Anomalous multiphonon features of hyper-Raman in ZnO NPs

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Abstract. This report is on the observation of unique anomalous multiphonon scattering of Raman and hyper-Raman at room temperature and low-temperature of 81K in ZnO nanoparticles prepared by dc arc plasma method. $E_{\text{LO}}$, $E_{\text{TO}}$, $A_{\text{LO}}$, $A_{\text{TO}}$, and $E_{\text{LO}}$ are among the fundamental modes that are also observed by hyper-Raman. In general, the anomalous modes are not usually observed in most ZnO samples. However, the presence of different types of anharmonic decay processes such as overtone, two phonon and three phonon combinations and their symmetry nature are discussed in detail. These ZnO materials have strong carrier-phonon coupling when irradiated with the 514 nm and 785 nm of excitation sources and also the material is highly responsive in the IR region.

Keywords: ZnO, Hyper-Raman, Multiphonon, electron-phonon interaction

1. Introduction

A lot of research has been done to study ZnO nanoparticle (NPs) due to its unique promising characteristics for optoelectronics and biomedical applications [1,2]. In addition, long-lived optical phonons in the polar crystals are playing an indispensable part in quantum processing. Due to the ionized vacancies such as $V_{\text{Zn}}$ and $V_{\text{O}}$, long-range Fröhlich interaction/deformation potential modify the phonon density locally [2,3]. A special interest of this work is to extract information of multiphonon such as two-phonon and three-phonon combination and their decay process by temperature dependent Raman and hyper-Raman scattering. Particularly, the anharmonic decay process of the observed low frequency vibrational modes in the range of Terahertz region is discussed. These ZnO NPs have a notably strong and high order non-linear optical response which may be beneficial for applications in biosensing[1]. Besides, hyper-Raman due to its different selection rules may help in observing anomalous along with most of the fundamental modes expected in a $C_{6v}$ point group symmetric structure [4].

2. Experiments

Nominally undoped ZnO NPs were prepared by dc dusty arc plasma method with an Arc current of 90 A at atmospheric pressure. The Zinc 3N metal was used as Zn source and unpurified air was used as Oxygen source[5]. The Raman spectra of ZnO NPs were recorded by using RenishawInVia micro-Raman spectrometer at excitation wavelengths of 514 nm and 785 nm with a resolution ~0.5 cm$^{-1}$. Low-temperature measurements were carried out at 81K using Linkam heating/cooling stage in nitrogen atmosphere.
Figure 1. Raman spectra of ZnO NPs at 300K and 81K from 0-4000 cm$^{-1}$ range

Figure 2. Second order Raman spectrum of ZnO of figure 1.

Figure 3. Raman spectra of ZnO NPs at 300K and 81K

Figure 4. Hyper-Raman spectra of the ZnO NPs irradiated with 785 nm laser.

3. Results
The Raman spectrum of the sample analyzed at 300K and 81K were generated by using 514 nm lasers as excitation source as shown in “figure 1-4”. Fundamental modes with peaks at 100 cm$^{-1}$ ($E_{2\text{low}}$), 441 cm$^{-1}$ ($E_{2\text{high}}$), 383 cm$^{-1}$ ($A_{1\text{-TO}}$), 411 cm$^{-1}$ ($E_{1\text{-TO}}$), 579 cm$^{-1}$ ($E_{1\text{-LO}}$) were observed in the spectra irrespective of temperature with excitation source at 515 nm and 785 nm. In addition, two silent modes were also observed at 242 cm$^{-1}$ ($B_{1\text{low}}$) and at 540 cm$^{-1}$ ($B_{1\text{high}}$) [6, 7]. Besides, several multiphonons modes were also observed. However, these multiphonon modes disappeared when the temperature was reduced down to 81K with 515 nm Raman. When the sample was irradiated with 785 nm laser, surprisingly, all the fundamental vibrational modesalong with multiphonons were observed (figure 4.) for both the temperature. Beyond 1500 cm$^{-1}$ the photoluminescence is highly dominating due to deep level defects.

