Lattice vibration of ZnSe$_{1-x}$Te$_x$ epilayers grown by molecular-beam epitaxy

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The lattice vibration of ZnSe$_{1-x}$Te$_x$ epilayers grown using molecular-beam epitaxy was investigated with Raman as well as Fourier transform infrared reflectance spectroscopy. The dependence of longitudinal-optical (LO) and transverse-optical (TO) phonon frequency on the Te concentration was found to follow previous theoretical predictions. However, additional vibration modes were observed at the energy between that of the LO and TO phonons. The microscopic force constants F_{ZnTe} and F_{ZnSe} were evaluated to be 6.46 $\times 10^6$ amu$\times$(cm^{-1})^2 and 2.91$\times 10^6$ amu$\times$(cm^{-1})^2, respectively. In addition, the Raman spectra were recorded at high pressure up to 20 GPa. The pressure at which the semiconductor to metal transition occurred is characterized by the disappearance of the LO phonon and found to decrease with the Te concentration. Current results imply the decreasing crystal stability with the Te concentration. [S0163-1829(99)01612-4]

I. INTRODUCTION

ZnSe$_{1-x}$Te$_x$ is an interesting class of ternary II-VI compound semiconductors. Spectacular atomic ordering has been observed by Ahrenkiel *et al.*[1] Freytag *et al.*[2] found that spontaneous ordering results in a different bowing parameter that is larger than the values obtained earlier from bulk material. Yao *et al.*[3] and Lee *et al.*[4] found the interesting optical phenomena of exciton bound to Te clusters in ZnSe$_{1-x}$Te$_x$. Brasil *et al.*[5] grew ZnSe$_{1-x}$Te$_x$ epilayers using molecular-beam epitaxy and found that the energy separation between the band gap and the transition energy of exciton bound to Te clusters depends upon the Te concentration. The effects of the substrate tilt angle on the optical properties of ZnSe$_{1-x}$Te$_x$ epilayers were studied by the present researchers.[6] Despite the intense research activities that have been carried out on ZnSe$_{1-x}$Te$_x$, detailed experimental results on lattice vibration have not been published. Until recently, the variation in the longitudinal-optical (LO) phonon frequency on the Te concentration (x) of ZnSe$_{1-x}$Te$_x$ was presented.[7] The Te concentration dependence on the transverse-optical (TO) phonon has yet to be found. In a current study, lattice vibrations of ZnSe$_{1-x}$Te$_x$ epilayers were studied using the phonon Raman scattering and Fourier transform infrared reflectance spectroscopy (FTIR). The concentration dependence of both LO and TO phonon frequency is found to follow the previous theoretical prediction.[8] However, additional vibration mode was observed at the energy between the TO and LO phonons.

Recently, the pressure effect on the physical properties of semiconductors has attracted a lot of attention. Ves *et al.*[9] observed the band-gap shift of ZnSe at high pressure. Itkin *et al.*[10] found the pressure-induced semiconductor to metal transition. Arora *et al.*[11] found the splitting of the TO phonon at 2.8 and 5.4 GPa. Li *et al.*[12] studied the luminescence of the deep phosphorous and arsenic impurities in ZnSe at high pressure. We have attributed the disappearance of the LO phonon at pressures around 10 to 13.5 GPa to the semiconductor to metal transition[13] for Zn$_{1-x}$Fe$_x$Se bulk crystals. In this paper, the effect of high pressure on the vibrational Raman spectra of ZnSe$_{1-x}$Te$_x$ was studied at high pressure, up to 20 GPa for the first time.

II. EXPERIMENT

ZnSe$_{1-x}$Te$_x$ epilayers ($0 \leq x \leq 1$) were grown on GaAs substrates using the EPI 620 molecular-beam-epitaxy system. Details of the growth conditions were described in a previous paper.[6] The 514.5-nm line from an argon-ion laser was used for the excitation of the Raman spectra. For the FTIR reflectance spectra, a normal incident beam was applied to the samples and a gold plate was used as a reference for the reflectance. The FTIR spectra were studied with the Bruker 120HR Fourier transform spectrometer at 1 cm^{-1} resolution.

For the high-pressure Raman scattering, the GaAs substrates were removed by mechanical polishing, followed by chemical etching using NaOH mixed with H$_2$O$_2$ (NaOH:H$_2$O$_2$=4:21). The epilayers without GaAs substrates were loaded along with ruby powder into a diamond anvil cell to obtain high pressure up to 20 GPa. The pressure dependence of the R1 and R2 photoluminescence lines of ruby powder was used for pressure calibration.

