Raman study of doped-ZnO thin films grown by rf sputtering

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Abstract. A Raman spectroscopy study of doped versus undoped ZnO layers is presented. The layers were grown by RF magnetron sputtering and the doping with Al, Sb and Mn was achieved by ion implantation with subsequent annealing. First-order Raman response measured under $\lambda=488$ nm excitation is discussed. It is shown that doping with any of the impurities used in this work produces a strong enhancement of the longitudinal optical (LO) phonon band, which is attributed to the intra-band Fröhlich mechanism. In addition, doping with Mn results in an extra mode located at 530 cm^{-1} , tentatively attributed to a local vibrational mode of Mn substituting Zn in the lattice sites.

1. Introduction

The increased interest in ZnO, in the form of thin films and nanostructure layers is due to their potential applications in a large variety of fields ranging from transparent electronics (requiring *n*- and *p*-type conductive layers) to spintronics relying on the material doped with magnetic ions such as Mn. To meet the demands of these applications, ZnO has to be doped with impurities such as Ga, Sb, Al, P, Mn, in a controllable way. Raman spectroscopy is one of the most suitable techniques to assess the distribution of impurity atoms between different lattice sites and interstitial positions by probing the characteristic phonon modes of the material.

As known, ZnO crystal (c-ZnO) has the wurtzite structure with the point symmetry group C_{6v} . The Raman-active phonon modes of c-ZnO are the non-polar ones of the E_2 symmetry located at 101 cm^{-1} (E_2 -low) and 437 cm^{-1} (E_2 -high), the A_1 and E_1 transverse optical (TO) phonons, with the frequencies of 380 cm^{-1} and 407 cm^{-1} , respectively, and the A_1 and E_1 longitudinal optical (LO) modes at, respectively, 574 cm^{-1} and 583 cm^{-1} [1]. In a back-scattering configuration, with the photon wave-vector

parallel to the c -axis of the crystal (the configuration used in this work), only the E2 and A1(LO) modes are allowed by first-order Raman scattering selection rules.[2] Raman spectra of high quality single-crystal undoped ZnO are in quite good correspondence with these selection rules [3]. However, despite the rather large number of studies reported, doubts still remain concerning the LO-modes ($500\text{-}600\text{ cm}^{-1}$) of doped ZnO layers. Indeed, a not unique association between the wavenumber and the vibrational modes ZnO-based systems persists [2,4, 5, 6, 7]. In this work, experimental results of Raman spectroscopy of Al, Sb and Mn-doped ZnO layers, grown by RF magnetron sputtering and carefully characterized, are presented and discussed by focusing on the LO phonon spectral region ($500\text{-}600\text{ cm}^{-1}$), in order to contribute to the non-ambiguous assignment of the observed Raman bands.

2. Experimental

Transparent ZnO layers were grown on glass substrates in an Alcatel SCM 650 sputtering system using a mixture of O₂ and Ar gases (relative oxygen fraction of 0.23), at a constant working pressure of 0.7 Pa and at a substrate temperature of 50°C. The target consisted of a hyper-pure (99.99%) metal zinc wafer spaced 60 mm away from the substrates. Radio frequency (13.56 MHz) reactive sputter deposition has been carried out after the camera had reached a base pressure of 5×10^{-5} Pa.

The as-grown films, which were 340 nm thick, were subsequently implanted with two different doses (D1 and D2) of Sb, Al and Mn ions using a high flux ion implanter (Danfysic model S1090). The implantation was performed following a Gaussian profile having its maximum at 100 nm in depth. For all doping ions, dose D1 corresponds to 1 at % and D2 to 3 at %, as confirmed either by Rutherford backscattering spectrometry (RBS) - in the case of Sb and Al - or by particle induced X-ray emission analysis (PIXE) - in Mn ions. In order to recover from the implantation damage and to activate the implanted ions, samples were annealed at 500°C for 60 min in vacuum. Along with ZnO films doped with a single impurity, layers co-doped with Al and Mn were fabricated, hereafter referred to as ZnO:Al:Mn. For these, equal doses (D1 and D2) of Mn were implanted into (previously characterized) ZnO:Al films. For comparison, we have also grown some ZnO:Mn films by RF co-sputtering, which are called ZnO:Mn(sp). The thickness of these sputtered films is 350 nm.

