

Photoluminescence and Raman spectroscopy of polycrystalline ZnO nanofibers deposited by electrospinning

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The technique of electrospinning offers the advantage of growing nanowires in bulk quantities in comparison to the traditional methods. We report optical studies of polycrystalline zinc oxide (ZnO) nanofibers (~ 100 nm thick and 5 μm long) deposited by electrospinning. Photoluminescence from the nanofibers shows a near UV peak corresponding to the near band edge emission and a strong broad peak in the visible region from oxygen antisite and interstitial defects. Temperature dependent photoluminescence spectroscopy reveals different carrier recombination mechanisms are dominant at low temperature. Our Raman spectroscopy results demonstrate that the characterization of the quasi-modes of longitudinal optical (LO) and transverse optical (TO) phonons present in an ensemble of polycrystalline nanofibers tilted at varied angles in addition to the dominant E_2 (high) mode provide a promising technique for assessing the quality of such randomly oriented nanowires.

Keywords: Zinc oxide, polycrystalline nanofibers, electrospinning, Raman spectroscopy

I. INTRODUCTION

Energy harvesting is necessary in order to satisfy the energy requirement for the ongoing advancements in all different fields ranging from military applications, medical purposes to home entertainment. Over the last few decades researchers around the world have been focusing on developing innovative nanotechnologies for energy harvesting, of which piezoelectric energy harvesting has recently drawn much attention [1]. Due to the wide band gap (3.4 eV) of ZnO with a large exciton binding energy (~ 60 meV), ZnO has been considered as a promising contender for application in solar cells, gas sensors and other optical devices. Recently, there has been much ongoing research on exploring the piezoelectric property of zinc oxide [1-3].

ZnO nanowires have been grown so far on various substrates with or without seeds, catalysts, surfactants, capping agents, and templates [4-7]. However, substrate-free ZnO nanowires would be more advantageous in various applications. Moreover, it is difficult to grow large quantities of nanowires using the traditional methods due to the equipment and substrate size limitations in contrast to electrospinning [8]. In this work we have investigated the optical properties of ZnO nanowires deposited by electrospinning from photoluminescence (PL) spectroscopy and Raman spectroscopy results.

II. EXPERIMENTAL DETAILS

ZnO nanofibers were deposited by electrospinning using zinc acetate ($\text{Zn}(\text{O}_2\text{CCH}_3)_2$) and polyvinylpyrrolidone ($\text{C}_6\text{H}_9\text{O}$)_n as the precursors under atmospheric conditions. The as-deposited fiber-mats were annealed at various temperatures ranging from 500 °C to

800 °C for different durations under different ambient conditions. The transmission electron microscopy (TEM) image of the nanofibers was studied using a JEOL JEM 3010 electron microscope. The photoluminescence (PL) of the nanofibers was studied using 325 nm laser line of a He-Cd laser. The scattered light was analyzed with an ACTON SpectraPro spectrometer equipped with a UV-enhanced liquid nitrogen cooled charged coupled device. The low temperature PL measurement was carried out with a closed-cycle Janis CCS-150, 10 K cryogenic system with standard UV grade quartz optical view ports. The Raman spectroscopy of the nanofibers was studied with Raman Reinshaw Microscope 2000 using 1800 grooves/mm grating providing 2 cm^{-1} resolution. The Raman spectrum was excited using the 514 nm laser line of an Argon ion laser.

III. RESULTS AND DISCUSSION

The as-deposited fiber-mats were annealed under different conditions to form ZnO nanofibers. The inset (a) of Fig.1 shows large scale of nanofibers has been synthesized by electrospinning. On annealing the fiber-mat at 800 °C at a very slow ramp rate for 1 h in oxygen ambient, about 100 nm thick and 5 μm long polycrystalline nanofibers were obtained as shown in Fig.1. It is important to note that the thickness of the crystals grown here is equal to the diameter of the nanofiber which makes it applicable for energy harvesting in contrast to the nanofibers composed of very small ($\sim 5\text{-}10\text{ nm}$) nanocrystallites reported in literature [9]. Since ZnO is piezoelectric, mechanical strain will generate some electric field for each crystal. However, if the fiber is composed of very small and unaligned nanocrystallites, there will be significant amount of field cancellation. Indeed, aligned single crystalline fibers would be the best for energy harvesting. However, our initial preliminary measurements show that with fibers with $\sim 100\text{ nm}$ crystals we could generate some electrical output.

The annealed fibers were stoichiometric in nature as confirmed by Energy Dispersion Spectrum (EDS) shown in inset (b) of Fig.1.

