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Raman scattering in narrow-gap semiconductors

KENJI KUMAZAKI
Hokkaido Institute of Technology, Teine, Sapporo 006, Japan

Abstract. Raman scattering by phonons has been measured in a narrow-gap semiconductor, $Zn_xHg_{1-x}Se$, with $x = 0$ to 0·4 near the $E_1 + \Delta_1$ energy gap at room temperature. Plasmon–LO phonon coupling modes have been explained by a model taking into account the two-mode behaviour of TO phonons. The photon energy dependence of scattering intensity has shown a strong enhancement near the $E_1 + \Delta_1$ energy gap. The experimental results have been compared with those of Raman scattering, far-infrared reflection and ellipsometric measurements.

Keywords. Raman scattering; narrow gap semiconductors; plasmon–LO phonon coupling modes; TO phonons.

1. Introduction

$Zn_xHg_{1-x}Se$ (ZnHgSe), is a family of narrow-gap semiconductors. This compound crystallizes in the zincblende structure in the whole range of composition x. The value of the fundamental energy gap varies with x continuously from $-0{\cdot}02$ to 2·8 eV. Recently, TO* and LO* phonon frequencies and plasmon–LO phonon coupling mode frequencies were measured in ZnHgSe with $x = 0$ to 0·40 from far-infrared (FIR) reflection spectra (Kumazaki and Nishiguchi 1986). The dependence of E_1 and $E_1 + \Delta_1$ gaps on the composition of ZnHgSe were measured by ellipsometry and its alloying effects were discussed (Kumazaki *et al* 1988). From resonant Raman scattering in $Cd_xHg_{1-x}Se$ (Kumazaki 1989), of a narrow-gap family, composition dependence of TO and LO mode frequencies and plasmon–LO phonon coupling effects were also measured at room temperature.

However, to our knowledge, there is no report on Raman scattering in ZnHgSe. In this paper we report Raman scattering of ZnHgSe crystals at room temperature under resonant conditions near the $E_1 + \Delta_1$ gap. The electron concentration dependence of plasmon–LO phonon coupling is also measured and compared with the results of FIR measurements.

2. Experimental procedure

Six crystals with $x = 0$ to 0·40 were grown by the Bridgman method (Kumazaki *et al* 1976). As-grown samples were annealed in an Se-saturated atmosphere for one

*LO–longitudinal optics; TO–transverse optics

month. The Raman scattering intensity was measured on the (100) surface with a Kr^+ laser in backscattering geometry at 300 K (Kumazaki 1989).

3. Results and discussion

Figure 1 shows the composition dependence of the Raman spectra in the $X(Y', Y')\bar{X}$ configuration with $X = (100)$ and $Y' = (01\bar{1})$ and with the 4067 Å line. For $x = 0$, two strong peaks are observed at 132 and 174 cm^{-1}, and a broad band is observed around 350 cm^{-1}. For other samples with $x = 0{\cdot}05$ to $0{\cdot}40$, the peaks observed around 130 cm^{-1} shift slightly to higher frequencies, while the broad bands shift to lower frequencies. Further new peaks for the samples with $x = 0{\cdot}05$ to $0{\cdot}40$ appear on both sides of the peak observed around 130 cm^{-1}. A small peak is seen at 210 cm^{-1} only for $x = 0{\cdot}40$.

According to the selection rules for allowed Raman scattering in zincblende-type crystals in backscattering (Cardona 1982), we should observe the LO phonons for the $X(Y', Y')\bar{X}$ configuration on the (100) surface. On this surface the TO phonon is forbidden for all other polarizations. However, under near-resonant excitation, Fröhlich interaction modifies the selection rules. Furthermore, the appearance of TO

