown by chemical bath deposition in a periodic honeycomb lattice formation. Mn-doping is accomplished by a diffusion process at a constant time of 8 h for different temperatures of 500 °C, 600 °C and 700 °C. Undoped and Mn-doped ZnO nanorods had a hexagonal wurtzite structure with a (0 0 2) preferred orientation. From SEM results, it was seen that Mn-doped ZnO nanorods grew vertically in the honeycomb lattice with lengths of 0.8 μm. XPS results showed that Mn^{3+} ions was successfully incorporated in the ZnO matrix by substituting for Zn^{2+} ions and that Mn-doping increased the number of oxygen vacancies in ZnO compared to undoped ZnO. This result was also supported by photoluminescence data at 10 K. Magnetic data showed that all the samples exhibited ferromagnetic character. Although the origin of undoped ZnO is related to oxygen vacancy-induced d^0 ferromagnetism, bound magnetic polarons are responsible from the ferromagnetism of Mn-doped ZnO samples which have T_c values above the room temperature.

Keywords: ZnO:Mn; Nanorods; Nanosphere lithography; Oxygen vacancy; BMP

1. Introduction

In recent years, diluted magnetic semiconductors (DMS) have attracted significant interest due to their potential applications in spintronic devices. Among II–VI group semiconductors, especially, ZnO has gained lots of interest since it has a wide band gap of 3.37 eV with an excitonic binding energy of 60 meV at room temperature that make it an important material for potential optoelectronic applications [1]. ZnO is also a promising material in the investigation of DMS systems that can be achieved by doping with 3-d group elements like Mn, Co, Fe etc. and by these means the optical and magnetic properties of ZnO materials can be tuned. In particular, Mn-doped ZnO nanostructures have attracted significant interest as Mn has the highest magnetic moment and the first half of the d band is fully occupied [2]. The literature contains some reports of experimental studies on ZnO:Mn grown with diverse morphologies such as thin films, nanocrystals and nanowires and exhibiting room temperature ferromagnetism. For instance, Yang et al. produced Mn-doped ZnO thin films by the sol–gel technique on both glass and Si substrates and they found that even though undoped ZnO exhibited diamagnetic behavior, all the ZnO:Mn samples had a ferromagnetic character at room temperature. The origin of ferromagnetism was explained by the substitution of Mn^{2+} ions on Zn^{2+} sites [3]. Sain et al. synthesized ZnO:Mn nanocrystalline samples by mechanical alloying using a mixture of ZnO and MnO powders for different doping concentrations and room temperature ferromagnetism for ZnO:Mn samples was obtained. The origin of ferromagnetism was attributed to RKKY exchange interactions [4]. Furthermore, Philipose et al. grew ZnO:Mn nanowires by the vapor phase transport technique on Au-catalyzed Si substrates with Mn concentrations of 1 at%, 2 at

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% and 4 at%. They observed room temperature ferromagnetic character for 1 at% Mn-doping and the ferromagnetism was attributed to the interactions between Mn ions and native defects [5].

ZnO material doped with transition-metal (TM) ions has been grown in various morphologies such as nanowires, nanorods and nanotubes [6–8]. Some methods to deposit TM-doped 1-D ZnO nanostructures include RF magnetron sputtering [9], vapor phase transport [10], pulsed laser deposition [11], spray pyrolysis [12] and chemical bath deposition (CBD) [13]. Among these methods, CBD is an attractive technique and offers advantages such as simple, low cost equipment and a low growth temperature [14]. To the best of our knowledge, this is the first study investigating the structural, optical and magnetic properties of Mn-doped ZnO nanorods grown into a periodic honeycomb pattern. Additionally, the study focuses on clarifying the origin of room temperature ferromagnetism observed in both undoped and Mn-doped ZnO nanorods grown this honeycomb lattice using both photoluminescence and X-ray photoelectron spectroscopy results.

