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Effect of thermal annealing on the structure and magnetism of Fe-doped ZnO nanocrystals synthesized by solid state reaction

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ABSTRACT

High purity Fe_2O_3/ZnO nanocomposites were annealed in air at different temperatures between 100 and 1200 °C to get Fe-doped ZnO nanocrystals. The structure and grain size of the Fe_2O_3/ZnO nanocomposites were investigated by X-ray diffraction 2θ scans. Annealing induces an increase of the grain size from 25 to 195 nm and appearance of franklinite phase of $ZnFe_2O_4$. Positron annihilation measurements reveal large number of vacancy defects in the interface region of the Fe_2O_3/ZnO nanocomposites, and they are gradually recovered with increasing annealing temperature. After annealing at temperatures higher than 1000 °C, the number of vacancies decreases to the lower detection limit of positrons. Room temperature ferromagnetism can be observed in Fe-doped ZnO nanocrystals using physical properties measurement system. The ferromagnetism remains after annealing up to 1000 °C, suggesting that it is not related with the interfacial defects.

1. Introduction

Recently, the emerging scientific field of spintronics becomes an active area because spin-based multifunctional electronic devices have several advantages over the conventional charge-based devices regarding data-processing speed, nonvolatility, higher integration densities, and decreased electric power consumption [1]. For the spin-based electronic devices, materials which can provide spin-polarized charge currents for spin injection into semiconductors are required. As potential candidates, diluted magnetic semiconductors (DMS) have aroused significant interest. The III–V and II–VI DMS have attracted considerable attention because the spin-dependent magnetic phenomena can be manipulated in these low-dimensional tailored magnetic thin films for various spin-based devices to unprecedented capabilities [2,3], such as spin-valve transistors, spin light-emitting diodes, nonvolatile memory, logic devices, gas sensor, optical isolators, and ultrafast optical switches, etc.

Among the studies of TM-doped conventional III–V and II–VI semiconductors, TM-doped ZnO became the most extensively studied topical materials since the prediction for Mn-doped p-type ZnO by Dietl et al. [4] based on Zener ferromagnetism model, as promising candidates to realize a diluted magnetic material with Curie temperature above room temperature. First-principles electronic structure calculations by Sato et al. [5,6] suggested that other 3d transition metal ions (such as V, Cr, Fe, Co, and Ni) doped ZnO could also exhibit room temperature ferromagnetism. The above-predicted ferromagnetism was later confirmed experimentally in Co-doped ZnO [7], V-doped ZnO [8], and Mn-doped ZnO [9]. Till now room temperature ferromagnetism has been obtained in various TM doped ZnO, such as Mn [10–12], Co [13–19], Ni [20–22], and Fe-doped ZnO [23].

Several methods have been utilized to produce ZnO based DMS, such as molecular beam epitaxy [18], solid state reaction [12], pulsed laser deposition [7,8,15,19–22], chemical pyrophoric reaction [24], and sol–gel coating methods [14], etc. Despite the successful fabrication of ferromagnetic ZnO based DMS, the origin of ferromagnetism is still under controversy. Doubts exist as to whether the ferromagnetism is intrinsic [15,18–20] or extrinsic in nature [14,22]. It is generally accepted that the ferromagnetism arises from TM ion substitution in Zn sites. However, in some other studies, formation of TM nanoclusters was proposed to be responsible for the observed ferromagnetism [14,25]. In addition, the intrinsic defects in ZnO were also suggested to be related with the ferromagnetism [26–28]. Recently Sundaresan et al. [29,30] reported the ferromagnetism as a universal feature of inorganic nanoparticles, and the ferromagnetism was suggested to be induced by the defects on the surface of ZnO nanoparticles.

In order to get a better understanding of the origin of ferromagnetism in Fe-doped ZnO, it is requisite to study the correlation between the ferromagnetism and microstructure. Positron annihilation spectroscopy (PAS) has been proved to be

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a powerful method to investigate microstructure in semiconductors [31]. Positrons are trapped preferentially by vacancy defects where electron density is lower than the bulk of material. Annihilation characteristics of positrons are different in the perfect bulk state and vacancy trapped state, thus the identification of vacancies is very straightforward. The positron lifetime measurements could provide information on both the nature and abundance of defects, while the Doppler broadening of positron annihilation radiation is useful to study the electron momentum distribution in materials. Especially the newly developed coincidence Doppler broadening (CDB) technique greatly reduces the background radiation by using two high-purity Ge detectors to record the two annihilation gamma-rays, respectively, thus improves the accuracy of the electron momentum distribution, and can provide chemical environment information where positron annihilates [32].

In this paper, room-temperature ferromagnetic ZnO was synthesized by Fe-doped ZnO nanocrystals using solid state reaction method. This technique offers several advantages such as low cost, easy controlling of the total dopant amounts, and facility of producing bulk materials. Studies of the structural and magnetic properties of Fe-doped ZnO nanocrystals were carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM), positron annihilation lifetime (PAL) spectroscopy, CDB, and physical properties measurement system (PPMS).

2. Experiment

Fe_2O_3/ZnO nanocomposites with proportion of 10 at% Fe were prepared through conventional solid-state reaction method [9]. The precursor ZnO (99.97%, Nanjing High Technology Nano CO., LTD) and α–Fe_2O_3 (99.96%, Nacheng Technology Development Corporation of Beijing) nanopowders were mixed and hand-milled in an agate mortar with pestle for 2 h. After hand-milling, the resultant powders were pressed under a static pressure of about 6 MPa at room temperature to get plane-faced pellets. The pellets were subsequently annealed in open air at 12 different temperatures ranging from 100 to 1200 °C for 2 h in an electric muffle furnace.

