

## Electron–phonon interaction and size effect study in catalyst based zinc oxide thin films

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### ABSTRACT

Nanocrystalline zinc oxide (ZnO) thin films have attracted great attention due to their possible applications in optoelectronic devices. The dependence of size and catalyst (indium and fluorine) in ZnO thin films synthesized by spray pyrolysis technique was studied. To understand the chemical bonding structure and electronic states of the catalyst based ZnO thin films, XPS analysis was carried out. A comprehensive micro-Raman scattering study of the phonons in catalyst based ZnO thin films grown in ambient air was made. Low temperature dependent Raman spectroscopy studies were carried out for the detailed structures, vibrations, and in situ size variation of nanostructured thin films. The size and catalyst dependence of the coupling strength between electron and LO phonon was experimentally estimated. The coupling strength determined by the ratio of second to first-order Raman scattering cross sections was found to diminish with decreasing crystallite size, and the Fröhlich interaction plays the vital role in electron–phonon-coupling in ZnO. Influence of catalyst on the luminescence properties was investigated.

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### 1. Introduction

Zinc oxide (ZnO) is a direct band gap II–VI compound semiconductor with the wurtzite-type crystal structure. Its high band gap energy (3.37 eV) and large exciton binding energy (60 meV) at room temperature, makes it a potential candidate for ultraviolet (UV) optoelectronic devices such as light emitting diodes, laser diodes for blue and ultraviolet spectral regions, dye-sensitized solar cells, transparent field effect transistors and photodetectors [1–5]. In addition, it proves to be suitable for the purpose of manufacturing room-temperature polariton lasers [6]. Doping in wide band gap semiconductors with transition metals is attracting great deal of attention for the research community to study the novel electronic devices of new generation. As we know, the size effects are crucial in a semiconductor; the electronic properties of a semiconductor start to change below the threshold size. The excitations become confined within the dimension of particles, and quantum size effects are clearly examined as a high energy shift of the optical band gap [7]. Raman scattering measurements are extensively carried out to study the substitution of dopant in the ZnO host

lattice [8–12]. This disfigures the crystal's local translational symmetry due to individuality (i.e. mass, electronic configuration, bond energy, atomic radii, etc.) of the dopant and host atoms. Raman spectroscopy senses these variations at molecular level and provides detailed and accurate information that other techniques like X-ray diffraction (XRD) cannot reveal. In polar semiconductors, carriers are excited highly in the conduction band and relaxation towards their ground state mainly by Fröhlich interaction with the longitudinal optical (LO) phonons. Raman scattering proves to be an important tool to obtain information about the transport properties and phonon interaction with the free carriers in both bulk and thin film forms of wide band gap semiconductors as well as to analyze more specific aspects of lattice dynamics, such as isotopic effects [13] and phonon lifetimes [14]. Therefore, a systematic study of the size dependence of the electron–phonon coupling strengths is of particular interest for understanding the fundamental physics and application to functional devices. The zone-center optical phonons can be classified according to the following irreducible representations:

$$\Gamma_{\text{opt}} = A_1 + E_1 + 2E_2 + 2B_1 \quad (1)$$

The  $B_1$  modes are silent modes; the  $A_1$  and  $E_1$  modes are polar modes and are both Raman and infrared active, whereas the  $E_2$  modes are non-polar and Raman active only.

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Polarized right-angle Raman scattering of ZnO was measured by Damen et al. [15] back in 1965. Arguello et al. [16] reported Raman spectra of ZnO in a variety of geometries, which allowed them to identify all Raman active modes from their selection rules. A few years later, a detailed study of the resonant behavior of the high frequency  $E_2$  mode ( $E_2^{\text{high}}$ ),  $A_1(\text{TO})$ , and  $E_1(\text{TO}, \text{LO})$  modes as well as several second-order features are presented by Calleja and Cardona [17]. In the past few years, the availability of ZnO films with very high optical quality and the technological relevance of this material have spurred the realization of fundamental and more detailed studies on ZnO lattice dynamics. Being a covalent compound, due to  $sp^3$  hybridization, ZnO exhibits a relatively open structure. Almost half its tetrahedral sites and all octahedral sites are unoccupied [18]. Due to presence of these sites, doping in ZnO is comparatively much easier than other compounds as they act as host sites for the dopant atoms. For low dopant concentrations, one-to-one substitution of a dopant at the host site does not affect local translational symmetry severely, if we ignore (for the moment) the identity or individuality of the dopant and host atom, and long-range order is maintained. However, fundamental properties of the host lattice still get affected but can be accepted due to opening of new characteristics. Inducing a higher concentration of dopant results in the formation of small metallic clusters or secondary phases and eventually breaks the long-range order. This ultimately results in severe degradation of the properties of host lattice and evolution of dopant-related ones.

In this paper, we present dependence of size and catalyst (indium and fluorine) on thin films synthesized by spray pyrolysis technique for their X-ray photoelectron spectroscopy, Raman spectroscopy and photoluminescence study. The chemical bonding structure and the electronic states of the dopant are verified by X-ray photoelectron spectroscopy (XPS). Second-order Raman features are discussed in the light of recently available DFT calculations of phonon DOS. To study the size and catalyst dependence of optical phonons in ZnO, the  $E_2^{\text{high}}$ ,  $A_1(\text{LO})$ ,  $E_1(\text{LO})$ , etc. modes is carried out for both catalysts. A visible line-shape asymmetry is observed for the  $E_2^{\text{high}}$  mode, which can be explained by the features of the two-phonon DOS around the  $E_2^{\text{high}}$  frequency. Also coupling between the lowest electronic excited state and LO modes in nanocrystalline ZnO thin films is studied. Temperature dependent Raman spectroscopy studies are carried out for the detailed structures, vibrations, and in situ size variation of nanostructured thin films. Luminescent behavior of prepared films is analyzed with the help of photoluminescence spectra.

