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Raman spectra, photoluminescence and ferromagnetism of pure, Co and Fe doped SnO_2 nanoparticles

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Abstract

The pure and transition metal (Co and Fe = 3 and 5 mol%) doped SnO_2 nanoparticles have been synthesized by a chemical route using polyvinyl alcohol as surfactant. These nanoparticles were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman, Fourier transform infrared (FTIR) spectroscopy, photoluminescence (PL) and magnetic measurements. The XRD patterns show that all the samples have tetragonal rutile structure without any extra phase and the value of average particle size using FWHM lies within 12–29 nm is also confirmed by TEM. FTIR spectrum has been used to confirm the formation of Sn–O bond. Raman spectroscopy shows the intensity loss of classical cassiterite SnO_2 vibration lines which is an indication of significant structural modifications. From PL, an intense blue luminescence centered at a wavelength ~530 nm is observed in the prepared SnO_2 nanoparticles, which is different from the yellow-red light emission observed in SnO_2 nanostructures prepared by other methods. The strong blue luminescence from the as-grown SnO_2 nanoparticles is attributed to oxygen-related defects that have been introduced during the growth process. These Co and Fe-doped SnO_2 nanoparticles exhibit room temperature ferromagnetism and the value of their magnetic moment and phase transition temperature are sensitive to their size and stoichiometric ratio.

Keywords: A. Sol–gel processes; B. Electron microscopy; E. Spintronics; Magnetic and optical properties; SnO_2

1. Introduction

Ferromagnetism of dilute magnetic semiconductors (DMSs) has been a subject of recent investigations because of their potential applications in the emerging fields such as spintronics, nanoelectronics, nanophotonics, magneto electronics and microwave devices [1,2]. A wide band gap oxide based DMSs such as TiO_2, ZnO, SnO_2, and HfO_2 have attracted considerable attention whenever doped with transition metal (TM) ions (Co, Mn, Ni, Fe, Cr, etc.) because their remarkable electronic, optical and magnetic properties resulting from a large sp–d exchange interactions between the magnetic ions and the band electrons.

Among above DMSs oxides, SnO_2 is an important n-type semiconductor of wide energy gap (E_g = 3.62 eV at 300 K) and presents special properties, such as transparency, chemical and thermal stabilities which are used in photodetectors, catalysts for oxidation and hydrogenation, solar cells, semiconducting gas sensors, liquid crystal displays, protective coatings, etc. [3,4]. There are a lot of works have been reported on ferromagnetic properties of TM-doped SnO_2 thin films and nanoparticles. Ogale et al. [5] reported room-temperature ferromagnetism of pulsed laser deposited SnO_2:Co thin films. More recently, Fitzgerald et al. [6] found ferromagnetism in Co-doped SnO_2 thin films with Co contents from 0.1 to 15%. On the other hand ferromagnetism of $Sn_{0.95}Fe_{0.05}O_2$ ceramic with magnetic moment of 0.95 μ_B/Fe, about 85% of the iron being in a magnetically order high-spin Fe^{3+} and Curie temperature of about 360 K were reported by Fitzgerald et al. [7]. However, Punnoose et al. [8] reported the paramagnetic behavior of chemically synthesized $Sn_{0.95}Fe_{0.05}O_2$, prepared above 600 °C and Adhikari et al. [9] observed antiferromagnetic behavior of 5% Fe-doped SnO_2 nanoparticles synthesized by chemical co-precipitation method. Overall, the origin of ferromagnetism in TM doped SnO_2 system is still an open issue.

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Nanometric size has great influence on the performance of several material systems and may affect various physical properties not only the host semiconductors but also of the DMS materials derived from them. For example, when the crystallite size in some of the DMS materials is reduced below 30 nm, they are found to exhibit better ferromagnetic properties as compared with those having microcrystalline particles (>100 nm) [10]. In addition, nanocrystalline oxide DMSs may be exploited for a variety of applications such as spintronic devices, biomedical applications, magnetic storage devices, and ferrofluids. DMSs SnO_2 also exhibits remarkable features such as native oxygen vacancies, high carrier density and transparency, and high chemical and thermal stabilities. A fewer studies [3,6,8,11] on nanocrystalline Co and Fe-doped SnO_2 DMSs with conflicting results especially on the existence of room temperature ferromagnetism have been reported. In view of above these discussions there is need for appropriate growth conditions which results to obtain room temperature ferromagnetism.

Moreover, bulk SnO_2 is a member of special class semiconductors which have direct band gaps and dipole forbidden due to their special wave function symmetry. Therefore, to pursue the potential for light emission near band edge, researchers have paid more attention to explore the luminescence properties of nanostructures, expecting that nanostructured materials may break the selection rule imposed on their bulk counterparts [12,13]. SnO_2 nanostructures showed broad emissions in the wavelength range of 400–600 nm at room temperature which is related to the deep level defects [14].