All the produced samples have been analyzed by X-ray diffraction and optical transmittance spectroscopy at room temperature (RT). The micro-structure of the films has been analysed by X-ray diffraction and Raman scattering. X-ray experiments have been performed in a Philips PW 1710 diffractometer using Cu-K α radiation, in a Bragg-Bretano geometry in the range $10^\circ < 2\theta < 80^\circ$. Optical transmittance spectra of the films were measured using a Shimadzu UV 3101 PC spectrophotometer from 300 to 2500 nm.

Micro-Raman spectra were measured on a Jobin-Yvon T64000 spectrometer equipped with a liquid nitrogen cooled CCD detector, in the back-scattering geometry, in a frequency range of 200-700 cm^{-1} , using the 488 nm (2.54 eV) excitation line of an Ar^+ laser with an incident power of 4 mW.

3. Results and discussion

All the produced ZnO films are polycrystalline. This also holds for the implanted films after annealing. According to the X-ray diffraction spectra, the micro-crystallites have the wurtzite structure and show a strongly preferential orientation with the c -axis perpendicular to the surface, independently of the dopant ion and implantation dose. From the XRD analysis of the samples performed prior to implantation, the crystalline grain size has been estimated at ≈ 200 Å. After implantation, this size was found to decrease and then partially recovered with annealing, reaching a value some 10% lower than the initial one.

Figure 1: Transmission spectra of the undoped ZnO film and of the three films implanted with D2 dose (after annealing).

Figure 1 depicts typical transmission spectra of the films implanted with dose D2. For comparison it is also shown the transmission spectra of the corresponding undoped film. From the fits obtained by the Minkov method using the classical Lorentz-Drude theory for the dispersion of the complex dielectric function, the film thickness and optical parameters were determined [8]. After doping, the films remained transparent in the visible and NIR region revealing good optical quality (only the Mn-doped films exhibit its typical yellowish colour) regardless the implantation ion. However, we observed a small shift of the absorption edge with the increase of the dopant content, in agreement with ref [9]. The estimated optical band gap energy is in the range 3.2-3.3 eV.

The essential Raman spectroscopy results are shown in Fig. 2. Figure 2a presents the Raman spectra of the original, non-doped ZnO thin film, and typical Al and Sb-implanted ZnO thin films after the annealing treatment. In Fig. 2b, the spectra of Mn-doped ZnO films prepared both by ion implantation (ZnO:Mn and ZnO:Al:Mn) and co-sputtering (ZnO:Mn(sp)) are shown.

Figure 2: (a) Raman spectra of the original ZnO film and of those implanted with Al and Sb-ZnO (the heaviest dose, i.e., dose D2) after annealing; (b) Raman spectra of the Mn-doped samples, ZnO:Mn and ZnO:Al:Mn obtained by implantation, and ZnO:Mn(sp) produced by co-sputtering.

In the Raman spectrum of undoped ZnO, only E2 (high) phonon mode is seen at 437 cm^{-1} , as expected in the used geometry (backscattering with $k||z$). Although the A1(LO) mode is also dipole-allowed in this geometry, for parallel polarizations of the incident and scattered light, in practice, it is hardly detectable. For instance, it was not observed for bulk c-ZnO unless under resonance excitation [10]. The low-intensity peak at 320 cm^{-1} seen for the undoped film and also in all the spectra presented in Figure 2 is assigned to a two-phonon-difference mode [3].

