

CHAPTER 4

FABRICATION, STRUCTURAL AND OPTICAL STUDIES OF INDIUM DOPED ZnO (IZO) NRs

In this chapter, the growth of 1-D ZnO NSs on the ITO coated glass substrate under various substrate temperatures and (Ar+O₂) deposition pressures has been described. The anisotropic transformation of 1-D ZnO NSs has been observed according to the variation in the deposition pressure at substrate temperature of 550 °C. The structural studies of IZO NRs demonstrate the hexagonal phase and good crystalline quality. The doping concentration and mobility of the NRs are determined to be $1.3 \times 10^{17} \text{ cm}^{-3}$ and $68 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ respectively by the Raman line shape analysis of the longitudinal optical phonon–plasmon coupled mode.

4.1 Introduction

The desirable electrical and optical properties of ZnO NSs are very important for device fabrications. To enhance the optical and electrical properties of ZnO, the doping is the simplest method. The group III and IV elements are usually doped to enhance the electrical parameters of ZnO. In particular, IZO is an attractive material due to its properties such as low resistivity and high optical transparency in both the visible and the infrared regions [90]. Hence, it is expected that IZO can be one of the most promising candidates for transparent conductors. Kyaw et al. reported that IZO semiconductor film is a suitable candidate for the charge collecting layer in organic solar cells due to its good optical transparency [91]. In recent years, it was accounted that IZO films with high mobility is an appropriate alternate for transparent electrodes in optoelectronic devices and it is also expected to increase the efficiency of copper indium gallium selenide based solar cells [92]. Further, well aligned arrays of vertically orientated IZO NRs are considered as a

suitable alternate to TiO₂ based dye sensitized solar cells owing to the poor crystalline quality of TiO₂ NWs on transparent conducting oxide substrates [93]. It was found that the electron diffusion coefficient of 1-D NSs is many times larger than that of ZnO or TiO₂ thin films and it increases the efficiency of the devices [94]. Hence, many research groups have been focused their attention on the growth and characterization of vertically aligned IZO NRs.

There are several possible ways to dope indium into ZnO lattice. Here, we have employed a physical deposition technique by exploiting the migration of indium adatoms from ITO coated glass substrate to dope into ZnO NRs. The thermal stability of ITO is poor and easily dissociate into indium and tin oxides at higher growth temperature. The indium can easily out-diffuse and incorporate into growing crystal lattice of ZnO. The migration length, vapor pressure and sublimation are the important factors on the control of indium incorporation into the host lattices. In this chapter, the growth of 1-D NSs on the ITO coated glass substrate under various growth temperatures and (Ar+O₂) pressures by RF magnetron sputtering has been discussed. Vertically aligned IZO NRs grown on ITO coated glass substrates are highly reproducible under the identical conditions. The structural, optical and electrical properties of the NRs grown under the pressure of 0.1 mbar at the substrate temperature of 550 °C are extensively investigated.

4.2 Experimental procedure

Depositions of 1-D ZnO NSs were carried out by RF magnetron sputtering using a pure 2 in. ZnO target on the commercially available ITO coated glass substrates. Prior to deposition, the substrates were cleaned by acetone and ethanol for 15 min each. The distance between the target and substrate was kept constant at 50 mm and the deposition was carried out with the rf power of 150 W for 60 min. In order to maintain the oxygen rich ambient within the chamber, the additional oxygen gas was supplied into the chamber through needle valve and the deposition was carried out at the total pressure of

0.1 mbar. In the deposition process, the oxygen rich atmosphere is maintained to induce the non-stoichiometry which evolves different NSs including 1-D NSs at elevated growth temperature. The deposition of ZnO was performed under various substrate temperatures (350, 450 and 550 °C) and (Ar+O₂) pressures (0.01, 0.05 and 0.1 mbar) at identical conditions.