Figure 2 shows the PL spectrum from the polycrystalline nanofibers. The PL spectrum shows a weak peak near the UV region and a strong broad peak in the visible region. The near UV emission can be attributed to near band edge emission. The broad strong peak in the visible region is due to a defect level in the mid gap region [10]. The point defects in a crystal include any foreign atom at a regular lattice site (i.e., substitutional site) or between lattice sites (i.e., interstitial site), antisite defects (e.g., Zn in O or O in Zn in the oxide), missing lattice atoms, and host atoms located between lattice sites and adjacent to a vacant site (i.e., Frenkel defects). The green emission from this oxide has been often related to O-vacancies [11]. However, in our case, since the fiber-mats have been annealed in oxygen rich environment, the probability of O-vacancies is much less which is in turn confirmed by the stoichiometric nature of the ZnO nanofibers. The green emission is also at times related to trace amount of carbon condensation in the nanowires [8]. Again, annealing the fiber-mat in O-rich environment also rules out this possibility. The fibers are stoichiometric; however there could be formation of interstitial defects leading to O-vacancies and Zn-vacancies at the lattice site or antisite related defects. Using full-potential linear muffin-tin orbital method, the energy levels obtained for the intrinsic defects in ZnO films are shown in the inset of Fig. 2 [12-14]. The energy interval ($\Delta E = 2.4$ eV) between the conduction band (E_C) and the oxygen antisite (O_{Zn}) level is consistent with the energy of the green emission (2.42 eV) observed in our experiment. Again, the energy interval ($\Delta E = 2.3$ eV) between the

conduction band (E_C) and the interstitial oxygen (O_i) level closely correlates to the green emission (2.42 eV) observed in our experiment. In case of Zn related defects, the energy interval between the Zn antisite level and the valence band is $\Delta E = 2.2$ eV as reported in literature [13-14] which is close to the green emission observed. The PL spectrum shows a very strong broad peak around 2.42 eV. Therefore, the broad strong green emission peak from ZnO nanofibers observed at 2.42 eV is likely due to O antisite, interstitial oxygen and Zn antisites in the oxide.

Figure 3 shows the PL spectra (UV emission) of the polycrystalline nanofibers measured at different temperatures. At low temperature (50 K), the PL features are found to be dominated by excitons bound to neutral donors with a very small free exciton peak visible at 3.36 eV (369.05 nm). As the temperature increases, the free exciton thermalizes and cannot be seen at higher temperature. The peak at 3.3 eV (375.5 nm) is attributed to the emission of excitons bound to neutral donors (D^0X). The peak at 3.23 eV (384.03 nm) is due to the emission of donor-acceptor (DA) pair and the peak at 3.16 eV (390 nm) is phonon replica of the DA pair transition [15]. The inset shows the temperature-dependence of the peak energies $E(T)$ of peak A at 3.36 eV (circles), peak B at 3.3 eV (up triangles) and peak C at 3.23 eV (down triangles) for the nanofibers. It can be observed that all peaks systematically shift to lower energy with increasing temperature and their

energy shifts can be well described by the Varshni equation $E(T) = E(0) - \frac{\alpha T^2}{\beta + T}$, where

$E(0)$ is the transition energy at 0 K, α is related to the exciton-average phonon interaction and β is closely related to the Debye temperature [16]. The α and β values obtained from

fitting the free excitons in ZnO nanofibers are 6.7×10^{-4} eV/K and 385 K, for the bound excitons are 9.4×10^{-4} eV/K and 645 K and for the third peak 5.7×10^{-4} eV/K and 645 K, respectively, which are in reasonable agreement with those reported in literature [17-18].

Figure 4 shows the Raman spectrum of the polycrystalline nanofiber measured at room temperature. According to group theory, the Raman active optical modes for the wurtzite crystal, ZnO, are A_1 , E_1 and the two E_2 modes. The selection rule depending on the crystal orientation relative to the propagation directions and polarizations of the incoming and outgoing light dictates the Raman mode that might be visible in a particular geometry. In our experiment, with 514 nm non-resonant excitation, E_2 (high) mode is the dominant feature in the spectrum. In general, for backscattering geometry, A_1 (LO) mode is also an allowed mode if the incident beam is parallel to the c-axis of the crystal [19]. However, in our experiment with disoriented nanowires, Raman mode frequencies seen at 385 cm^{-1} and 586.7 cm^{-1} are different from either the A_1 or E_1 modes reported for ZnO single crystal [19]. This discrepancy may be addressed in terms of the quasimode-nature of the phonons. In our case, the Raman signal is collected from an ensemble of ZnO nanofibers (which might be tilted at different angles) in backscattering geometry. From an ensemble of nanofibers tilted at different angles, the A_1 modes are expected to interact with E_1 modes and create a quasi mode of mixed A_1 - E_1 symmetry. According to Loudon's model, the quasi- mode frequency should lie between the frequency of pure A_1 (TO) and that of the pure E_1 (TO) modes and quasi-LO mode frequency should lie between the frequency of pure A_1 (LO) and that of the pure E_1 (LO) modes according to the relation