III. RESULTS AND DISCUSSION

The Raman spectra from ZnSe$_{1-x}$Te$_x$ epilayers are shown in Fig. 1. For $x=0.08$, the peak positions of the LO and TO phonons are at 248 and 198 cm^{-1}, respectively. The overtone of the LO phonon is observed at 495 cm^{-1}. The weak peak at 443 cm^{-1} is attributed to the overtone of the weak structure (''A''), which is on the low-energy side shoulder of the LO phonon at 222 cm^{-1}. A weak peak at 293 cm^{-1} is identified as the LO phonon of the GaAs substrate. As x is increased, LO, TO, and also the weak peak (''A'') exhibit a redshift, which implies the softening of the lattice. As x is increased
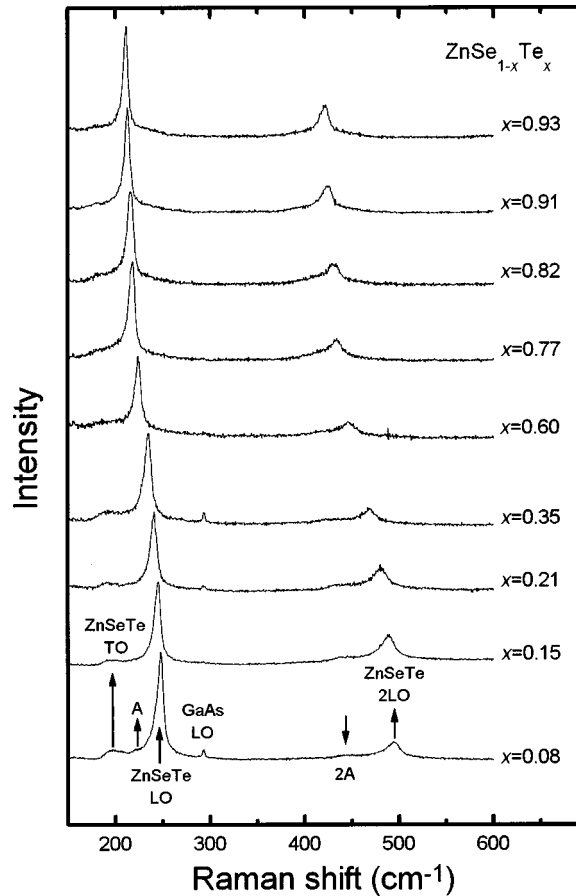
FIG. 1. Raman spectra from ZnSe$_{1-x}$Te$_x$ epilayers.
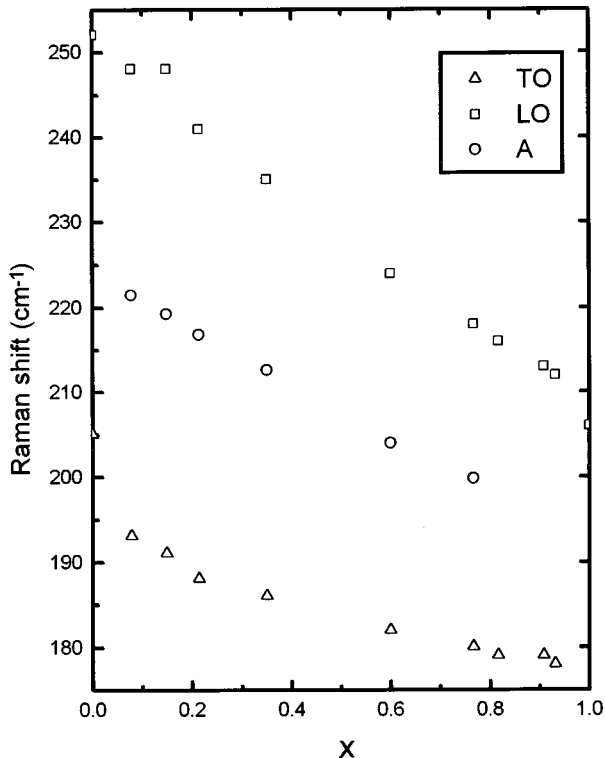

FIG. 2. Concentration (x) dependence of LO (open squares), peak A (open circles), and TO (open triangles) frequencies for ZnSe$_{1-x}$Te$_x$ epilayers.