4.3 Results and discussion

4.3.1 Morphological and structural studies of IZO NRs

The FESEM images of ZnO deposited on ITO coated glass substrates under various substrate temperatures are shown in Fig. 4.1. The substrate temperature is varied at 350, 450 and 550 °C, while the rest of the growth parameters are kept constant including the pressure at 0.1 mbar for 60 min growth duration. The evolution of the NSs under various substrate temperatures is analyzed.

At a substrate temperature of 350 °C, the thin film like structures was found with the rough surfaces as shown in Fig. 4.1(a). The high density nuclei are observed at 450 °C as shown in Fig. 4.1(b) and the surface becomes rough with coalesced nucleation. Further increasing the substrate temperature to 550 °C, the nuclei confine the diameter and promote the growth of vertically aligned NRs with the average diameter of 90 nm and its length up to 1 μm for 60 min growth duration. Fig. 4.1(c) shows the FESEM image of the vertically aligned NRs and its inset depicts the diameter distribution of the NRs. The self-assembled NRs are vertically aligned along the c-axis with the hexagonal cross section. The NRs are found to be homogeneously distributed over the substrate with uniform diameter and length. The density of the NRs is calculated to be $4 \pm 0.5 \times 10^9 / \text{cm}^2$.

In order to understand the structural variation of ZnO NSs, the deposition pressure has been varied between pure Ar and (Ar+O₂) ambient at constant growth temperature. Fig. 4.2 shows the FESEM images of ZnO NSs grown on

ITO coated glass substrates under different (Ar+O₂) pressures (0.01, 0.05 and 0.1 mbar) and the other growth parameters are kept constant. Under pure Ar ambient with the pressure of 0.01 mbar at 550 °C, the NWs are grown laterally on the substrate with the average diameter of 320 nm and its length up to 4 μm as shown in Fig. 4.2 (a). The lateral NWs are distributed uniformly on the substrate with low density. It is well known that the sputtering rate strongly depends on the pressure within chamber. Under low chamber pressure, the growth rate of the NSs is high due to the reduced number of collisions. The high sputtering rate promotes the lateral growth of NWs [47]. On the other hand, when the O₂ was introduced into the chamber up to the growth pressure of 0.05 mbar (Ar: 0.01 mbar; O₂: 0.04 mbar) at 550 °C for 60 min, the anisotropic growth transformation have occurred from lateral to vertical standing NRs as shown in Fig. 4.2 (b) owing to the influence of Zn adatom mobility under the over pressure of O₂. The average diameter and the length of NRs are 85 and 600 nm respectively. Further, we noticed that there is a small cavity on the top of the NRs and its depth is approximately 30 nm. The density of the vertically aligned NRs is relatively high as compared to lateral NWs. Further, increasing the oxygen pressure to 0.1 mbar, the NRs remain vertical and grew up to 1 μm with the average diameter of 90 nm as shown in Fig. 4.2 (c). The density and aspect ratio of the NRs are increased as compared to the Fig. 4.2 (b) grown at 0.05 mbar. NRs exhibit a small cavity on the top and its diameter and depth are 40 and 50 nm respectively.

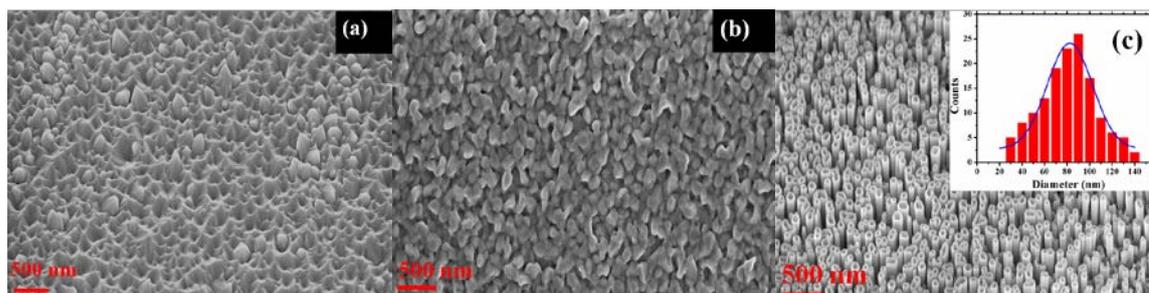


Fig. 4.1 FESEM images of ZnO nanostructures grown under various substrate temperatures at constant (Ar + O₂) pressure of 0.1 mbar. (a) 350 °C, (b) 450 °C, (c) 550 °C and the inset shows the diameter distribution of the NRs.

