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Probing local structure of co doped polyvinylidene fluoride-ZnO thin films using X-ray absorption spectroscopy

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ABSTRACT

Nanocrystalline ZnO doped with cobalt ($Co_xZn_{1-x}O$) as a filler was added to polyvinylidene fluoride (PVDF) host matrix to produce a free-standing flexible composite film by sol-gel technique. Three different amounts of cobalt ($x = 0.01, 0.04, 0.07$) were used in the above synthesis. The as-deposited and the poled composite Co-ZnO/PVDF films were subjected to extensive study by X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy. Detailed information regarding the valence states of the host and the filler ions in the samples was derived from XPS and XANES (X-ray absorption near edge structure) studies. Local structures surrounding the Zn and Co sites were obtained from EXAFS (Extended X-ray absorption fine structure) data analysis. Combined XPS, XANES and EXAFS studies confirm that substitution of Zn sites by Co ions in wurtzite ZnO lattice without forming any significant metallic cluster phase in the samples.

1. Introduction

Synthesis of dilute magnetic semiconductor (DMS) by doping of magnetic impurities in a semiconductor has drawn considerable attraction in the last decade for the potential applications of these materials in spintronics [1–7]. Room temperature ferromagnetism with suitable magnetic dopant ions in ZnO lattice was studied extensively. Dopants in ZnO included transition metals like: Co, V, Fe, Ni, Mn, etc. These materials showed Curie temperature values higher than 300 K [8–11]. Most of the studies reported on transition metal doped ZnO are related to Mn or Ni doped systems [12–20] and Co-doped systems have not been studied so critically yet. A few reports on Co-doped ZnO in nanopowder, thin film and nanocrystal forms are available in the literature [21–24]. Studies on Co-doped ZnO nanopowders prepared by a co-precipitation method were reported by He et al. [21]. Location of dopant ions in the ZnO matrix and the effect of doping level on the photocatalytic activity were investigated. It was reported in the above study that Co atoms successfully replaced the Zn atoms in the ZnO lattice which might have created deep band gap energy levels for the recombination of photo-generated electrons and holes. The sol-gel technique was adopted by Neamatu et al. [22] for the synthesis of Co-doped ZnO thin films. It was indicated from the magnetometric and local structure studies carried out by them that most of the Co atoms (around 87%) were placed in environments similar to that of Co (II) oxide and quite a few (around 13%) had substituted Zn in the ZnO lattice. Giuli et al. [23] reported an in-depth investigation by X-ray diffraction (XRD) and XAS (X-ray absorption spectroscopy) to study the major differences between Co and Fe-doped ZnO nanoparticles prepared by chemical route regarding the dopant oxidation state and the presence of local defects such as cationic vacancies or anionic interstitials caused by the substitution. Atomistic information on the dissolution of Co ions in wurtzite ZnO were also obtained by Extended X-ray absorption fine structure (EXAFS) on Co-ZnO films prepared by sol-gel coating route by Park et al. [24].

Irrespective of the substitution, brittleness and high loss factors with highly hysteretic behavior are the general characteristic features of piezo-ceramics like ZnO [25]. The increasing demand of printable resistance, transistors and sensor devices, etc. on flexible substrates [26,27] has accelerated the search for new materials in free-standing and flexible form for application in flexible electronics device technology. There exists a challenge for synthesizing ZnO based DMS material in a free-standing flexible form in cost effective, scalable and reproducible method. Polymer-based composites with high dielectric constant [28–33] or high permeability [34–37] are treated as a possible candidate for the

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above due to their flexible nature. In this regard, polyvinylidene fluoride (PVDF) has become one of the most suitable and potential materials for advanced applications. This is basically due to the extraordinary electroactive properties among other polymer systems. Inherent combination of properties conducive to various device applications like: processability, mechanical and chemical resistance, and low mechanical and acoustic impedance [38,39] are present in PVDF material. These properties have ushered in hope of utilizing it for various device applications, especially in the fields of sensors and actuators [40,41].

In the present study, the sol-gel technique has been exploited for the deposition of free-standing flexible films of Co-doped nanocrystalline ZnO/PVDF ($Co_xZn_{1-x}O$/PVDF) composites. Different Co doping concentrations (x = 0.01, 0.04, 0.07) were used in the composite films. Surface morphology of the films has been studied by Field Emission Scanning Electron Microscopy (FESEM) measurements. Local structure surrounding the Zn and Co sites was probed by XAS (combined techniques of X-ray absorption near edge structure (XANES) and EXAFS). Both the unpoled and poled samples were subjected to the above measurements. It appears that this is the first kind of report on preparation of Co-doped ZnO/PVDF free-standing flexible polymer films and their characterisation by synchrotron radiation based XAS techniques.

2. Experimental procedure

The synthesis protocol followed for the deposition of ~50 μm thick (surface area ~ 5 mm × 5 mm) free standing Co-ZnO/PVDF or $Co_xZn_{1-x}O$/PVDF films is identical to that reported by us for Mn doped ZnO/PVDF films [42] with the exception that Co-acetate tetrahydrate has been used for Co doping instead of Mn-acetate.