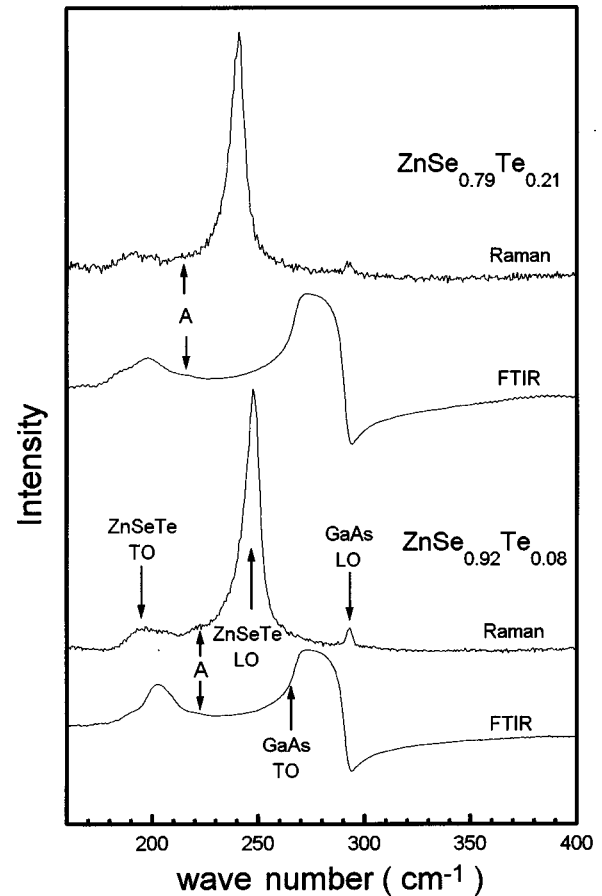FIG. 3. Raman spectra and FTIR reflectance spectra for ZnSe$_{0.92}$Te$_{0.08}$ and ZnSe$_{0.79}$Te$_{0.21}$ epilayers.

further, the weak structure (''A''), whose energy is between that of the TO and LO phonon, becomes weaker and difficult to resolve from the LO phonon peak. However, the Te-concentration (x) dependence of peak A can be observed better from its overtone. For $x = 0.21$, the overtone of the weak structure A is at 432 cm^{-1}, while the overtone of the LO phonon is at 480 cm^{-1}.

The x dependence of the Raman shifts for LO, TO and the weak peak A of ZnSe$_{1-x}$Te$_x$ epilayers are summarized in Fig. 2. For high-x samples, the TO and peak A become invisible in the Raman spectra. The energy determination of these two peaks was made from the FTIR spectra, shown in Fig. 3 for $x = 0.08$ and $x = 0.21$. In Fig. 3, the LO phonon of ZnSe$_{1-x}$Te$_x$ epilayer is invisible in the FTIR spectra due to the selection rule, which prohibits the existence of a LO phonon in the FTIR spectra. The TO phonons of the ZnSe$_{1-x}$Te$_x$ epilayer and GaAs substrate dominate the FTIR spectra. However, peak A, which is relatively weak compared to LO in the Raman spectra, exists in the FTIR spectra where LO is not observed. It implies peak A exhibits TO character. On the other hand, in the Raman spectra, overtones of both peak A and LO are observed in Fig. 1. While, the TO overtone is not observable. The above investigations suggest that peak A exhibits both TO and LO phonon character. Therefore, we attribute peak A to the degenerate LO-TO phonon mode.

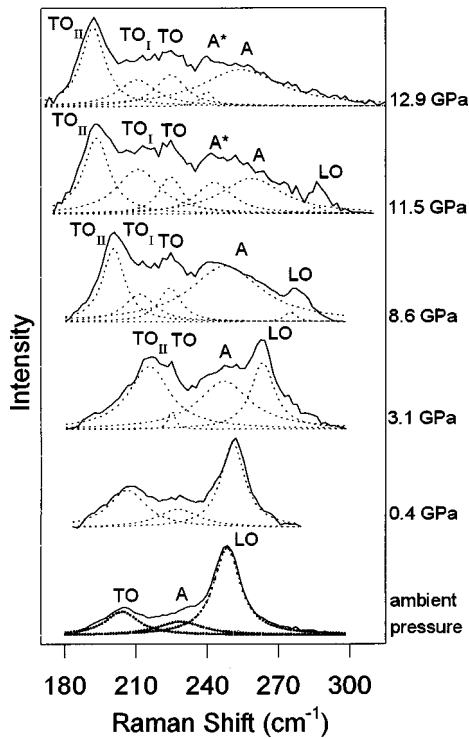In Fig. 2, the x dependence of the Raman shifts for LO and TO phonons are similar to the previous theoretical pre-

FIG. 4. Raman spectra of $ZnSe_{0.96}Te_{0.04}$ epilayers at high pressure.

