

# Raman and Photoluminescence Spectroscopy Investigations of ZnO Nanostructures

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## ABSTRACT

We discussed the Raman and photoluminescence studies of ZnO in solid, thin film and nanowire samples. The resonant laser excitations varies from near infrared to ultra violet are used in order to observe and analyze the vibration modes of the nanostructures in response to the changing optical emissions and electronic band gaps simultaneously. The spectroscopy analysis to the nanostructure, electronic band gaps and photo emission demonstrated importance of phonon-electron interactions, which plays the important role in the polar semiconductor such as ZnO.

**Keywords:** Raman spectroscopy, photoluminescence spectroscopy, zinc oxides nanostructures, thin films.

## 1. INTRODUCTION

ZnO is a polar semiconductor exhibit important optoelectronic property such as the lasing ability in the blue light region<sup>1</sup>. The exciton near band gap emission is sensitive to the ZnO nanostructures. As the boundary condition changes from crystalline form to quasi one-dimensional nanowire, the effect of the surface phonon can change the electronic properties. The confined periodicity of phonon wave is related to the polarity of the excitation field, as well the dielectric media the nanosize material is embedded. The latter is recently reported in the GaP nanowires studies<sup>2</sup>. The effect of the aspect ratio in the nanostructure domain is the third possible cause for the symmetry change<sup>3</sup>. Comparing the cylindrical high aspect nanowire columns with the presumably spherical nanocrystalline particles in the solids and thin film, the GaP theoretical investigations reveal the distinct Raman shifts due to induced polarity change in the samples. Besides changing the dielectric property of the media to fabricate the semiconducting nanowires, the aspect ratio of the nanostructures, which is typically controlled by the growth condition, can similarly change the optoelectronic property in the semiconducting materials to tailor for various device applications. For example, the efficiency of the field enhancement waveguide can be greatly improved with high aspect ratio and the surface plasmon resonance of the nanostructural materials.

We preformed systematic Raman spectroscopy studies to investigate the vibrational symmetry characteristics of the ZnO solids, thin films and nanowires. The correlation between the nanostructure and the optical property provides us a controllable approach to tailor the nanostructure growth conditions for the different device application and architecture.

## 2. EXPERIMENT

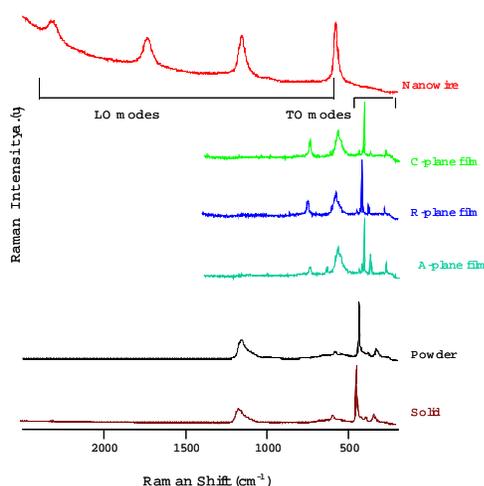
ZnO solid is purchased from Aldrich without further purifications. The ZnO thin films are produced in two methods with Ar ion sputtering onto three sapphire planes as the substrates: A, R and C, and onto semiconducting Si wafer substrate with laser ablation. The ZnO nanowire is synthesized with CVD method, which was reported elsewhere<sup>4</sup>. All the samples are studied without further preparation.

Raman and photoluminescence spectra are taken with UV system 1000 spectrometer (Renishaw Product Inc.) in back scattering configurations. A He:Cd laser is used for excitations at 325 nm and an Argon ion laser for 488 nm. In the 325 nm excitation, the laser power on the 2  $\mu\text{m}$  focused sample spot is 4-5 mW. An UV coated x40 objectives from Leica is used for the incident and scattering light. 2400 lines/mm grating is used to achieve the optimized resolution and throughput in the Raman analysis. The spectral resolution is 8  $\text{cm}^{-1}$ . The photoluminescence measurement is done with 1800 lines/mm grating for collecting the emission spectra. Similarly, 488 nm laser excitation is also used for Raman measurement with the slightly higher laser power, up to 8 mW on the 2 $\mu\text{m}$  sample spot. The spectral resolution is 4 or 6  $\text{cm}^{-1}$  depending on either 2400 or 1800 lines/mm grating is used. Spectra are taken at least in 3 different spots to ensure the reproducibility for peak intensities. The spectrometer is calibrated with atomic emission from Neon lamp, and checked by the silicon lines before the spectrum is taken.