There are several methods used by researchers to prepare DMS SnO_2 such as chemical co-precipitation, conventional mixed oxide, sol–gel, and hydrothermal process [15,16]. However, most of them have been directed toward the preparation of particles with a large size distribution of few micrometers economically, despite complicated experimental steps and high reaction temperatures. In the present paper, we have prepared Co and Fe-doped SnO_2 nanoparticles by sol–gel method in which polyvinyl alcohol (PVA) is used as surfactant and the resulting size of the prepared nanoparticles is comparatively smaller and the quality is even better. We have prepared samples of pure SnO_2 (S0), $Sn_{0.97}Co_{0.03}O_2$ (SC3), $Sn_{0.95}Co_{0.05}O_2$ (SC5), $Sn_{0.97}Fe_{0.03}O_2$ (SF3), $Sn_{0.95}Fe_{0.05}O_2$ (SF5) nanoparticles. The Raman shifts support the existing phase structure and nano effect of TM doped SnO_2. The PL spectra depict its optical nature and exhibit an intense blue luminescence. The magnetic properties depend not only on the oxygen vacancies but also on electronic and structural modifications and the surface nature of the nano crystallites.

2. Experimental procedure

Pure and doped SnO_2 nanoparticles were prepared by a chemical route using PVA as surfactant. The precursor solutions were prepared from stannic chloride pentahydrate ($SnCl_4{\cdot}5H_2O$), ferric chloride ($FeCl_3$) and cobalt chloride ($CoCl_2{\cdot}6H_2O$) with desired molar concentration. In this method, ethanol and acetic acid were mixed in the ratio of 3:1. $SnCl_4{\cdot}5H_2O$ was added to it and stirred for 2 h on a magnetic stirrer. In this solution a calculated amount of dopants Co and Fe was added and again stirred for 1 h. The precursor solutions (M) were mixed in PVA solution in the molar ratio of M:PVA::5:2. The solution was dried at 250 °C and annealed at 700 °C for 2 h to crystallize. The reaction mechanism of PVA with metal ions ($M^+ = Sn^{4+}$, Co^{2+}, Fe^{3+} etc.) is shown in Fig. 1. During heating there exist two sites namely hydrophobic (H_b) and hydrophilic (H_p) of PVA and form clusters. The H_b keeps

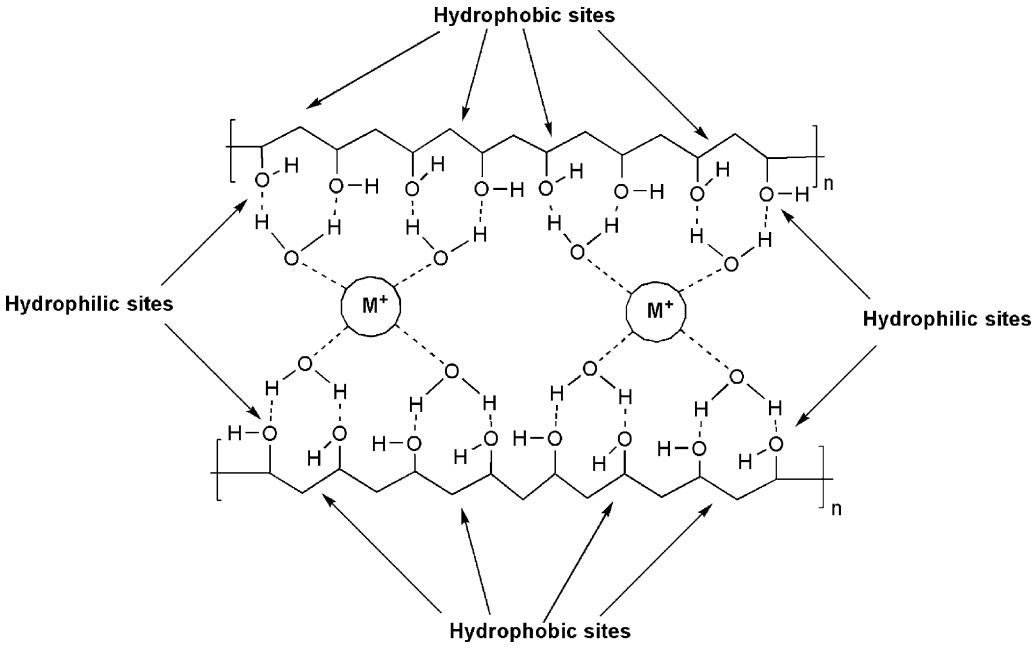

Fig. 1. Mechanism during growth of metal ions in the presence of PVA.