4. Discussion
The phonon decay life time of $E_{2\text{high}}$ and $E_{2\text{low}}$ modes are 0.55 ps and 1.13 ps, respectively for 514 nm excitation source. While decreasing the temperature to 80K life time increased to 0.75 ps and 1.4ps respectively. Similar trend has been observed when the samples were irradiated with 785 nm, however the overall life time decreased by a value of 0.2 ps.

The 441 cm$^{-1}$ ($E_{2\text{high}}$) can be expressed as the overtone scattering of the 221 cm$^{-1}$ ($2TA_{1}$) which may belong to $K$/M/Brillouin zone point. In the low frequency region, two modes were deconvoluted using a Gaussian fit and are at 70.9 cm$^{-1}$ and 87.4 cm$^{-1}$ asshown in the “figure.3&4” inset. The first mode observed at $\approx 71$ cm$^{-1}$ was due to the decay process of 221 cm$^{-1}$ ($2TA_{1}$) into 71 cm$^{-1}$ and 144 cm$^{-1}$[8]. Rather, the peak $E_{2\text{high}}$ can also decay into the two modes of 353 cm$^{-1} + 87.4$ cm$^{-1}$, the 87.4 cm$^{-1}$ peakis
found to have a 0.49 ps lifetime. The two modes 70.9 cm\textsuperscript{-1}, 87.4 cm\textsuperscript{-1}, 144 cm\textsuperscript{-1} and 221 cm\textsuperscript{-1} may be due to scattering from zone centre \Gamma to M-K and A-M zones [7]. Moreover, 353 cm\textsuperscript{-1} may belong to 700 overtones with class E\textsubscript{2} TO. The three modes 353 cm\textsuperscript{-1}, 88 cm\textsuperscript{-1}, 441 cm\textsuperscript{-1} have strong temperature dependency. The 353 cm\textsuperscript{-1} modes got more resolved with a considerable change in intensity when the temperature was decreased; which would lead to an argument that this mode must have contributions from optical modes as these modes are observed to get more distinguished with decrease in temperature as thermal interaction of the phonons increase with higher temperature which in turn decreases the mean free path [9].

Additionally, Millot et al described the decay of 441 cm\textsuperscript{-1} into two acoustic modes 190 cm\textsuperscript{-1} and 250 cm\textsuperscript{-1} as calculated from ab initio density of states [10]. It has been argued that the up-conversion process of E\textsubscript{2} high is not feasible and thus the temperature dependence of the 441 cm\textsuperscript{-1} has to be due to the possible decay of this mode into low energy phonons. It has also been argued that these decay modes which correspond to two phonon processes that can be used to describe the E\textsubscript{2} high \textsubscript{lin}ewidth based on temperature [3, 9]. A moderate 333 cm\textsuperscript{-1} (E\textsubscript{2} high \textsubscript{lo}w - E\textsubscript{2} low) has also been observed, which shows strong temperature dependence [6]. The 333 cm\textsuperscript{-1} mode can also be expressed as a difference mode (TO - E\textsubscript{2} low) [8] although the possibility of this combination is unlikely due to the general observed behavior of optical modes. An asymmetric mode is observed at 324 cm\textsuperscript{-1}, which has clearly convoluted with 333 cm\textsuperscript{-1} and it belongs to 3E\textsubscript{2L} symmetry group [11]. However, the origin of some of the mode is unclear. At 1056 cm\textsuperscript{-1} a strong peak is observed, this mode is due to a three phonon process which is a combination of 579 cm\textsuperscript{-1} (E\textsubscript{1}(LO) \textsubscript{\Gamma}), 410 cm\textsuperscript{-1} (E\textsubscript{1}(TO) \textsubscript{\Gamma}) and 100 cm\textsuperscript{-1} ((E\textsubscript{2} low) \textsubscript{\Gamma}). Usually multiphonon do not show intense peak; however the observed intense mode at 1056 cm\textsuperscript{-1} may also be due to contributions from surface impurities.

5. Conclusion
The ZnO NPs were prepared by dc arc plasma method. The nature of phonon decay process has been studied with Raman and hyper-Raman. These ZnO NPs have strong carrier-phonon interaction and high order non-linear optical response which may be beneficial for applications in quantum process and biosensing.

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