MULTI-PHONON RAMAN SCATTERING OF ZnSe NANOWIRES

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Abstract: Multi-phonon Raman spectrum containing up to six order of phonon peaks were observed in ZnSe nanowires. The intensity variation among the different orders of phonon peaks was investigated by changing the incident laser power. The observed relative intensity change of the 4\textsuperscript{th} order to the 5\textsuperscript{th} Raman peak is explained by the laser heating effect.

Zincblende-structured ZnSe nanowires were grown on (001) silicon substrates by metalorganic chemical vapor deposition. They are found to be single crystals with shapes elongated along the \textlangle 11\bar{2}\rangle \textrangle crystallographic direction by TEM. The diameters of the nanowires range from a few to 100 nm and typical lengths in tens of micrometers \cite{1}.

Raman spectra of the sample excited by 442nm laser line shows that, at first order, there are a LO mode at 252 cm\textsuperscript{-1} and a very weak TO mode at 209 cm\textsuperscript{-1}, frequencies which are not different from those of bulk ZnSe \cite{2}. Moreover, multiple LO phonon Raman spectra up to six orders are observed. The dependence of the excitation power on multiple phonon Raman spectra is investigated. The resultant spectra are shown in Fig 1.

From Fig 1 we find that all of the phonon peaks sit on a broad PL background and the relative intensity of Raman peaks changes with the incident laser power. To describe the change of the intensity of the two most intense peaks, we define a parameter, $I_{4th}/I_{5th}$, i.e. the relative intensity of the 4\textsuperscript{th} order peak to the 5\textsuperscript{th} order peak. The dependence of $I_{4th}/I_{5th}$ with the laser power is shown in the inset of Fig 1. From the inset, we see that $I_{4th}/I_{5th}$ increases with the laser power. Since the energy position of the order that shows the strongest resonance in the Raman spectrum corresponds to an electron transition of the samples, the increase of the $I_{4th}/I_{5th}$ implies that the PL peak position moves progressively from under the 4\textsuperscript{th} order Raman peak to the 5\textsuperscript{th} order as laser power increases. Had the laser power used been sufficiently high, the position of the most intense resonant Raman
peak would have shifted by one order, which corresponds to a shift of the electron level by a phonon energy of 31 meV (252 cm\(^{-1}\)). On the other hand, we observed that high laser power would permanently damage the nanowires; so we limited the laser power to within a safe range, with the result that the shift of the resonance is not quite one complete order in our experiments. To locate the exact position of the PL peak we fitted the background of Raman spectra measured at different laser powers. Fig 2 shows this fitted PL background. From Fig. 2 we learn that the largest shift of the PL peak is \(\sim 25\) meV.

From the energy shift of the PL peak, the temperature at the laser irradiated spot on the nanowire may be estimated by the expression [3],

\[
E_0(T) = E_0(0) - 2a_B/[\exp(\theta_B/T) - 1]
\]  

(1)

Where \(E_0(0) = 2.80\) eV is the bandgap at temperature \(T=0\), \(a_B = 73\) meV and \(\theta_B = 260\) K for ZnSe. Then the value of \(T\) is about 360 K at the largest excitation power of 2.23 mW.

One of an accepted the measured method of the temperature of the irradiated spot is by comparing the intensity ratio of Stokes peak to anti-Stokes peak through the relationship [4].

\[
\frac{I_{k-S}}{I_{k-as}} = \left[ \frac{(\omega_L - \omega)}{(\omega_L + \omega)} \right]^4 \exp\left(\frac{\hbar \omega}{kT} \right)
\]  

(2)

The temperature of spot irradiated by 2.23 mw of excitation power calculated by this method is about 374 K, which matches that extracted from formula (1). The agreement of the two temperatures strongly indicates the shift of the electron level is due to laser heating.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Fitted PL background excited by increasing laser powers}
\end{figure}

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