## 3. RESULTS AND DISCUSSIONS

The bulk ZnO has the wurtzite structure belongs to the  $C_{6v}^4$  space group, the zone center optical phonons are:  $A_1+2E_2+E_1$ . Figure 1 is the Raman spectra of ZnO solids, thin film excited by 488 nm Ar ion laser. Since the collection volume of the ultra thin nanowire film on the sapphire substrate is very small, the 488 nm excitation is used as preresonant UV excitation for enhanced signal to

noise ratio. 325 nm laser excitation on the thin film sample lacks the deep penetration depth to yield sufficient scattering volume to generate good signal to noise ratio. We have not obtained the thin film spectrum with 325 nm excitation. ZnO in both solid (both powder and window target) and thin film (in the different sapphire planes) forms exhibit the predominant Raman modes in the vibrations of transverse acoustic (TA) modes below 500  $\text{cm}^{-1}$ , and broader and weaker longitudinal optical (LO) modes in the frequency region between 500 to 1300  $\text{cm}^{-1}$ . However, the vibration symmetry differences of TO modes in the frequency region of 380 to 430  $\text{cm}^{-1}$  between solid and thin film ZnO samples are quite different in their relative ratios (for an example, the TO modes of 439  $\text{cm}^{-1}$  in solids vs. 430  $\text{cm}^{-1}$  in the thin film), possibly due to more polarized nanostructure domain ensemble in the thin film.

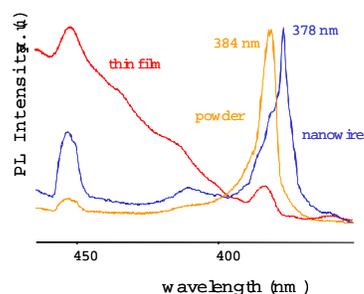


**Figure 1** 488 nm excitations on the ZnO nanostructures in various forms.

The enhanced acoustic Raman modes (TA) below 300  $\text{cm}^{-1}$  are also likely attribute to the 488 nm preresonant excitation. We also observed the unique relative ratio of transverse acoustic (TA) modes to longitudinal modes in the solids and thin film respectively. Since both solids and thin film consist of polycrystalline domains, the confined dimension in the thin film appears to play significant role in the overall polarity through lattice packing orientation. The broadening of the longitudinal optical modes is likely due to the excess Zn particles in the thin film which can reduce the ZnO bandgap<sup>5</sup>. The longitudinal optical (LO) modes, on the other hand, are much more significant in the thin film than in the solids. It becomes the dominant Raman modes in the nanowires under 325 nm resonant excitation condition, in which the multiple phonon modes are observed up to 4<sup>th</sup> order of LO frequency, with negligible TA frequency. This strong electron phonon interactions present in the polar semiconductor like ZnO appear to be more dominant in both thin film and nanowire than that in the solids. It is interesting to observe the enhanced 1<sup>st</sup> and 2<sup>nd</sup> order LO modes at 580 and 1152  $\text{cm}^{-1}$  presented in the

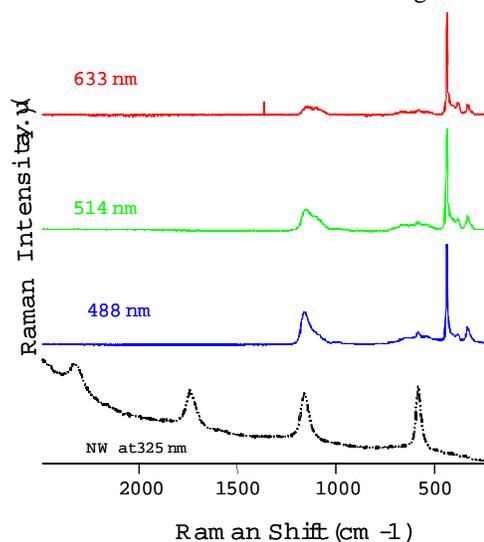
preresonant scattering at 488 nm excitation as this energy is lower than the bulk band gap by more than 0.3 eV.