FIG. 6. Concentration dependence of semiconductor to metal-transition pressure for $ZnSe_{1-x}Te_x$ epilayers.

diction made by Genzel et al.[8] However, in their work, no lattice vibration mode, whose energy is between that of the LO and TO phonons, was predicted. Genzel et al.[8] reported that the lattice vibration of $ZnSe_{1-x}Te_x$ exhibits a one-mode behavior. The predicted second LO (LO_2) and second TO (TO_2) lie below the first LO (LO_1) and first TO (TO_1), which are mentioned above. In this paper, we have observed that a weak peak "A," which is the degenerate LO and TO phonon mode lies between LO and TO. As a result, the cur-
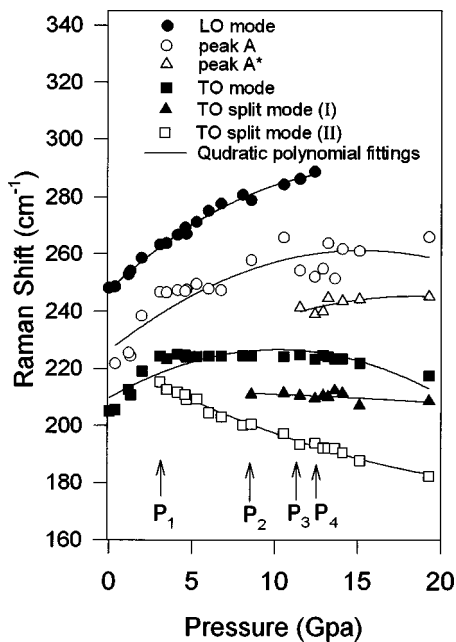
rent investigation suggests that the lattice vibration mode behavior of $ZnSe_{1-x}Te_x$ epilayers is intermediate mode behavior rather than one-mode behavior. This calls for a modification in the theoretical calculation. Let us recall the novel optical properties of Te-bound exciton observed in $ZnSe_{1-x}Te_x$.[3,4,6] The existence of Te-bound exciton results from the large difference in electric negativity (between the Te and Se atoms)[14] which induces a particular local electric field to trap excitons. The local electric field also affects the strength of the chemical bonding, which can be expressed by the strength of the force constant of the lattice vibration in $ZnSe_{1-x}Te_x$. Note that the macroscopic force constant is related to the microscopic dielectric constant, which is very sensitive to the variation of polarization induced by the local electric field, using the Born-Huang procedure,[8] which is $F/M = \omega_T^2(\varepsilon_0 + 2/\varepsilon_\infty + 2)$, where F and M are the microscopic force constant and mass of the atom. ε_0 and ε_∞ are the static and high-frequency dielectric constant. ω_T is the frequency of the TO phonon. Therefore, in the theoretical calculation, the impurity mode frequencies $f_{Te} = (F_{ZnTe}/M_{Te})^{1/2}$ and $f_{Se} = (F_{ZnSe}/M_{Se})^{1/2}$, which correspond to the vibration of Te in ZnSe ($x=0$ limit) and Se in ZnTe ($x=1$ limit) have to be modified for better fitting.[8,15] Where, F_{ZnTe} (F_{ZnSe}) is the force constant, which reflects the strength of the chemical bonding, between the Zn and Te (Zn and Se) atoms. M_{Te} and M_{Se} are the masses of the Te and Se atoms. The force constant, $F_{ZnTe} = 1.73 \times 10^6$ $amu \times (cm^{-1})^2$, and $F_{ZnSe} = 2.01 \times 10^6$ $amu \times (cm^{-1})^2$ which were obtained by the theoretical fitting to the impurity mode frequencies of mixed crystals,[8] should be adjusted to $F_{ZnTe} = 6.46 \times 10^6$ $amu \times (cm^{-1})^2$ and $Fe_{ZnSe} = 2.91 \times 10^6$ $amu \times (cm^{-1})^2$ for a proper fit to the current experimental data. Compared with the force constant, $F_{ZnSe} = 2.16 \times 10^6$ $amu \times (cm^{-1})^2$ (Ref. 16) and $F_{ZnTe} = 1.57 \times 10^6$ $amu \times (cm^{-1})^2$ (Ref. 17), the modification of the force constant is very substantial due to the unique physical property of $ZnSe_{1-x}Te_x$.[6]