## 2. Experimental

The experiments were performed for high-quality catalysts (i.e. fluorine and indium) based ZnO thin films obtained by the chemical spray pyrolysis technique. The growth and physicochemical (structural, morphological, electrical and optical) properties of catalyst based ZnO thin films obtained by this method have been published elsewhere [19–21]. XPS spectra were recorded by using an ESCA spectrometer (ULVAC-PHI 5600). Monochromatized X-ray ( $K\alpha$ : 1486.61 eV) from an Al anode was used for excitation. An electron flood gun was employed to compensate for the sample charging under X-ray irradiation. The room-temperature photoluminescence spectra were recorded using Perkin-Elmer Luminescence Spectrometer (Model: LS-55) with Xenon source. Raman scattering experiments were performed in air at room temperature with micro-Raman system from Jobin Yvon Horibra LABRAM-HR visible within 200–1400  $\text{cm}^{-1}$ . The low temperature Raman spectra were measured at liquid nitrogen ( $\text{LN}_2$ ) cooling up to 100 K with spectral resolution of 1  $\text{cm}^{-1}$ . The Raman spectra were obtained at excitations from Argon 488 nm laser source for different catalyst.

The 600 and 1800 lines/mm gratings – detector: CCD detector were used.

## 3. Results and discussion

To understand the chemical bonding structure in catalyst (indium and fluorine) based ZnO thin films, the valence band states are examined using XPS technique. The pronounced splitting of the Zn 2p spectral line into the  $2p_{1/2}$  and  $2p_{3/2}$  lines is observed (Fig. 1), despite the instrument operating set-up, which aimed at an improvement of the sensitivity with some sacrifice of resolution. The doublet lines of Zn corresponding to  $2p_{3/2}$  and  $2p_{1/2}$  are observed at 1022.8 and 1045.9 eV, respectively. The Zn ( $2p_{3/2}$ ) line has been shifted by  $\Delta E_{\text{Zn}} = 1.1$  eV from the binding energy position of 1021.5 eV for elemental zinc [22]. These results are attributed to the substitution of  $\text{In}^{3+}$  ions into  $\text{Zn}^{2+}$  sites in ZnO lattice. The binding energy values of Zn  $2p_{3/2}$  and In  $3d_{3/2}$  are higher than those of the host material ZnO (1021.5 eV). The slight enhancement in the binding energy may be due to the increase in the surface energy of the nanocrystalline In:ZnO thin films. No metallic Zn with a binding energy of 1021.50 eV [23] was observed, which confirms again that Zn exists only in the oxidized state.

Fig. 2a and b shows deconvoluted O 1s three component XPS peaks for In:ZnO and F:ZnO films. The major O 1s peak of In:ZnO film is observed at 532.32 eV with two satellite peaks at 534.18 and 530.78 eV. The main O 1s peak of F:ZnO is observed at 532.68 eV with small satellite peaks at about 533.79 and 531.40 eV. The peak is assigned to oxygen atoms bound to Zn in ZnO while the satellite peak has been assigned to the presence of moisture as its binding energy lies between 531.5 eV (OH) and 533 eV ( $\text{H}_2\text{O}$ ) due to chemisorbed oxygen [22]. Generally the O 1s peak has been observed in the binding energy (BE) region of 529–535 eV. The peak around 529–530 eV has been attributed to lattice oxygen and the peak around 530.7–531.6 eV to oxygen in non-stoichiometric oxides in the surface region and the peak at 533 eV to a weakly bound surface oxygen. For chemisorbed  $\text{O}_2$  on the metal surface the BE's found to be in the region 530–530.9 eV, for the surface oxides and hydroxides in the region 529.6–531.0 eV and 533.3 eV, respectively. For water it is observed in the range 533.9–535.7 eV [24]. The peak positions of In  $3d_{5/2}$  and  $3d_{3/2}$  are located at 445 and 453 eV respectively for In:ZnO thin films (Fig. 3) and are consistent with Ref. [22]. The splitting of 3d core levels is about 8 eV. Thus In can be incorporated into the ZnO lattice as a dopant (donor impurity, both occupying a Zn site

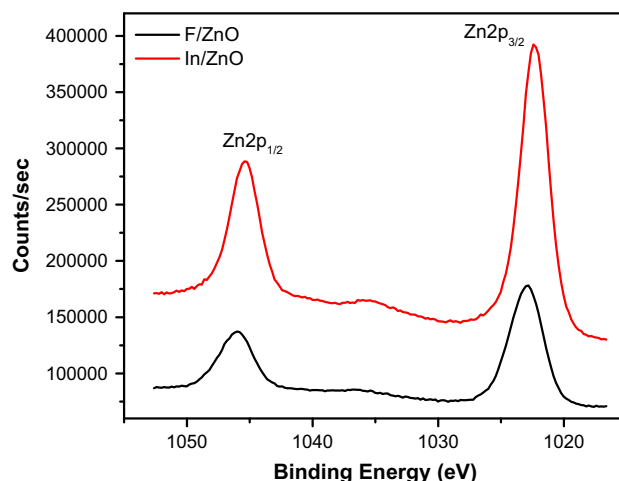


Fig. 1. Photoelectron Al  $K\alpha$  spectrum of the Zn  $2p_{3/2}$  and  $2p_{1/2}$  region of polycrystalline 3 at.% indium and 15 at.% fluorine based ZnO thin films.

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