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ARTICLE

Remarkable Magnetic Properties of Co-doped ZnO Nanorods Array at Room Temperature Originated from Vertical Growth on Zn Foil

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Abstract: Large-area arrays of highly oriented Co-doped ZnO nanorods with hexagonal structure were grown on Zn substrates by single-step hydrothermal process. Structure analysis indicates that the as-prepared products have wurtzite structure, and no other secondary phase is found in the nanorods. The intensity of UV emission peak decreases with the increase of Co doping concentration. When Co is doped into ZnO lattice, oxygen vacancies and Zn interstitials are created. The concentration of these defects increases with rise of the Co concentration. Magnetic measurement reveals that the Co doped ZnO nanorod arrays exhibit obvious room-temperature ferromagnetic behavior with a large coercive field H_c of 52.8 kA/m, which makes them potentially useful as building components for spintronics.

Key words: semiconductor; magnetic material; nanorod array; ZnO; hydrothermal

Diluted magnetic semiconductors (DMSs) have attracted considerable research interest in recent years due to their great potential applications in spintronic devices, such as spin field-effect transistors, non-volatile memory devices and quantum computer [1,2]. A key work to realize spintronic devices is to develop ferromagnetic DMSs with a Curie temperature above room temperature. Transition metal-doped ZnO DMSs have been extensively investigated since theoretic studies of Dietl et al. predicted their Curie temperature (T_c) to be above room temperature in 2000 [3]. Following the original research by Ueda et al.[4], many reports have been given about Co doped ZnO thin films exhibiting ferromagnetism with Tc above room temperature. Wu et al. [5] prepared $Zn_{1-x}Co_xO$ nanowires using chemical vapor deposition (CVD) methods. Chen et al. [6] reported that room temperature ferromagnetism was observed in Co doped ZnO nanoneedle array prepared by pulsed laser deposition. L. Q. Liu et al.[7] reported the room temperature ferromagnetism of $Zn_{1-x}(FeCo)_xO$ nanowires synthesized via a CVD growth method.

Recently, solution growth methods, for example, the bottom-up approach is becoming attractive to grow semiconducting magnetic nanostructures as they are expected to allow better control over chemical composition and dopant speciation compared to those of the physical methods. The chemical synthesis, in addition to being cost-effective, also offers advantages such as bulk synthesis and easy processing. Although there are a number of reports on the chemical synthesis of ZnO nanostructures, only few of them are related to the synthesis of doped nanostructure of ZnO. Yang et al. [8] reported the synthesis of Co-doped ZnO nanorods using the hydrothermal method. Wang et al. [9] reported a two-step chemical method for the synthesis of Co-doped single-crystalline ZnO nanorods. The first step involved the preparation of ZnO nanoparticles (seeds), which acted as nucleating centers for nanorods, and in the second step nanorods were grown from the solution. In the chemical

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methods reported so far, the final products were obtained in powder form. Hence, there is a need to further process these powders so as to prepare their films for making devices. Nowadays, substrate-anchored thin film with oriented nanostructures are often more desirable for applications. Three-dimensional (3D) arrays of nanostructured materials have been widely introduced to enable to improve unique performances in electronics [10], optical devices [11], light emitting diodes [12], and so on. The low dimensional, wide band gap (3.37 eV) semiconductor-zinc oxide (ZnO) with large excition binding energy (60 meV) at room temperature has been so far applied in many aspects. Particularly, one dimensional ZnO oriented nanostructures are confirmed to be able to further enhance the performances of various devices, including field emission flat panel displays [13], shore-wavelength lasers [14], solar cell [15] and chemical sensors [16]. However, there are few researches on magnetic materials based on oriented ZnO nanostructure arrays. In particular, one-step template-free synthesizing route for one-dimensional ZnO array is still a significant challenge for researchers. In this paper, we reported a single-step simple wet chemical process to directly produce films of Co-doped ZnO nanorod arrays on zinc substrate in an aqueous medium. Zinc substrate can not only act as the carrier of the nanorods arrays, but also be the excellent conductor, which ensure the good ohmic contact between the ZnO nanorods and Zn substrate. At the same time, the ZnO nanorods film layer in-situ-generated on the zinc foil surface can improve the interface adhesive force.

