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Synthesis of sol–gel based nanostructured Cr(III)-doped indium tin oxide films on glass and their optical and magnetic characterizations

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ABSTRACT

Sol–gel based nanostructured Cr(III)-doped indium tin oxide (ITO) films (In:Sn:Cr = 84.6:9.4:6.0) deposited on silica glass were cured at 350 °C, 450 °C, 600 °C, 700 °C and 900 °C. EDX, absorption spectra and TEM images confirmed formation of Cr(III)-doped ITO nanoclusters close to Bohr radius of ITO. Excitonic and phonon interactions were studied by absorption, photoluminescence (PL) and Raman spectra. The photon energy between the satellite peaks of PL spectra predicted phonon vibrations. Strong hybridization between s–p-states of host and d-states of Cr(III) resulted in stable exciton–phonon coupling as revealed from excitonic and lattice phonon vibrations. Soft room temperature ferromagnetism was observed in the films.

1. Introduction

We have already reported [1] the synthesis and characterizations of Mn(II), a transition metal (TM) ion doped indium tin oxide (ITO) films on silica glass using cost-effective sol–gel dip coating technique. The morphological and spectroscopic study of the films revealed the incorporation of Mn(II) in the cubic nanoclusters of ITO of different sizes obtained by curing at different temperatures. The cluster sizes were close to Bohr radius of ITO [2–5] and showed the photoluminescence (PL) properties due to HOMO–LUMO transitions of free and bound excitons where strong hybridization [3–5] between s–p-states of host and d-state of the dopant was proposed. Probably this type of hybridization enhanced the exciton–phonon interaction which implied the presence of satellite PL bands around the PL of excitons. We have also reported room temperature ferromagnetism (~1.5 BM) in Mn(II)-doped transparent ITO films on glass [6].

Though Mn(II) (d^5 ion) is the mostly studied transition metal ion used as a dopant in different system by several researchers [5,7], other TM ion like Cr(III) (d^3 ion), Cu(II) (d^9 ion) doped system may also lead to similar optical and magnetic properties [8–10]. Recently many researches are going on for the development of other TM ion doped systems [11–22] but to the best of our knowledge, the present methodology for the preparation of Cr(III) doped system is not reported.

In the present work, similar to Mn(II) doped ITO, attempt has been made to prepare nanoclusters of Cr(III) doped ITO by sol–gel film deposition technique and their excitonic and phonon features were studied by absorption, photoluminescence and Raman spectra.

We have also studied the ferromagnetic properties of selected Cr(III) doped ITO films at different temperatures from 5 K to 300 K.

2. Experimental

2.1. Preparation of precursor

The aquo-organic based precursor solution for the Cr(III) doped ITO films was prepared from hydrated indium and tin salts, $In(NO_3)_3{\cdot}3H_2O$ and $SnCl_4{\cdot}5H_2O$ respectively. Polyvinyl alcohol (PVA) (molecular weight 22,000, BDH,UK) and $Cr(NO_3)_3{\cdot}9H_2O$,(ACROS ORGANICS) were used as binder and dopant respectively. Initially an ITO precursor was prepared following the procedure as described in our earlier work [2]. In the present case, Cr(III) doping was done by incorporation of requisite quantity of aqueous Cr(III) nitrate solution into the ITO precursor maintaining the atomic ratio, In:Sn:Cr = 84.6:9.4:6.0. Next the solution was stirred for 2 h. Concentration of the sol, 6.0 wt.% equivalent metal oxides was

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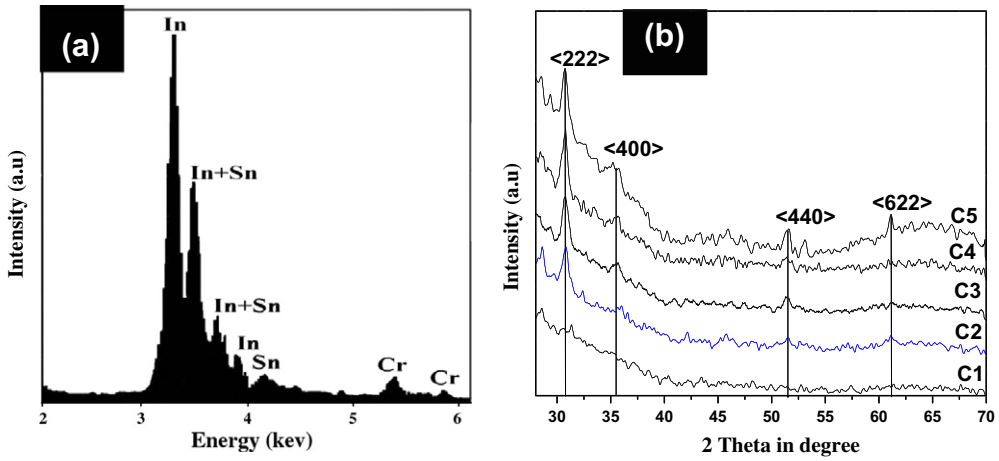