Doping with Al or Sb (Fig. 2a) results in the appearance of an intense and broad band in the spectral region close to the LO phonon frequencies of undoped c-ZnO (574 cm^{-1} for A1-mode and 583 cm^{-1} for E1-mode) [11]. For ZnO:Sb and ZnO:Al samples, the maximum of this band (particularly intense for the ZnO:Sb sample) lies at approximately 572 cm^{-1} . It becomes more and more important with the increasing implantation dose, as it can be seen in Fig. 3 for ZnO:Sb samples. Similar effect has been observed in the literature for a number of doping impurities [1] and was attributed to point defects. However, the universal behavior of this band observed for ZnO doped with several impurities (also

Mn, see Fig. 2b) hints that it may be related to LO-type lattice phonons. The enhancement of the LO-phonon mode can be due to the intra-band Frohlich interaction. It is known that in III-V semiconductors, where LO-phonon scattering is dipole-forbidden, it is often seen under (or close to) resonant conditions. This mode is also strongly enhanced in nanostructures, e.g. QDs due to the (partial) separation of electron and hole clouds in space (created by the incident photon) [12]. Indeed, Raman spectra of "ZnO submicron crystals" presented in Ref. 6 are dominated by the LO phonon mode (in addition, the authors of this work used resonant excitation at 325 nm). Probably something similar happens when the ZnO thin films are rather heavily doped, whatever the type of impurity (n or p) is. Then the strong scattering of the electrons and holes on the impurities can relax the $q=0$ selection rule of the dipole-allowed Raman scattering. One can also expect that LO phonons participating in the scattering will be a mixture of A1 and E1 modes because of the symmetry breaking introduced by the impurities. This may explain the slight shift of the peak position with doping.

Figure 3: Raman spectra of two different doses of ZnO:Sb thin films.

Doping ZnO with Mn introduces an extra mode at $\approx 530 \text{ cm}^{-1}$ that appears in all Mn-doped spectra and is not observed for any other impurity. In order to clarify the origin of this mode, Raman spectroscopy was performed for ZnO:Mn films implanted with two different doses, D1 and D2. The results are depicted in Fig. 4a and show that the intensity of the Raman signal at this frequency increases with increasing the concentration of Mn. In order to eliminate the possibility that this 530 cm^{-1} peak would be due to the defects in ZnO lattice resulting from the implantation, our Raman studies were extended to two samples of ZnO:Mn produced by co-sputtering (ZnO:Mn (sp)). With this alternative doping method, the extra Raman mode is also present as can be seen in Fig 4b. Moreover, layers co-doped with two

impurities (ZnO:Al:Mn) show essentially the same behavior, as far as the 530 cm^{-1} mode is concerned, and its relative importance increases with the Mn dose as can be seen in Fig 4c. Thus, we conclude that the extra mode is undoubtedly associated with Mn ions or atoms. As a matter of fact, such an extra mode has been observed before in ZnO:Mn doped films [4, 13] and has been interpreted as a local mode due to Mn substituting Zn in a lattice site [14]. Although such an assignment seems reasonable, the effects of plasmon-phonon coupling, known to be important for GaAs:Mn [15], should be investigated by combining Raman and FIR spectroscopies.

Figure 4: Raman spectra of Mn doped ZnO films (a), the dose effect in ZnO:Mn implanted films; (b) the dose effect in ZnO:Mn(sp) films produced by co-sputtering; (c) the dose effect in ZnO:Al:Mn films where also shown, for comparison, the spectrum of (Mn free) ZnO:Al.

4. Conclusion

In conclusion, we have been able to produce polycrystalline transparent doped-ZnO layers by RF sputtering technique. Their doping with Sb, Al and Mn can be achieved by ion implantation and subsequent annealing without spoiling their optical transparency and structural properties. Our studies of the films by means of Raman spectroscopy show that doping with Al or Sb results in the appearance of an intense and broad band in the spectral region close to the LO phonon frequencies of undoped c-ZnO. Together with the previously reported data, the list of different impurities that provoke this effect

becomes long enough to believe that it has a universal origin, a doping-activated enhancement of the (forbidden) scattering on polar LO phonons through the intra-band Fröhlich mechanism. Doping with Mn induces an extra mode at about 530 cm^{-1} . Although, following the opinion published in the literature, we tentatively assign it to the local mode vibration mode of Mn in substitution position, further studies are necessary to confirm this assertion.

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