To ascertain the reason for the appearance of cavity on the top of the NRs, the deposition was carried out under various time durations such as 15, 30 and 60 min at constant temperature and pressure of 550 °C and 0.1 mbar respectively. For the 15 min deposition, only short NRs of 90 nm diameter with flat top is observed. But, for the 30 and 60 min growth, a clear cavity is found on the top of the vertically aligned NRs. As compared to 30 min growth, the depth of the cavity is increased from 30 to 50 nm for 60 min growth duration. Hence, we suggest that the cavity on the top of the NRs may be formed due to the insufficient free radicals of zinc under oxygen rich ambient. Generally, the low sputtering rate at high pressure is attributed to the increased number of collisions between the sputtered molecules and gas molecules within the chamber. Here, the growth of the NRs is carried under higher pressure; subsequently the mean free path is expected to be reduced. Hence, the migration of Zn adatoms on the facet of NRs will be suppressed due to O₂ rich condition. However, the out-diffusion of indium adatoms due to sublimation of ITO at 550 °C migrates along the sidewalls of the NRs and incorporates into the ZnO lattice as a dopant. The indium adatoms lowers the Gibbs free energy and crystallizes the available free radicals of zinc and oxygen on the growth front and this may be responsible for

the cavity on the top of the NRs. The direct impingement and diffusion induced mechanism are responsible for the growth of NRs.

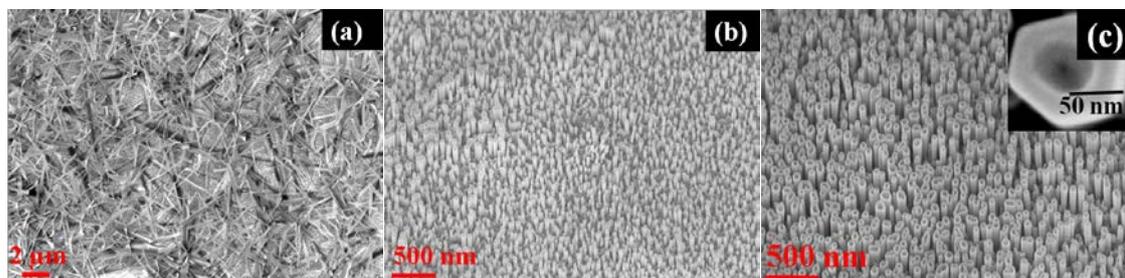


Fig. 4.2 FESEM images of ZnO nanostructures grown under various (Ar+O₂) pressures at constant temperature of 550 °C. (a) Pure Ar under the pressure of 0.01 mbar, (b) (Ar + O₂) pressure of 0.05 mbar and (c) (Ar + O₂) pressure of 0.1 mbar and the enlarged view of a single NR.

The surface migration continues to enhance the growth if the length of NRs is shorter than the migration length, otherwise it will be desorbed from the facet of the NRs. The inset of the Fig. 4.2 (c) clearly depicts the enlarged view of the cavity on the top of a NR. Vertically aligned IZO NRs are expected to be a potential candidate for transparent conducting oxide anode applications for both in optoelectronics and photovoltaics. Hence, a detailed investigation is extended to the IZO NRs grown at 550 °C under the oxygen rich condition with the pressure of 0.1 mbar.