$$\omega_{Q(TO)}^2 = \omega_{E_1(TO)}^2 \cos^2 \beta + \omega_{A_1(TO)}^2 \sin^2 \beta \quad \text{for TO modes} \quad \dots\dots\dots(1a)$$

$$\omega_{Q(LO)}^2 = \omega_{A_1(LO)}^2 \cos^2 \beta + \omega_{E_1(LO)}^2 \sin^2 \beta \quad \text{for LO modes} \quad \dots\dots\dots(1b)$$

where β is the angle of phonon propagation relative to the c-axis of the crystal [20]. By rearranging equation (1a) we have

$$\omega_{Q(TO)}^2 = \omega_0^2 \left[1 + \left\{ \frac{\omega_{E_1(TO)}^2 - \omega_0^2}{\omega_0^2} \cos^2 \beta + \frac{\omega_{A_1(TO)}^2 - \omega_0^2}{\omega_0^2} \sin^2 \beta \right\} \right] \quad \dots\dots\dots(2a)$$

where ω_0 will be shown later to be the average frequency of the quasimode [21]. By expanding equation 2(a) and neglecting the higher order terms we have

$$\omega_{Q(TO)} \approx \omega_0 \left[1 + \frac{1}{2} \left\{ \frac{\omega_{E_1(TO)}^2 - \omega_0^2}{\omega_0^2} \cos^2 \beta + \frac{\omega_{A_1(TO)}^2 - \omega_0^2}{\omega_0^2} \sin^2 \beta \right\} \right] \quad \dots\dots\dots(2b)$$

On averaging equation 2(b) over the angles β (with volume element of $\sin \beta d\beta$), we have

$$\langle \omega_{Q(TO)} \rangle = \omega_0 \left[1 + \frac{1}{6} \frac{\omega_{E_1(TO)}^2 - \omega_0^2}{\omega_0^2} + \frac{1}{3} \frac{\omega_{A_1(TO)}^2 - \omega_0^2}{\omega_0^2} \right] \quad \dots\dots\dots(3)$$

Now we can choose the value of ω_0 such that the last two terms in equation (3) cancels each other giving the quasi-TO mode frequency

$$\langle \omega_{Q(TO)} \rangle^2 = \frac{\omega_{E_1(TO)}^2 + 2\omega_{A_1(TO)}^2}{3} = \omega_0^2 \quad \dots\dots\dots(4)$$

Inserting the values of the two symmetry, A_1 (TO) = 374.7 cm^{-1} and E_1 (TO) = 407.1 cm^{-1} as reported in literature [3] we obtain, $\omega_{Q(TO)} = 385.8 \text{ cm}^{-1}$ which is very close to the one observed at 385 cm^{-1} in our study. Applying the same formula for the quasi-LO mode, and using the frequency of 579 cm^{-1} for the A_1 (LO) and 591 cm^{-1} for the E_1 (LO) [19] we

obtain, $\omega_{Q(LO)} = 587 \text{ cm}^{-1}$ which is also very close to the peak observed at 586.7 cm^{-1} in our study. Therefore the Raman peaks seen at 385 cm^{-1} and 586.7 cm^{-1} may be attributed to the quasi phonon modes. The peak seen at 334.9 cm^{-1} may be attributed to the E_2 (high) - E_2 (low) multiphonon mode [20]. This is also related to second order Raman processes by some researchers and is assigned to $2E_2$ (low) mode which needs further confirmation [23-24].

ZnO nanofibers deposited by electrospinning reported so far were comprised of very small nanocrystallites ($< 10 \text{ nm}$) which pose limitation for its application in piezoelectric energy harvesting. However with our polycrystalline nanofibers (with crystals $\sim 100 \text{ nm}$ diameter) we could successfully generate an electrical output by stretching the polycrystalline fiber mat which will be reported in detail in the future.