2. Experimental details

The experimental details concerning the growth of a ZnO buffer layer on Si substrates using both a seed layer followed by chemical bath deposition (CBD) can be found in [10]. To ensure spatially ordered nanostructure growth, ZnO buffer layer coated Si substrates were patterned using a modified nanosphere lithography (NSL) technique [15] whereby a close packed monolayer of polystyrene nanospheres (diameter 1 μm) are deposited on the sample. This nanosphere layer is then used as a template for a secondary silica mask [16]. Once deposited, the nanosphere layer is annealed at 110 °C for 40 s to ensure that each sphere has made good contact with the underlying ZnO buffer layer. Then a silica sol (prepared by mixing 1 ml of TEOS with 1 ml of 0.1 M HCl in 20 ml of absolute ethanol for 3 h) is diluted 1:1 with absolute ethanol. 20 μl of this diluted sol is drop coated onto the annealed nanosphere layer. This is allowed to evaporate for a short period time before any excess is removed by spinning at 2500 rpm for 30 s. The silica is then left to dry in air before being heated to 90 °C for 10 min. The nanospheres are then removed by dissolution in toluene, the substrate is rinsed in DI water and dried under a stream of nitrogen. Finally, the silica layer is densified by heating to 550 °C at a ramp rate of 15 °C/min. Using this method a periodic honeycomb silica lattice with periodic apertures exposing the underlying ZnO layer was formed. Vertically aligned ZnO nanorods were then deposited into the honeycomb pattern by the CBD process where 25 mM zinc acetate was dissolved in deionized water and the solution was heated at 70 °C and the substrates were submerged into the solution and kept at this temperature for 2 h under stirring. After deposition, the samples were taken from the solution and cleaned with deionized water for five minutes. Finally, they were dried with nitrogen gas flow at room temperature. Introduction of Mn into ZnO nanorods was achieved by the evaporation of Mn metal using a thermal evaporation (Leybold Univex 350) system that had a pressure $\sim 10^{-6}$ Torr during deposition. A thickness monitor (Inficon XTM/2) was used to control the evaporated Mn amount onto ZnO nanorods and thickness of the Mn layer was maintained at ~5 nm. After this process, the samples were annealed in a quartz tube at temperatures of 500 °C, 600 °C and 700 °C for 8 h in a vacuum of $\sim 10^{-2}$ Torr.

X-ray diffraction (XRD) and X-ray rocking curve (XRC) studies were performed to investigate the crystal structure of the samples by means of a Bruker AXS D8 diffractometer with Cu$K\alpha$ radiation in the range of $2\theta = 20$–60° with a step of 0.01°. Studies of surface morphology and chemical composition were done with a Zeiss EVOLS 15 scanning electron microscope (SEM) which had an energy dispersive X-ray spectroscopy (EDS) attachment at an acceleration voltage of 20 kV. Detailed information about bonding at the surface was possessed via X-ray photoelectron spectroscopy (XPS) with Al$K\alpha$ radiation (1486.6 eV). The C 1s peak located at 285.0 eV was used as a reference for the charge-correction of binding energies of all the peaks. For the photoluminescence (PL) measurements at 10 K, a SPEX 1704 monochromator was employed with a closed cycle cryostat (Janis SHI-950-5) using an excitation 325 nm line of a He–Cd laser. Magnetization measurements of the specimens were conducted using a Quantum Design Physical Property Measurement System (PPMS) system.

3. Results and discussion

Fig. 1(a)–(d) shows the XRD patterns of undoped and Mn-doped ZnO nanorods annealed at 500 °C, 600 °C and 700 °C for 8 h in vacuum, respectively. In all cases a dominant peak at 34.4° is seen, corresponding to the ZnO (0 0 2) reflection (JCPDS card no:36-1451), confirming the deposit as ZnO material with the normal hexagonal wurtzite structure. As seen from the figure, the strong (0 0 2) preferred orientation perpendicular to the substrate was observed for all the samples, indicating a highly textured deposit, following the seed layer

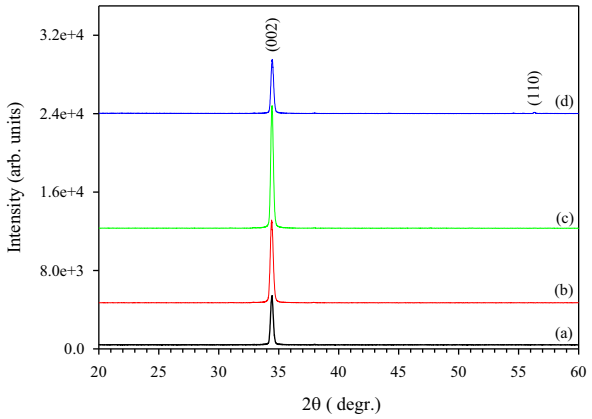

Fig. 1. XRD patterns of undoped ZnO (a) and Mn-doped ZnO nanorods (grown into the honeycomb lattice) annealed at 500 °C (b), 600 °C (c), 700 °C (d) for 8 h.