XRD pattern of IZO NRs grown on ITO coated glass substrate is shown in Fig. 4.3 and the inset shows the XRD pattern of the bare ITO coated glass substrate. ITO films are polycrystalline with the preferential orientation along (222) direction and all the diffraction peaks of the ITO films correspond to cubic phase and it is in good agreement with standard results. It could be noticed that IZO NRs show a dominant (002) reflection peak at $\sim 34.23^\circ$ representing a preferential growth along the c-axis normal to the ITO coated glass substrate. The intense diffraction peak along (002) relative to the background with narrow full width at half maximum (FWHM) (~ 1177 arc-sec) demonstrates the

hexagonal phase and good crystalline quality of IZO NRs. The diffraction peaks of the NRs marginally shift towards lower diffraction angle as compared to the strain free ZnO NWs grown on silicon substrate [95]. The (002) diffraction peak shift indicates the increase of out-plane lattice parameter 'c' in ZnO lattice. The increase of lattice parameter is expected due to the incorporation of indium into the ZnO lattice by the migration of indium atoms from ITO buffer layer. The larger ionic radii of In^{3+} (0.76 Å) substitutes into the smaller Zn^{2+} (0.64 Å) site, leads to an increase in the lattice parameter to $c=0.5237$ nm from its standard bulk value of 0.5213 nm. Thus the peak shift and the corresponding lattice parameter provide conclusive evidence for the substitution of In^{3+} partly into the ZnO lattice [96]. Using Vegard's law, the incorporation of cations (In^{3+}) into the host lattice of ZnO NRs is calculated to be approximately 1%.

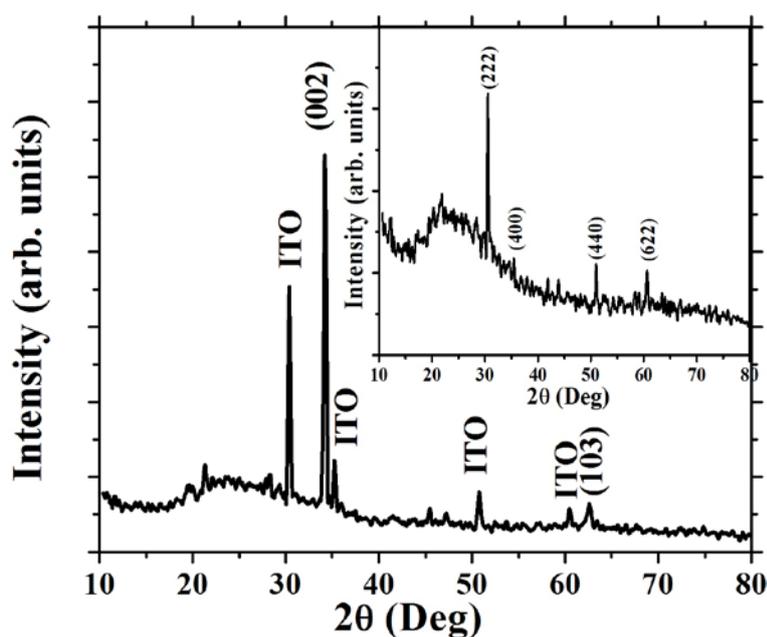


Fig. 4.3 XRD pattern of the IZO NRs grown on ITO coated glass substrate by RF magnetron sputtering. The inset shows the XRD pattern of the ITO coated glass substrate.

Fig. 4.4 (a) depicts the HRTEM lattice fringes with an interplanar spacing of about 2.62 Å corresponding to the (0002) crystallographic direction. This agrees well with the interplanar distance calculated from X-ray diffraction

pattern. Fig. 4.4 (b) shows the selected area electron diffraction (SAED) pattern of a single IZO NR, which provides more evidence for the c-axis oriented growth and single crystalline nature of IZO NR grown on the ITO coated glass substrates. These results provide a strong confirmation of wurtzite crystalline nature of IZO NRs and consistent with XRD observation.