IV. CONCLUSION

Large quantities of polycrystalline stoichiometric ZnO nanofibers ($\sim 100 \text{ nm}$ thick and $5 \mu\text{m}$ long) were produced on annealing the electrospun fiber mat in oxygen ambient at a very slow ramp rate at $800 \text{ }^\circ\text{C}$ for 1 h. The room temperature PL spectra show a UV peak due to the near band transition and a broad visible emission due to the antisite oxygen and oxygen interstitial defect levels in the oxide. The temperature dependent PL spectra reveal the different carrier recombination mechanisms, also confirmed by Varshni fitting. In addition to the dominating E_2 (high) mode, the Raman spectrum also shows the quasi-TO and quasi-LO modes of mixed A_1 and E_1 symmetry which can be addressed by modifying Loudon's model for a random ensemble of nanowires. This method

demonstrates the use of the non-destructive Raman spectroscopy to characterize an ensemble of randomly oriented polycrystalline nanowires where a very cost-effective technique and annealing has been utilized for bulk-volume growth of nanowires of promising quality and which has potential for use in energy harvesting.

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Figure captions

Figure 1: TEM image of polycrystalline ZnO nanofiber annealed at 800 °C for 1 h in oxygen ambient at a very slow ramp rate. Inset (a) shows an image of the fibers under optical microscope. Inset (b) shows the EDS image of the fiber.

Figure 2: Photoluminescence spectrum of ZnO nanofibers annealed at 800 °C for 1 h in oxygen ambient. Inset shows the intrinsic defect levels in ZnO film [12-14].

Figure 3: Temperature dependent Photoluminescence spectra (near UV region) of ZnO nanofibers annealed at 800 °C for 1 h in oxygen ambient. Inset shows Varshni fitting for the PL peaks at (A) 3.36 eV, (B) 3.3 eV and (C) 3.23 eV.

Figure 4: Raman spectrum of ZnO nanofibers annealed at 800 °C for 1 h in oxygen ambient.