The Raman-scattering spectra of the $ZnSe_{0.96}Te_{0.04}$ epilayer at high pressure is shown in Fig. 4. At ambient pressure, the Raman shifts for LO, peak A, and TO are at 250, 230, and 208 cm^{-1}, respectively. As pressure is increased to 3.1

FIG. 5. Pressure dependence of Raman shifts for TO, TO_I, TO_{II}, peak A, peak A*, and LO of $ZnSe_{0.96}Te_{0.04}$ epilayers.
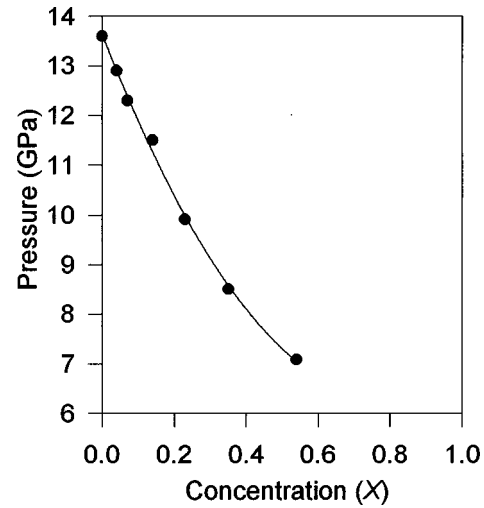
GPa, LO, peak A, and TO phonon energies exhibit a blue-shift. This implies the increasing force constant, which results from the shortening of lattice constant (hardening of lattice). As pressure is increased further, the LO peak becomes weaker. Above 12.9 GPa, the LO phonon is no longer observed in the spectra. The disappearance of LO is attributed to the semiconductor to metal transition.[13] As the semiconductor becomes metal, the excitation laser beam for the Raman spectrum is not allowed to penetrate into the sample. As a result, LO is not observed. Whereas, Raman peaks that exhibit TO character are still observable due to the fact that transverse surface lattice vibrations are allowed regardless if the sample is semiconductor or metal. The current result is consistent with the previous investigation of ZnSe and Zn$_{1-x}$Fe$_x$Se crystals.[13]

In Fig. 4, the dotted lines represent the curve fitting to the Raman spectra, although for some peaks the curve fitting looks quite artificial. However, the focus is to point out the disappearance of the LO phonon at high pressure, which is clear in the spectra. In Fig. 4, for TO and peak A, pressure-induced splittings are observed. TO$_{II}$ and TO$_I$ split from TO mode at 3.1 and 8.6 GPa. While peak A^* splits from peak A at 11.5 GPa. The splitting of the vibration mode implies the occurrence of a new phase, which results from the structural transition caused by applied pressure.[11] The splitting can be observed in the summary plot in Fig. 5. The curves represent quadratic polynomial fitting. The phase-transition pressure labeled in Fig. 5 by P_1, P_2, and P_3 mark the pressures where the splitting of TO phonon and peak A occur. These types of phase transition (structure transition) are not identified. However, this is not the major concern in our current article. The main point is to study the Te-concentration dependence of the P_4, semiconductor to metal-transition pressure.

The Raman spectra taken at high pressure for the other ZnSe$_{1-x}$Te$_x$ epilayers are similar to Fig. 4. As x is increased, the semiconductor to metal-transition pressure decreases. The transition pressures of the ZnSe$_{1-x}$Te$_x$ epilayers for x up to 0.54 are plotted in Fig. 6. The decrease in transition pressure with x implies the decreasing crystal stability with x. At $x = 0.54$, the transition pressure drops to 7.3 GPa. The decreasing crystal stability with the concentration of the third element was also observed in the Cd$_{1-x}$Mn$_x$Te mixed crystals. Qadri *et al.* found that the B_3-B_1 phase-transition pressure of Cd$_{1-x}$Mn$_x$Te mixed crystals drops from 3.2 to 2.4 Gpa as x is increased from 0 to 0.7.[18] The elastic stiffness moduli of the Cd$_{1-x}$Mn$_x$Te mixed crystals drops about 20% as x is increased to 0.52.[19]

IV. CONCLUSION

To summarize this paper, we have found that the lattice vibration mode behavior of ZnSe$_{1-x}$Te$_x$ epilayers belongs to the intermediate mode behavior. The microscopic force constants F_{ZnTe} and F_{ZnSe} were evaluated to be 6.46×10^6 amu$\times$(cm^{-1})^2 and 2.91×10^6 amu$\times$(cm^{-1})^2, respectively. The disappearance of the LO phonon in the Raman scattering at high pressure is attributed to the semiconductor to metal transition. The transition pressure was found to decrease with Te concentration

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