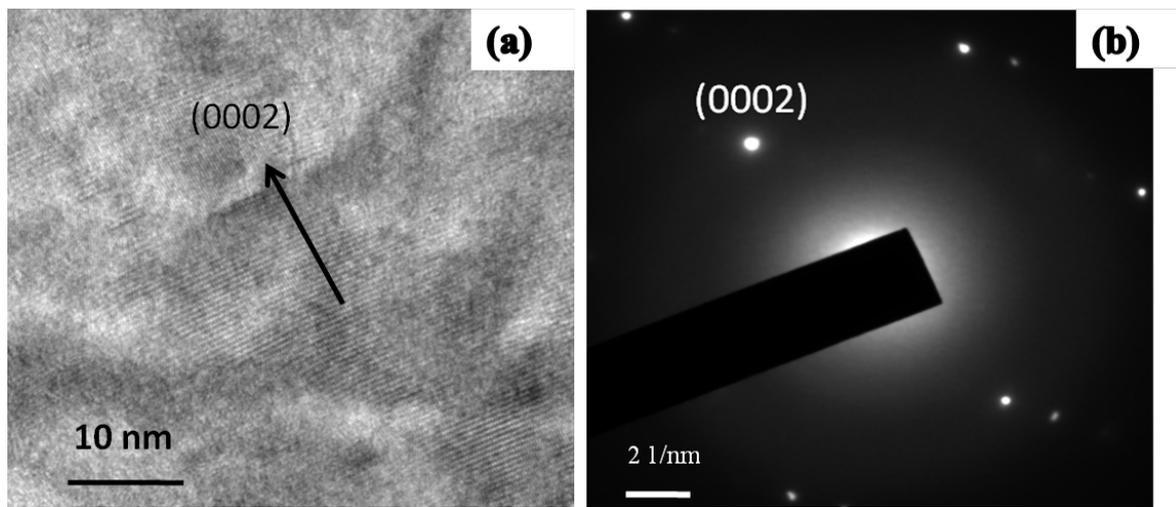


Fig. 4.4 (a) HRTEM image of IZO NRs indicating the perfect wurtzite structure and (b) SAED pattern describes the (002) orientation of IZO NR.

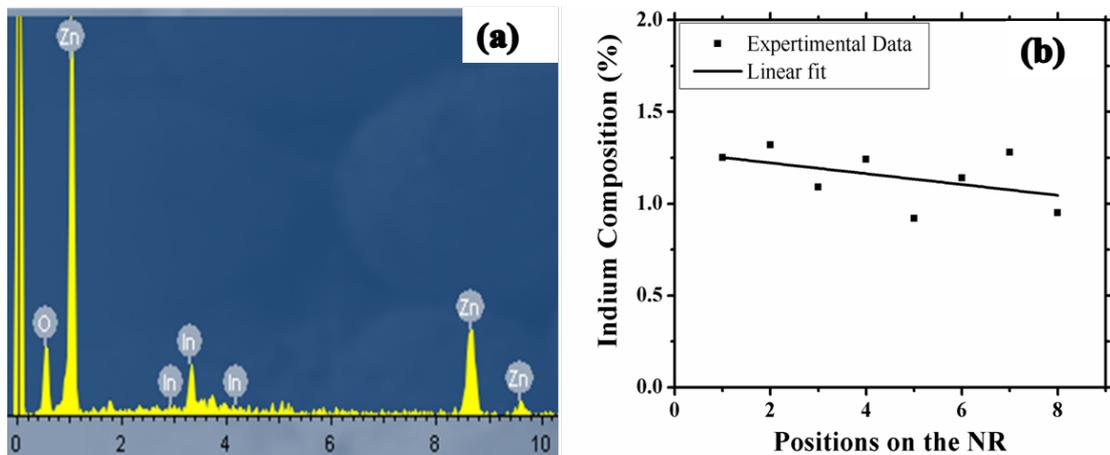


Fig. 4.5 (a) EDX spectrum of IZO NRs grown on ITO coated glass substrate and (b) Spatial distribution of indium composition on the single IZO NR along the growth direction.