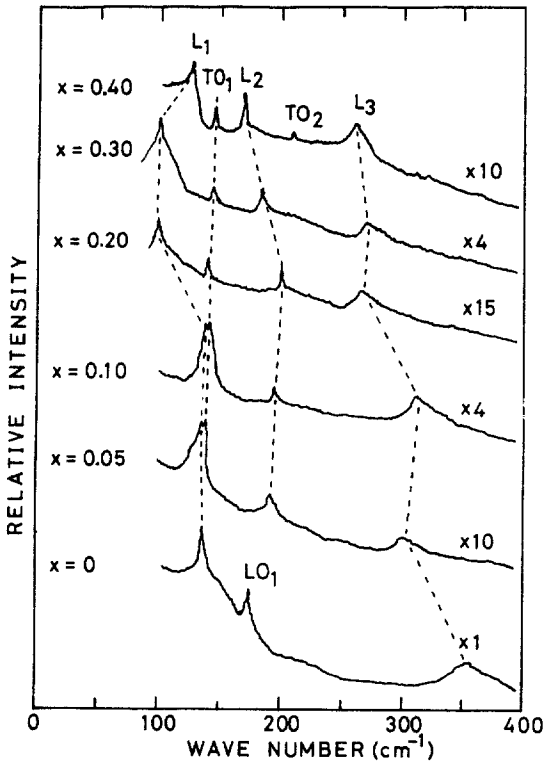

Figure 1. Raman spectra for $Zn_xHg_{1-x}Se$ on the (100) surface with 4067 Å laser line at 300 K in the configuration $X(Y', Y')\bar{X}$ with $X = (100)$ and $Y' = (01\bar{1})$. L_1, L_2 and L_3 are the plasmon–LO phonon coupled modes.

phonons arises from breakdown of selection rules due to native defects or microscopic compositional disorder.

From the Raman selection rules and reported FIR data (Kumazaki *et al* 1986; Kumazaki and Nishiguchi 1986; Kumazaki 1989; and references therein) we propose that the peaks around $130\,cm^{-1}$ observed for all compositions are that of TO_1(HgSe) and the peak at $210\,cm^{-1}$ observed only for $x = 0{\cdot}40$ is due to TO_2(ZnSe). The appearance of two TO modes indicates the two-mode behavior of this material. These two TO phonons were also observed by measurements of FIR reflection spectra (Kumazaki and Nishiguchi 1986).

The peak at $174\,cm^{-1}$ for $x = 0$ is due to unscreened LO_1 from a surface depletion layer (Kumazaki 1989). The peaks (L_1 and L_2) on both sides of TO_1 and broad bands (L_3) between ~ 250 and $\sim 350\,cm^{-1}$ are plasmon–LO phonon coupling modes because of their sensitive frequency-dependence on electron concentration. Corresponding three peaks were observed for FIR reflection spectra in this material (Kumazaki and Nishiguchi 1986). These were explained by a dispersion relation of the order of six with respect to frequency, obtained by the well-known plasmon–LO phonon coupling theory (Burstein 1969) taking into account both HgSe-like and ZnSe-like oscillator terms. This dispersion relation, as a function of the square root of ratio of electron concentration N to effective mass m^*, gives us three curves (Kumazaki 1986), L_3 in the region above LO_2(ZnSe), L_2 in the middle region between LO_1(HgSe) and TO_2(ZnSe) and L_1 in the region below TO_1(HgSe). The three peaks, as a function of $(N/m^*)^{\frac{1}{2}}$, are plotted together with the data of FIR reflection in figure 2. The solid curves are the three dispersion curves (L_1, L_2 and L_3) calculated

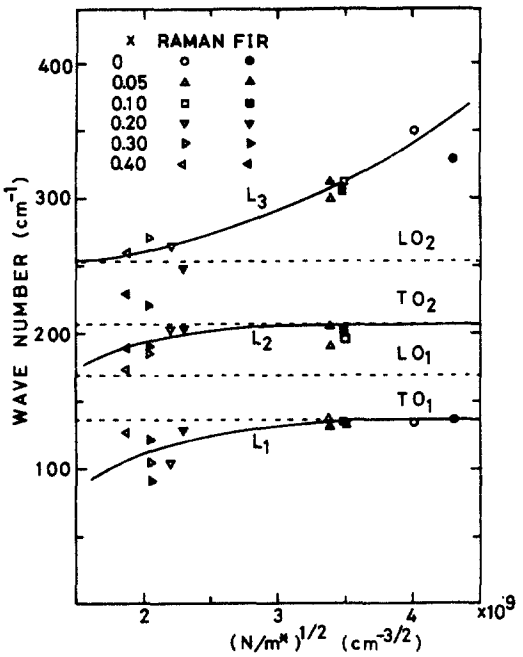

Figure 2. Plasmon–LO phonon coupled frequency as a function of electron concentration and effective mass for $Zn_xHg_{1-x}Se$. The solid lines (L_1, L_2 and L_3) are calculated by using our model.