Figure 2 is the photoluminescence emissions of the ZnO solids, thin film and nanowire. The onsite emission threshold is the same; however, nanowire shows the discrete emission levels near the band edge while solid and thin film samples have broad bound exciton emissions. This is indicative of the possible bound and free exciton confinement in the nanowires due to phonon and electron interactions, as it has not observed in the thin film and amorphous solids. This leads an explanation to the trapped exciton level or as quantized exciton level due to the confinement in the cylindrical nanowire. It is also evident that the band gap in the nanowire is blue shifted, consistent with the confinement exhibited by the nanometer size nanowires. The green emission in PL is believed to due to the O<sub>2</sub> deficiency.



**Figure 2** Photoluminescence of ZnO in the solid, thin film and nanowire forms.

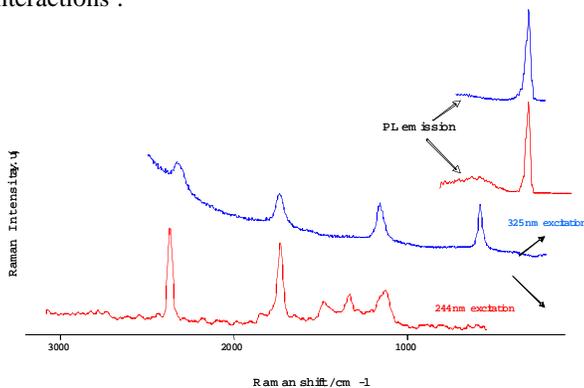
Figure 3 shows the ZnO powder vibration symmetry responses towards different laser excitation energies.



**Figure 3** Raman Spectra of ZnO powder excited with different laser wavelengths. The multiphonon ZnO nanowire resonant spectra are used for comparison.

It is interesting to observe the enhanced 1<sup>st</sup> and 2<sup>nd</sup> order LO modes at 580 and 1152  $\text{cm}^{-1}$  are presented in the preresonant scattering at 488 nm excitation even this energy is lower than the bulk band gap by more than 0.3 eV.

The resonant excitation can also be further illustrated with the bulk ZnO spectroscopy analysis. Figure 4 shows the ultra violet Raman and photoluminescence results of the solids and nanowire excited with 244 nm and 325 nm wavelength respectively. The 244 nm excitation energy is much higher than the bandgap which is just above 325 nm, thus there is much higher photon flux to the exciton emission near the band edge. It is observed that the 4<sup>th</sup> and 3<sup>rd</sup> orders of the electron phonon interaction are even stronger than that under resonant excitation at 325 nm. We observed four major bands, centered at 577, 1152, 1734, and 2319  $\text{cm}^{-1}$ , with bandwidths at 30, 46, 55, and 53  $\text{cm}^{-1}$ , respectively. This result is consistent with the resonant excitations shown before. Since different phonons display different degree of enhancement with the resonant excitations. This is depending on their contribution to the electronic polarizability via the electron-phonon interactions<sup>6</sup>.



**Figure 4** UV Raman and photoluminescence spectra of ZnO nanowires excited at 244 nm (red) and 325 nm (blue) respectively, showing the multiphonon vibration modes. The inset is the photoluminescence spectra.

#### 4. CONCLUSION

We conclude with the Raman spectroscopy observations that the aspect ratio of ZnO nanostructure and domain ensemble can significantly affect the electronic and optical properties of the materials. We observed simultaneous changes of the frequency shift of the near band edge emissions and the nanostructures from the ZnO nanowire to its corresponding solids. Through changing the ZnO polarity by changing the surface phonon density of states, we will be able to tune the ZnO bandgap, or the electronic and optical properties to tailor for different device applications. Resonant Raman spectroscopy is a very sensitive technique to study the nanowire electronic structures in relation to nanostructure analysis. The simultaneous Raman and photoluminescence investigations have the advantage to correlate the nanostructure with the

electronic band gap and the optical property changes of the semiconducting materials.

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