Fig. 4.5 (a) shows the EDX spectrum of a single IZO NR which depicts the existence of the zinc, indium and oxygen with no other secondary traces. Here, we have recorded the EDX spectrum from the magnified cross sectional view and hence one can easily avoid the substrate influence in this spectrum. The distribution and composition of indium are probed at several points periodically at a distance of ~ 100 nm along the axial direction from the bottom of a single IZO NR. The indium is found to be homogeneously distributed from bottom to top of a NR, which is represented in Fig. 4.5 (b). The indium composition identified by the EDX analysis corroborates with the XRD result of 1% doping determined by the Vegard's law and this confirms the unintentional doping of indium in ZnO NRs. ITO is known to be thermodynamically unstable and indium atoms can out-diffuse into the neighboring interface or accumulate on the surface by depletion at the growth temperature of ~ 550 °C. The indium adatom migration length on the facets of ZnO is about $25 \mu\text{m}$ [97]. However, the incorporation of indium into the ZnO lattice highly depends on the solid solubility, diffusion rate and vapor pressure of indium that vary with temperature and pressure, especially oxygen rich pressure [98]. At 550 °C, the indium has a low vapor pressure ($\sim 1 \times 10^{-6}$ mbar). Consequently, the diffusion rate of indium is expected to be reduced and hence only a low concentration of indium incorporation occurs in ZnO lattice.

4.3.2 Optical properties of IZO NRs

Fig. 4.6 (a) depicts the micro-Raman spectrum of vertically aligned IZO NRs grown on ITO coated glass substrate at 550 °C. The dominant peaks at 99 and 439 cm^{-1} are attributed to the lattice vibrations of the optical phonons E_2^{low} and E_2^{high} respectively. E_2^{high} is the characteristic Raman active mode of hexagonal wurtzite ZnO, which is very sensitive to strain, composition, crystalline quality and laser induced localized heating of NRs. The sharp FWHM of 1.9 cm^{-1} for E_2^{low} at 99 cm^{-1} evidences the good optical quality of NRs. Here, the peak position of the E_2^{high} phonon shifts towards the higher wave number

side of the spectrum by 2 cm^{-1} with FWHM of 6.4 cm^{-1} as compared to the strain free ZnO single crystal [86]. However, this considerable shift in the E_2^{high} phonon peak can be attributed to either the laser induced localized heating or the incorporation of foreign impurities into the ZnO host matrix [85]. If laser induced heating plays a role, the shifts would have been effected for all the observed Raman lines. In our case, only E_2^{high} mode exhibits the shift and hence laser heating cannot be responsible for this peak shift of E_2^{high} phonon mode. On the other hand, it is presumed that the doping of indium in ZnO lattice is more pronounced for the E_2^{high} phonon shift. The adatom migration length of indium is several micrometers and could easily migrate and incorporate into the growing lattice. Hence, the intrinsic doping of volatile impurities from the substrate can be unavoidable. The spectrum has been analyzed by the Lorentz peak fit to deconvolute ZnO and ITO peaks. The fitting reveals a peak at 577 cm^{-1} which corresponds to $A_1(\text{LO})$ Raman phonon mode of IZO NRs and it is red shifted about 3 cm^{-1} as compared to the relaxed $A_1(\text{LO})$ phonon mode of ZnO (574 cm^{-1}) which indicates that the collective oscillation of free carriers (plasmons) are coupled with LO phonons through the longitudinal electric fields, represented as longitudinal optical plasmon coupled (LOPC) mode. The additional peaks at 131 cm^{-1} and 566 cm^{-1} arise from the ITO coated glass substrate.

Generally, the electrical properties are studied by Hall, impedance and capacitance–voltage (C-V) measurements. However, these measurement techniques require electrical contacts and give information about the transport properties of the sample averaged over relatively large volumes. Raman scattering is one of the non-destructive methods to determine the electrical properties of 1-D NSs on the spatially defined area by the focal size of the optical beam. The carrier concentration of the polar semiconductors can be determined using Raman scattering without the need of ohmic contacts from LOPC mode. The $A_1(\text{LO})$ mode splits into the lower (L_-) and upper (L_+)

branches to phonon-plasmon coupling. With the increase of the free carrier concentration, the L_+ mode shifts to high wavenumbers with broadening and weak intensity [70].