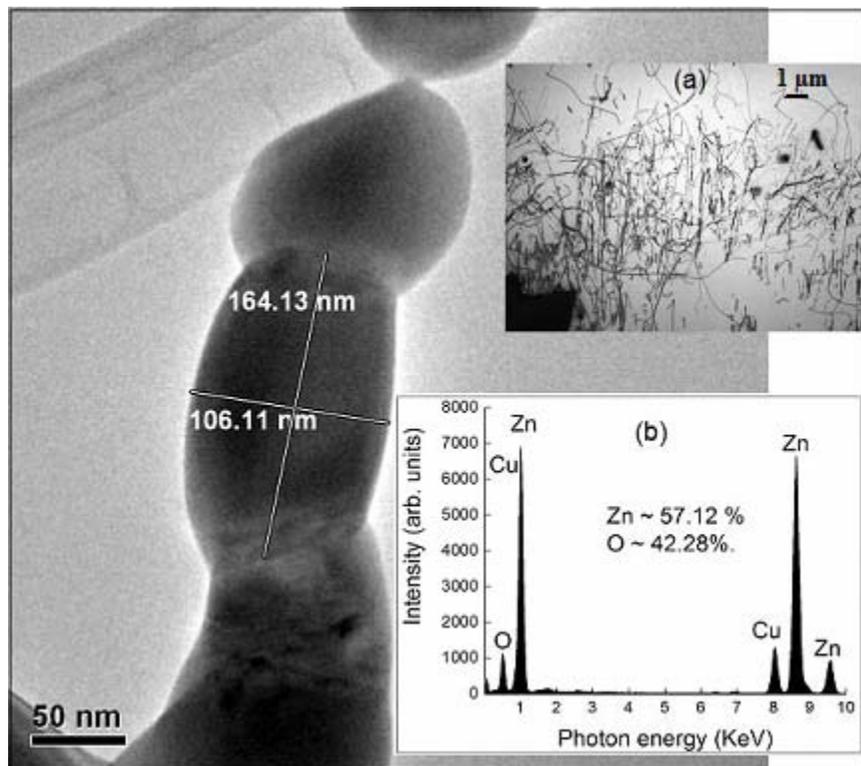


Figure 1

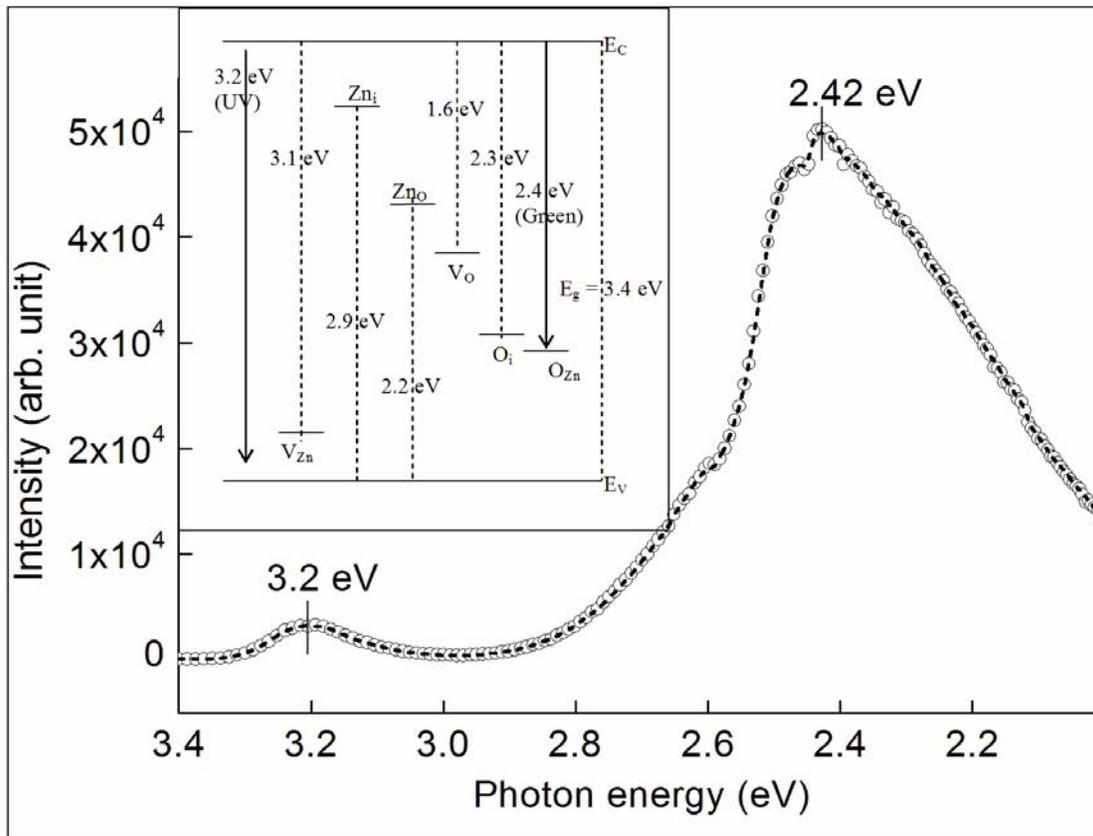


Figure 2