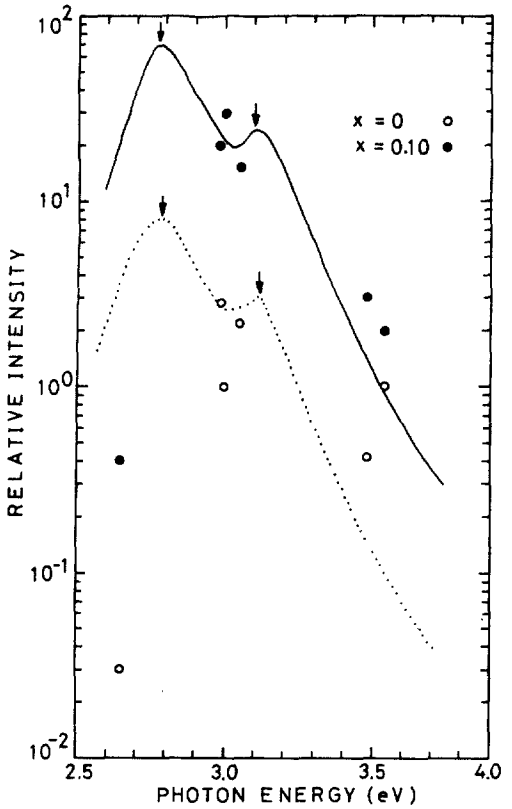

Figure 3. Relative Raman scattering intensity of unscreened LO_1 phonon as a function of photon energy for $Zn_xHg_{1-x}Se$ with $X(Y,Z)\bar{X}$ configuration and $X = (100)$, $Y = (010)$ and $Z = (001)$. The dotted line for $x = 0$ and the solid line for $x = 0{\cdot}10$ indicate the curve calculated only by a model taking into account the two-band terms.

by above mentioned relation. Because of the large value of N the L_1 modes for $x = 0{\cdot}05$ and $0{\cdot}10$ are very close to the TO_1 mode and that for $x = 0$ is not separable in figure 1. Our experimental points are in good agreement with calculated curves.

Figure 3 shows the dependence of Raman scattering intensity on photon energy for LO_1 phonons of the samples with $x = 0$ and $0{\cdot}10$. The scattering intensity of the LO_1 phonon was obtained on the samples with a surface depletion layer of about 200 Å depth. In these samples we can observe the unscreened LO mode from the surface depletion layer and the plasmon–LO phonon coupled modes from the region where the carrier concentration reached the bulk value. Six laser lines with 4680 to 3507 Å were used. These spectra were measured for the $X(Y,Z)\bar{X}$ configuration with $Y = (010)$ and $Z = (001)$. The values of E_1 and $E_1 + \Delta_1$, obtained from the ellipsometric measurements (Kumazaki *et al* 1988), are denoted by the arrows in the figure. Data were corrected by the ellipsometric data. The scattering intensities for both samples show a similar tendency and a strong enhancement of two orders of magnitude in our experimental region.

For the E_1 and $E_1 + \Delta_1$ gaps there are two main contributions to the Raman tensor, i.e. two-band terms due to the modulation of gaps by phonons and three-band terms corresponding to the coupling by phonons of the spin-orbit valence bands

(Cardona 1982). We can calculate only the intensities due to two-band terms by using our ellipsometric data (Kumazaki 1989) since we have no information about deformation potentials for ZnHgSe. Relative values calculated from the square of the first derivative of susceptibility with respect to energy are denoted by a dotted line for $x = 0$ and a solid line for $x = 0{\cdot}10$. The solid line for $x = 0{\cdot}10$ agrees roughly with the measured points, but the dotted line for $x = 0$ does not show good agreement with experiments. Thus we cannot see good agreement with experiments and theory for both samples. The reasons for the disagreement are mainly due to neglecting the three-band terms and to the effects of the surface depletion layer.

In summary, by resonant Raman scattering of ZnHgSe at room temperature, plasmon–LO phonon coupling modes have been explained by theory taking the two-mode behavior of TO phonons into account. These results, obtained by Raman measurements, agree well with those obtained by FIR measurements. Raman intensities as a function of photon energy have shown a strong resonance of the order of magnitude two near $E_1 + \Delta_1$. We can roughly explain our experiments with a simplified theory but we recognize a disagreement because of neglecting the three-band terms.

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