

Raman spectra of cubic $Zn_{1-x}Cd_xS$

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We report Raman spectra of cubic $Zn_{1-x}Cd_xS$ grown by metalorganic vapor-phase epitaxy and metalorganic molecular-beam epitaxy on (001) GaAs substrates. Two longitudinal-optical (LO) modes and one transverse-optical mode are observed, and their behavior is similar to that of the one-mode type. However, the signal intensity of the lower-frequency LO phonon is strong compared with that in hexagonal $Zn_{1-x}Cd_xS$, which exhibits a typical one-mode behavior. We also observe two additional peaks that are tentatively attributed to disorder-activated modes.

I. INTRODUCTION

$Zn_{1-x}Cd_xS$ bulk alloys are stabilized in a hexagonal wurzite structure. However, Fujita *et al.* recently demonstrated that $Zn_{1-x}Cd_xS$ exhibits a cubic zinc-blende structure when grown on (001) GaAs substrates.^{1,2} They also showed that cubic $Zn_{1-x}Cd_xS$ possesses promising characteristics for short-wavelength optoelectronic application. However, fundamental physical properties of cubic $Zn_{1-x}Cd_xS$ are scarcely known, since almost all of previous investigations of this alloy system dealt with hexagonal materials. In Refs. 1 and 2, cubic $Zn_{1-x}Cd_xS$ was characterized by x-ray diffraction (XRD) and photoluminescence measurements. In this paper, we report results of a Raman study of cubic $Zn_{1-x}Cd_xS$.

Behavior of zone-center optical phonons in $A_{1-x}B_xC$ ternary alloys can be classified into one-mode type, two-mode type, and some intermediate types.³ (Although slightly different definitions of the mode type have been proposed,^{3,4} we follow the definition of Brodsky *et al.*³) The phonon properties of hexagonal $Zn_{1-x}Cd_xS$ have been investigated by infrared reflection spectroscopy and Raman-scattering method.⁵⁻⁷ In both cases, the one-mode type was attributed to this system. Recently, Karasawa *et al.* reported a Raman spectrum of cubic $Zn_{0.56}Cd_{0.44}S$.⁸ In their results, two peaks having nearly the same intensity appear in the optical-phonon frequency range. On the basis of this observation, they ascribed the two-mode type to cubic $Zn_{1-x}Cd_xS$. In this study, we investigate phonon properties of this alloy more comprehensively. The results given in Sec. III show that cubic $Zn_{1-x}Cd_xS$ does not display a typical two-mode behavior, but a one-mode behavior.

II. EXPERIMENT

Alloy composition, thickness, and growth method of $Zn_{1-x}Cd_xS$ layers characterized in this study are listed in Table I. Samples 2 and 7 were grown by metalorganic molecular-beam epitaxy (MOMBE) at 280 °C and others

by metalorganic vapor-phase epitaxy (MOVPE) at 420 °C. (001) just-oriented GaAs is used as a substrate except for sample 3, which was grown on a GaAs substrate with the orientation of (001) 2° off toward $\langle 011 \rangle$. It was confirmed by XRD that all the layers are dominantly of zinc-blende structure. The alloy composition was determined from the lattice constant measured by XRD assuming the Vegard law.

Raman spectra were obtained at room temperature using the 514.5-nm line of an Ar laser as an exciting source in a backscattering geometry. The alloy layers are transparent for the laser light, but the band gap of CdS is slightly smaller than the photon energy. In order to observe the transverse-optical (TO) phonon, we obtained spectra on a (110) cleaved face of the grown layer using the micro-Raman system, i.e., focusing the laser beam by an optical microscope. Spectra on a (001) face were taken by a conventional (macroscopic) Raman measurement. The spectral resolution is 3 cm^{-1} .

III. RESULTS

Figure 1 shows Raman spectra for $Zn_{0.43}Cd_{0.57}S$ (sample 3). The spectra in Fig. 1(a) were obtained on the (001) surface with the incident light beam polarized along the [100] direction. The configuration $z(xy)\bar{z}$ corresponds to the cross polarization of the incident and scattered light, and the configuration $z(xx)\bar{z}$ to the parallel polarization.

TABLE I. Alloy composition, thickness, and growth method of the layers characterized in this study.

Sample	Cd content	Thickness (μm)	Growth method
1	0.32	0.47	MOVPE
2	0.54	0.96	MOMBE
3	0.57	0.81	MOVPE
4	0.59	0.88	MOVPE
5	0.62	0.93	MOVPE
6	0.825	1.19	MOVPE
7	1	0.9	MOMBE

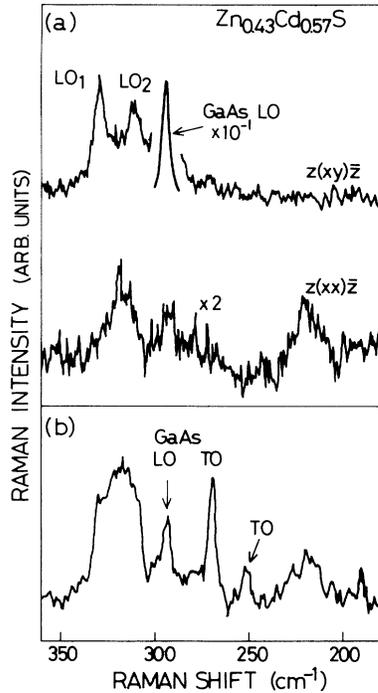


FIG. 1. Raman spectra of $\text{Zn}_{0.43}\text{Cd}_{0.57}\text{S}$. (a) Analyzed spectra on a (001) face with incident light polarized along [001]. (b) Unanalyzed spectrum on a (110) cleaved face.