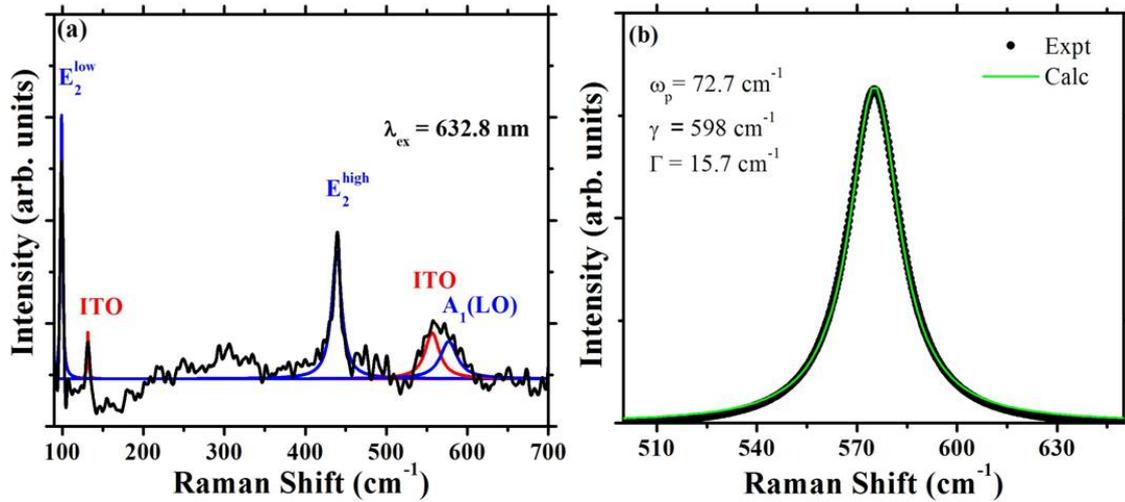


Fig. 4.6 (a) Micro-Raman spectrum of IZO NRs recorded in the back scattering geometry and (b) Comparison of the experimental and calculated line shapes of the LO phonon-plasmon coupled mode of the IZO NRs.

From the Raman line shape analysis, the free carrier concentration (n) and mobility (μ) can be determined more precisely with the considerations of deformation potential and electro-optical mechanisms [70]. The following constants have been used for the line shape analysis of coupled $A_1(\text{LO})$ mode ($\omega_{\text{TO}} = 382 \text{ cm}^{-1}$, $\omega_{\text{LO}} = 574 \text{ cm}^{-1}$ and $\epsilon_{\infty} = 3.68$). Fig. 4.6 (b) shows a typical line shape of the experimental and the theoretical curves of the $A_1(\text{LO})$ phonon-plasmon coupled mode. The reproducible fitting parameters plasmon damping constant (γ), phonon damping constant (Γ) and plasmon frequency (ω_p) have been obtained from the above line shape analysis and given in Fig. 4.6 (b). Plasmon frequency (ω_p) and plasmon damping constant (γ) can be related to the free carrier concentration (n), effective electron mass ($0.23m_e$) and mobility (μ).

$$\omega_p^2 = \frac{\pi n e^2}{\epsilon_a m^*} \text{-----} (4.1)$$

and

$$\mu = \frac{e}{m^* \gamma} \text{-----} (4.2)$$

The estimated free carrier concentration (n) and mobility (μ) from the above relation are $1.3 \times 10^{17} \text{ cm}^{-3}$ and $68 \text{ cm}^2/\text{Vs}$ respectively. These estimated values are in the same order of the reported values, however, the difference can be attributed to the enhanced surface scattering due to the low dimension of the IZO NRs (diameter $D = 90 \text{ nm}$) and experimental growth parameters.