A field of 5 MV/m was applied across the films surfaces for 2 h for poling the composite films. The poling unit [42] consisted of a spring loaded electrode and a film holder acting as the second electrode. A pyrex glass vacuum chamber which could be evacuated to a level of ~10^{-6} Torr was used to house above assembly. HT connections were introduced in the poling chamber by appropriate feed-throughs. The electrodes are connected to a regulated d.c. power supply (0–10 KV at 50 mA) with appropriate protection for short circuit.

The surface morphology of the films was recorded by FESEM (Carl Zeiss AURIGA). XPS (X-ray photoelectron spectroscopy) measurements were carried out in a SPECS (Germany) spectrometer with delay line detector at 300 W power and measurements were carried out at a chamber pressure of ~4×10^{-10} Torr with Al Kα line source of 1486.74 eV.

EXAFS measurements were carried out at the Energy-Scanning EXAFS beamline (BL-9) at the INDUS-2 Synchrotron Source (2.5 GeV, 100 mA: with 0.5 mm × 0.5 mm beam size) at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India [43,44] operating in the energy range of 4 KeV to 25 KeV. The beamline optics consists of a Rh/Pt coated collimating meridional cylindrical mirror and the collimated beam reflected by the mirror is monochromatized by a Si (111) (2d = 6.2709) based double crystal monochromator (DCM). The second crystal of DCM is a sagittal cylinder used for horizontal focusing while a Rh/Pt coated bendable post mirror facing down is used for vertical focusing of the beam at the sample position. Rejection of the higher harmonics content in the X-ray beam is performed by detuning the second crystal of the DCM. In the present case, EXAFS measurements at the Zn K-edge (9659 eV) have been performed in transmission mode while measurements at the Co K edge (8333 eV) have been carried out in fluorescence mode.

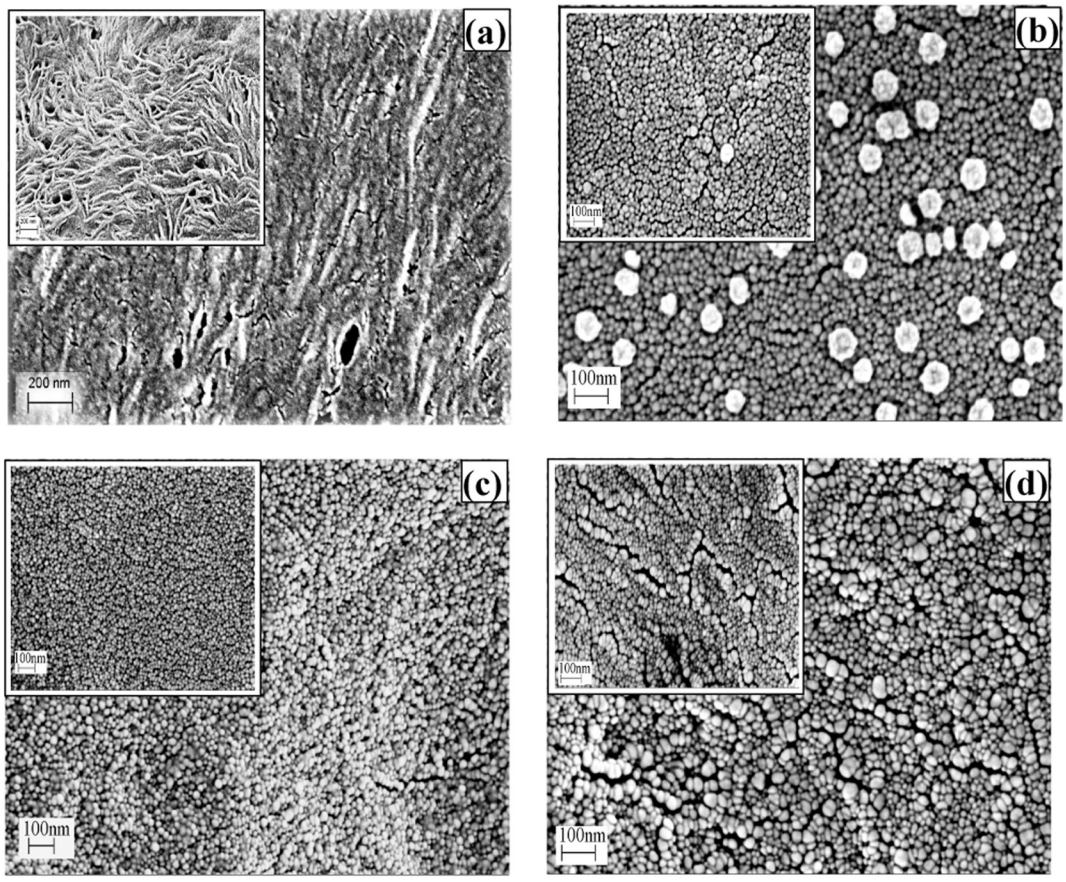

Fig. 1. FESEM pictures of poled: (a) pristine PVDF film, (b) $Co_xZn_{1-x}O$/PVDF (x = 0.01) sample, (c) $Co_xZn_{1-x}O$/PVDF (x = 0.04) and (d) $Co_xZn_{1-x}O$/PVDF (x = 0.07) sample. Insets show the corresponding FESEM pictures of unpoled films.