Fig. 1. (a) Energy dispersive X-ray (EDX) spectrum of Cr(III) doped ITO film cured at 450 °C; (b) XRD patterns of Cr(III) doped ITO films cured at 350 °C (C1), 450 °C (C2), 600 °C (C3), 700 °C (C4) and 900 °C (C5).

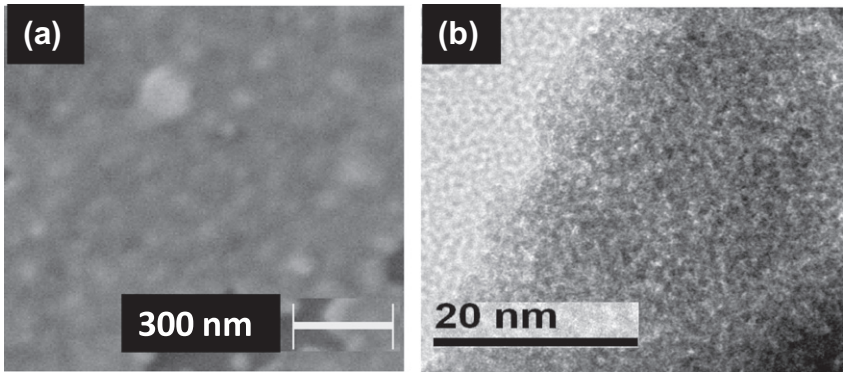

Fig. 2. (a) FESEM and (b) TEM images of Cr(III) doped ITO film cured at 350 °C.

Table 1
Cluster size of the Cr(III) doped ITO films cured at different temperatures measured from the TEM and calculated from band gap studies.

Sample no.	Curing temperature (°C)	Band gap		Cluster size (nm)	
		$E_{g(bulk)}$ (eV)	$E_{g(QD)}$ (eV)	Experimental (TEM)	Calculated
C1	350	3.60	4.32	2.4	2.9
C2	450		4.21	4.2	3.1
C3	600		4.20	6.1	3.2
C4	700		4.11	7.3	3.4

maintained by adding water. The sol was aged for a few days before coating.

2.2. Deposition of film

The above precursor was used for the deposition of layers onto the cleaned Heraeus (Germany) make suprasil grade pure silica glass (dimensions, 25 mm × 75 mm, thickness 1 mm) following the dipping technique with an optimum withdrawal speed of 5 cm/min. The coated samples were placed in an air oven and heated to 100 °C for 30 min. The dried films were then put into an electrical furnace and cured in air at different temperatures viz. 350 °C, 450 °C, 600 °C, 700 °C and 900 ± 5 °C with 30 min soaking. These films (thickness ~ 100 nm) were designated as C1, C2, C3, C4 and C5 respectively.

2.3. Characterization

The crystalline phase of the films were detected by X-ray diffraction (XRD) study (Philips PW 1730 X-ray diffraction unit employed with nickel filter CuKα radiation source, 1.5418 Å radiation). The surface morphology and the particle size distribution were measured from Field Emission Scanning Electron Microscopy [FESEM (LEO)] and high resolution Transmission Electron Microscopy [TEM (JEOL)] respectively. The incorporation of Cr(III) in the ITO films were identified from Energy Dispersive X-ray Spectroscopy (EDX) study. The UV–Vis spectra of the films were recorded at room temperature using Shimadzu UV–VIS–NIR (model UV 3101 PC) spectrophotometer. Room temperature photoluminescence (the lamp corrected for emission and excitation spectra of the sample) was recorded by Perkin–Elmer LS55 Luminiscence spectrofluorometer. Dispersive Raman spectral study (micro-Raman, Renishaw in-Via Raman microscope) of the film after subtracting the data for silica glass was done at room temperature using argon ion laser with an incident wavelength of 514 nm as the excitation source. The magnetizations versus temperature patterns and the hysteresis loops at different temperatures have been measured in a SQUID magnetometer (MPMS; Quantum Design) over a temperature range 5–300 K.

3. Results and discussion

Hydrated Cr(III) nitrate was chosen as the starting material for Cr(III) doping because it has very low melting point (~60 °C) [23]