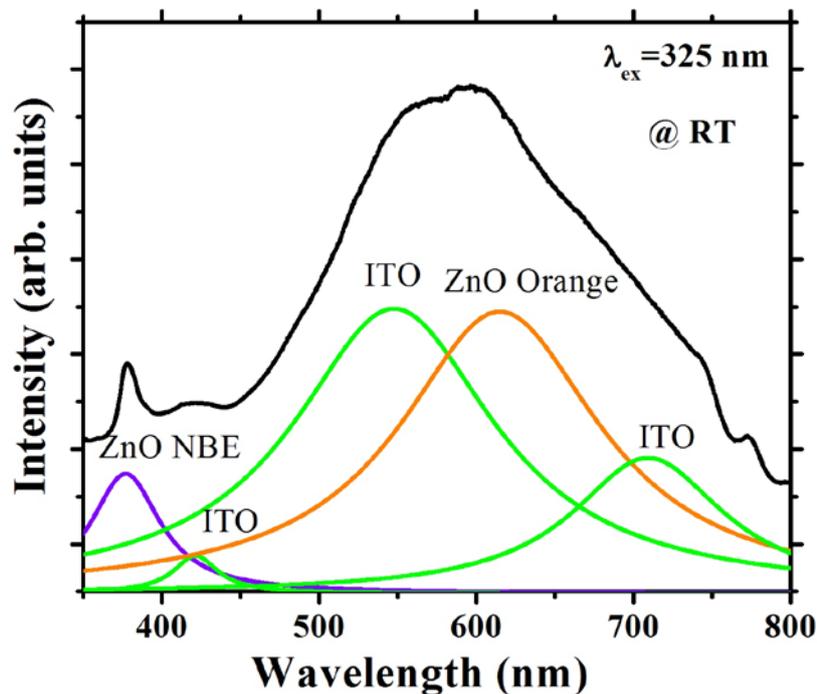


Fig. 4.7 RTPL spectrum of IZO NRs grown on ITO coated glass substrate.

Fig. 4.7 illustrates the RTPL spectrum of IZO NRs grown on ITO coated glass substrate. The PL spectrum is fitted with Lorentz function. The fitted peaks are centered at 377, 421, 547, 615 and 709 nm. The fitted peaks at 377 and 615 nm are attributed to IZO NRs and assigned as near band edge (NBE) and orange

emissions respectively. The NBE emission of IZO NRs grown under oxygen rich environment looks broad with the FWHM of 53 nm. Further, the oxygen interstitial related defects are considered as the most probable culprit for the generation of dominant orange emission and quenching of band edge emission in the NRs grown under oxygen rich ambient [99]. The observed additional peaks at 421, 547 and 709 nm are arise from the base of the ITO coated glass substrate and related to the defects of the ITO film.

4.4 Summary

The fabrication and characterization of vertically aligned IZO NRs on ITO coated glass substrates by RF magnetron sputtering at 550 °C have been discussed in this chapter. The anisotropic transformation from lateral NWs to vertical standing NRs has occurred at 550 °C under the (Ar+O₂) pressure range of 0.01-0.1 mbar. Uniformly distributed high density ($4 \times 10^9/\text{cm}^2$) and well isolated ZnO NRs with homogeneous diameter (90 nm) were achieved by varying the growth parameters such as substrate temperature and pressure. The structural investigation reveals the hexagonal wurtzite nature of IZO NRs with preferential growth along (002) crystallographic plane. The indium atoms are spatially incorporated into the ZnO lattice through migration from the ITO coated glass substrate during the growth. Uniform distribution of dopant along the axial direction is relying on the adatom diffusion length and 1% doping is expected to be within the solid solubility. The spatial distribution of indium into ZnO matrix substantially enhances the optical quality of ZnO NRs as substantiated by the symmetry allowed E_2^{low} and E_2^{high} of Raman stokes lines. The line shape analysis of the coupled $A_1(\text{LO})$ mode has been found to be a non-contact versatile tool to measure the carrier concentration and mobility of IZO NRs ($n = 1.3 \times 10^{17}/\text{cm}^3$ and $\mu = 68 \text{ cm}^2/\text{V sec}$). The defect mediated orange emission in IZO NRs evidences the presence of oxygen interstitial related point defects in IZO NRs.