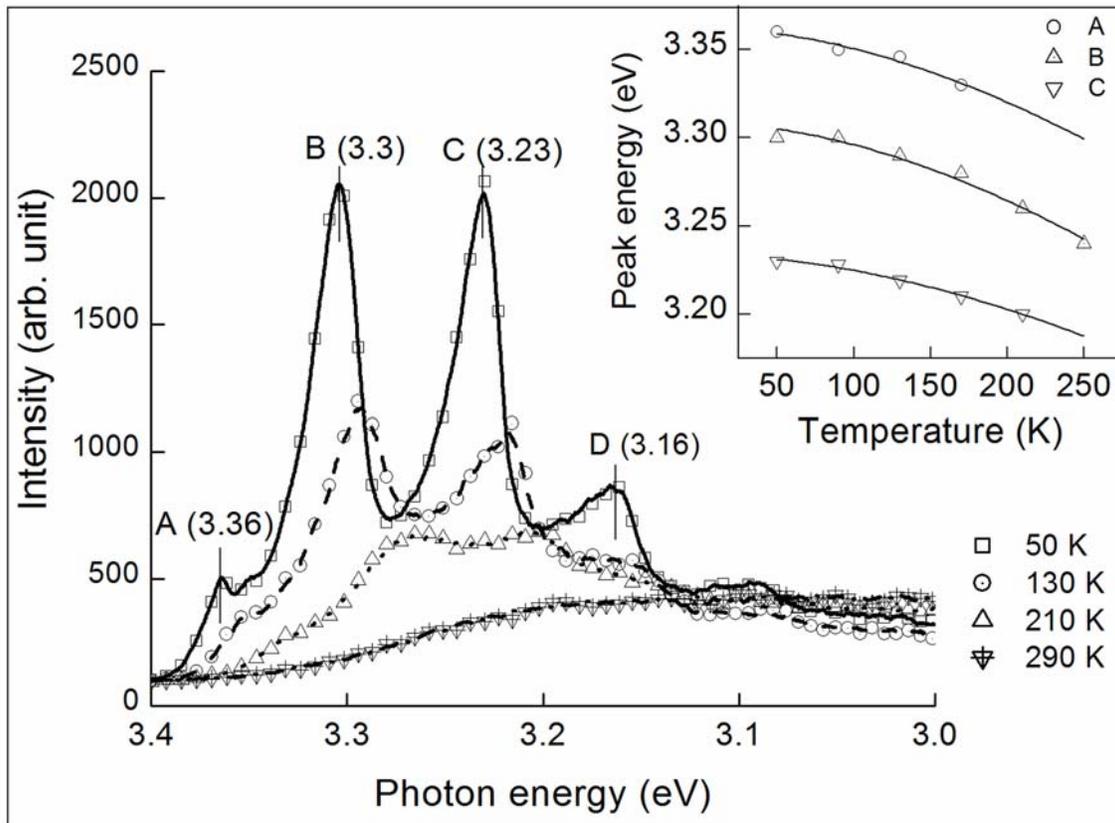


Figure 3

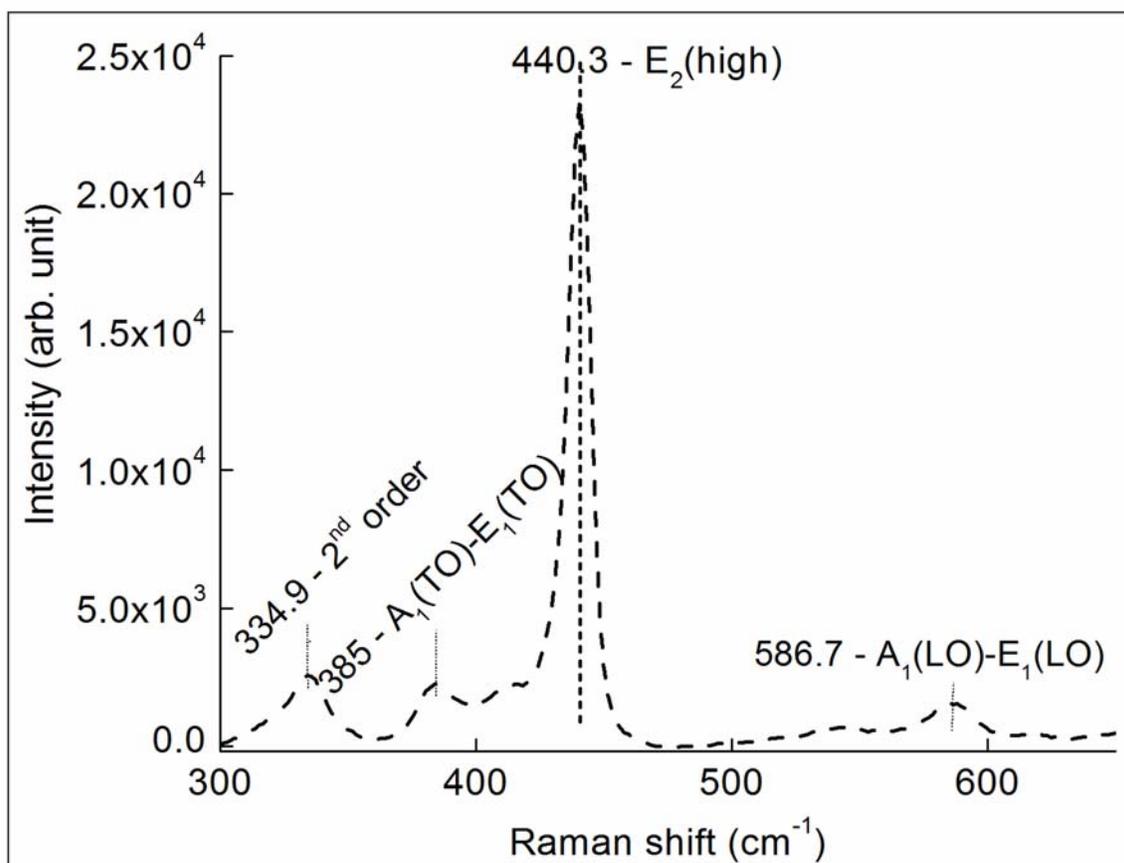


Figure 4