1 Experiment

All chemicals were analytical-grade reagents and purchased from Shanghai Chemical Reagent Corp. The zinc foil (99.99% purity) with a size of 2.5 cm×2.0 cm×0.1 cm was polished, washed by acetone, ethanol and distilled water for several times, and dried in an oven. Cobalt acetate [$Co(Ac)_2 \cdot H_2O$] and tetramethylammonium hydroxide (TMAOH, 25%) were used as reactants without further purification.

The Zn foil substrates were put up-side down into a 50 mL Teflon-lined stainless steel autoclave within 40 mL aqueous solution of 0.3 mol/L TMAOH and required amount $Co(Ac)_2 \cdot H_2O$. The autoclave was heated to 170 °C for 12 h in the oven. After the reaction, the specimens were completely washed with absolute ethanol and Milli-Q water for several times, and then dried in vacuum at 60 °C for 8 h.

The morphologies of the as-synthesized Co-doped ZnO nanorods arrays were observed by field-emission scanning electron microscopy (FE-SEM, LEO1550). The crystal structures of the obtained samples were characterized by X-ray diffraction with graphite monochromatized CuKα radiation (BrukerD8, λ=0.154 05 nm). Photoluminescence measurement was carried out by employing a CARY Eclipse Fluorescence spectrum. The Raman spectra were collected at room temperature with a confocal Raman microscope (NT-MDT NTEGRA Spectra) using a 514 nm laser as the excitation source. A vibrating sample magnetometer (VSM) was used to study the magnetic properties.

2 Results and Discussion

In the present experiment, we couldn't confirm the quantity of the zinc atoms involved in the reaction, so we assumed all the TMAOH reacted with Zn substrates and calculated the quantity of the Zn^{2+}. Then the $Co(Ac)_2 \cdot H_2O$ were added in the solution with the mass fractions 1%, 5%, and 10% of the Zn^{2+}. The samples are denoted as ZnO:1wt%Co, and ZnO:5wt%Co, ZnO:10wt%Co.

Figs.1a~1g show the SEM images of the ZnO nanorods arrays with different Co doping concentrations and the pure ZnO nanorods arrays. Remarkably, the uniformity of the nanorods over a large area is obviously shown in a top view image, taken in a low magnification of the nanorods arrays (Fig.1a, 1c, 1e). Uniform growth of nanomaterials on large scale is important to nanodevice fabrication. The high-magnification FE-SEM images of the arrays (Fig.1b, 1d, 1f) suggest that the nanorods of high density grow nearly vertically from the substrates. The diameters of the nanorods in a hexagonal shape with the pencil shape tip are estimated to

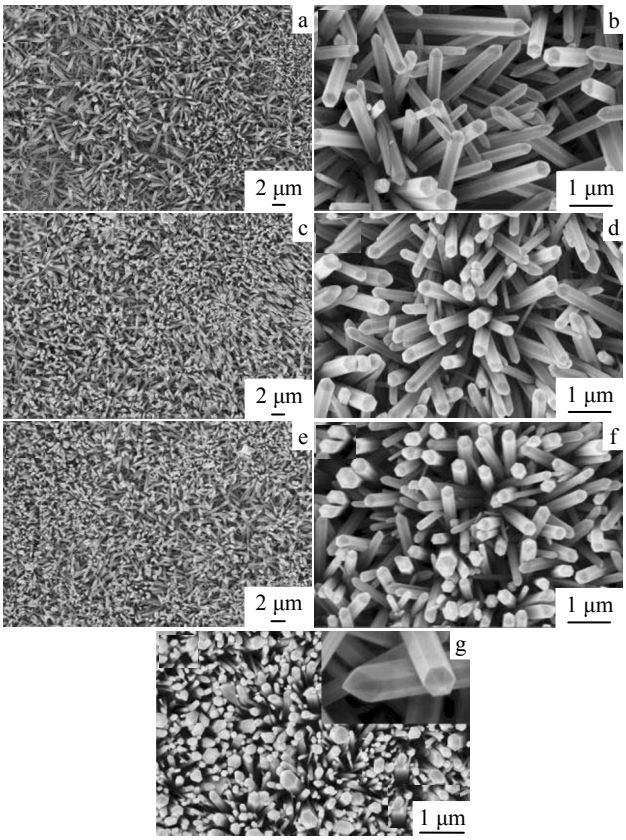

Fig.1 SEM images of ZnO nanorods arrays with different Co doping concentrations and pure ZnO nanorods arrays: (a, b) ZnO:1wt%Co; (c, d) ZnO:5wt%Co; (e, f) ZnO: 10%Co; (g) pure ZnO nanorods arrays