The microstructure of the Fe_2O_3/ZnO nanocomposites after each annealing step was investigated by positron annihilation spectroscopy (PAS). Pure ZnO and α–Fe_2O_3 pellets were also studied for comparison. The positron source prepared by depositing ^{22}NaCl onto a Ni thin film with a thickness of 3 μm was sandwiched between two identical plane-faced pellets. Positron lifetime measurements were performed at room temperature using a conventional fast–fast coincidence system with a time resolution of 280 ps in full width at half maximum (FWHM). No less than 10^6 total counts were accumulated in each measurement. The lifetime spectra were analyzed by the computer program PATFIT [33]. The contribution of positrons annihilating within the source and the foil was determined to be 530 ps with an intensity of 2% using a silicon single crystal. Coincidence Doppler broadening (CDB) spectra were measured using two high purity (HP)-Ge detectors with energy resolution of about 1.64 and 1.76 keV (FWHM) at 1.33 MeV, respectively. At least 10^7 annihilation events were collected in each two-dimensional spectrum.

In order to study the grain size and the structural changes after annealing, all the samples were subjected to X-ray diffraction analysis using Cu K_α radiation (Bruker D8 Advance) with a Ni filter. The morphologies of the samples were examined by a field-emission scanning electron microscopy (FE-SEM, Philips XL30). The magnetization behaviors of the Fe_2O_3/ZnO nanocomposites annealed at different temperatures were investigated by a Quantum Design physical properties measurement system. All the above measurements were carried out at room temperature.

3. Results and discussion

Fig. 1 depicts XRD patterns for the 10 at% Fe-doped Fe_2O_3/ZnO nanocomposites annealed at 100, 400, 700, and 1000 °C. For Fe_2O_3/ZnO samples annealed at 100 °C, the observed peaks can be indexed with the wurtzite phase of ZnO (JCPDS Card No. 36-1451) and hematite phase of Fe_2O_3 (JCPDS Card No. 33-0664). After annealing at 400 °C, the XRD pattern shows a decrease in peak intensity of hematite phase and the (3 0 0) peak disappears. After annealing at 700 °C, most peaks of hematite phase disappear, whereas (1 0 4) peak of hematite phase can be observed. Peaks attributed to franklinite phase of $ZnFe_2O_4$ (JCPDS Card No. 22-1012) appear, indicating the majority of α–Fe_2O_3 have reacted with ZnO to form $ZnFe_2O_4$ when the annealing temperature reaches 700 °C. After annealing above 1000 °C, no peaks of hematite phase can be observed, suggesting all the α–Fe_2O_3 have reacted with ZnO in the annealing process. In addition, the intensity of the peaks increases and the full width at half maximum (FWHM) decreases with the elevated annealing temperature, which indicates a possible change in the grain size.

The average grain size of the annealed samples is calculated by Scherer's formula [34]:

$$D_{hkl} = K\lambda/\beta\cos\theta, \quad (1)$$

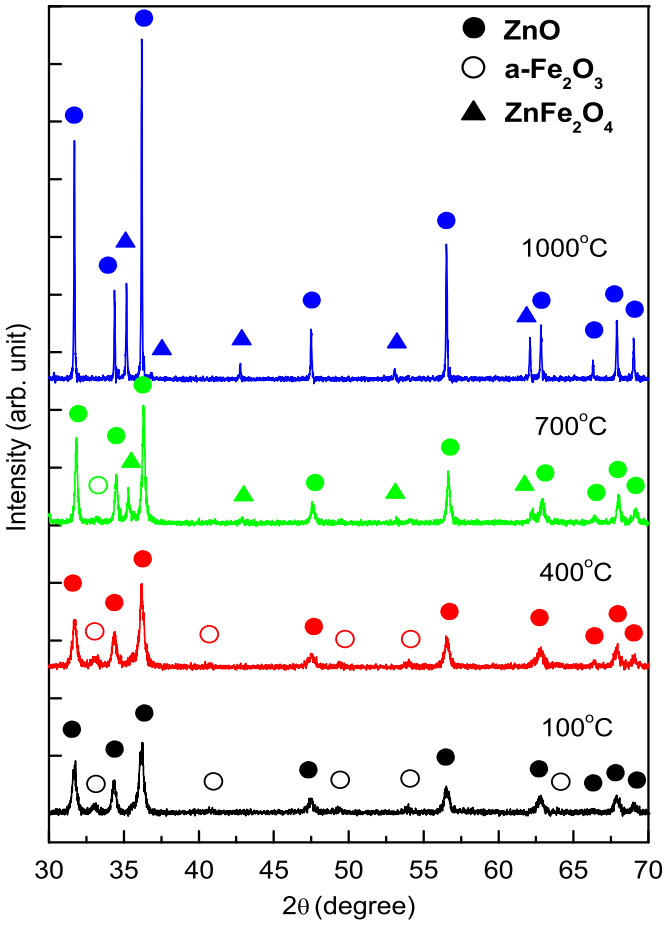

Fig. 1. X-ray diffraction patterns for Fe_2O_3/ZnO nanocomposites annealed at 100, 400, 700, 1000 °C. The diffraction lines can be assigned to ZnO (solid circles), α–Fe_2O_3 (open circles), and Fe_2ZnO_4 (solid triangles).