The scattering by the longitudinal-optical (LO) mode in a zinc-blende crystal is allowed in $z(xy)\bar{z}$. As can be seen in the figure, the two peaks at 328.5 and 310 cm^{-1} are observed in the configuration $z(xy)\bar{z}$ and not in $z(xx)\bar{z}$. Therefore, they can be attributed to the LO phonons in $\text{Zn}_{0.43}\text{Cd}_{0.57}\text{S}$. In the spectrum of $z(xx)\bar{z}$, another peak appears between the frequencies of the two LO peaks. A broad peak is also present at 220 cm^{-1} in the $z(xx)\bar{z}$ spectrum. These two modes are not considered to be a zone-center optical mode. We tentatively assign them to disorder-activated modes that result from the breakdown of the selection rule in a random alloy and have been observed in many alloy systems. The small peak at 293 cm^{-1} in the $z(xx)\bar{z}$ spectrum is due to the LO phonon in GaAs; it is observed probably because of a small departure from the exact $z(xx)\bar{z}$ configuration.

Scattering by the TO phonon is forbidden in a back-scattering geometry on a (001) face, but it is allowed on a (110) face. Figure 1(b) shows an unanalyzed spectrum taken on the cleaved face of the grown layer. In addition to the TO mode at 270 cm^{-1} and the forbidden LO mode at 293 cm^{-1} of the GaAs substrate, three peaks are observed. The broad peaks at 220 and 310 cm^{-1} will be the same modes as those appearing in the $z(xx)\bar{z}$ spectrum in Fig. 1(a). The peak at 251 cm^{-1} is absent in the spectra on the (001) face but clearly observed in Fig. 1(b). Thus, it can be assigned to the TO mode in the zinc-blende structure.

Figure 2 shows results for $\text{Zn}_{0.175}\text{Cd}_{0.825}\text{S}$ (sample 6). The signal from the $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ layer is much stronger than in Fig. 1 because the experimental condition is rath-

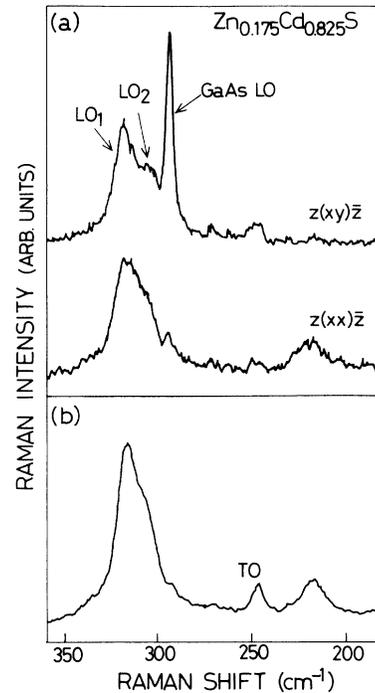


FIG. 2. Raman spectra of $\text{Zn}_{0.175}\text{Cd}_{0.825}\text{S}$. (a) Analyzed spectra on a (001) face with incident light polarized along [001]. (b) Unanalyzed spectrum on a (110) cleaved face.

er close to the E_0 resonance. Two LO modes are observed in the $z(xy)\bar{z}$ spectrum, as in the case of $\text{Zn}_{0.43}\text{Cd}_{0.57}\text{S}$. The lower-frequency LO mode (LO_2) corresponds to the broad structure around 305 cm^{-1} , whereas the peak of the higher-frequency LO (LO_1) broadens only slightly as compared with Fig. 1. The peak at 246 cm^{-1} will be due to the TO mode. Although it is observed clearly in the spectrum on the (110) face [Fig. 2(b)], it also appears in the spectra on the (001) face. This could be due to the near-resonant condition of the experiment.

The relative intensity of each peak in other alloy samples does not differ significantly from that of the corresponding peak in Fig. 1. For CdS (sample 7), the E_0 resonance occurs, and the luminescence band overlaps the Raman band. A single LO mode was observed in CdS.

Figure 3 shows peak frequencies as a function of Cd content x . The LO frequencies are represented by the circles and the TO frequency by the squares. The triangles represent the modes tentatively assigned to the disorder-activated modes. The solid and broken lines show the frequencies in hexagonal $\text{Zn}_{1-x}\text{Cd}_x\text{S}$.⁵ The TO and LO branches in a hexagonal lattice are split because of the lower symmetry, although the splitting is negligible for the LO mode. The mode shown by the broken line is a weak secondary mode. In hexagonal $\text{Zn}_{1-x}\text{Cd}_x\text{S}$, the signal due to the secondary mode is much weaker than that of the dominant mode in both the Raman and infrared reflection measurements.⁵⁻⁷ As shown in the figure, the frequencies of the higher-frequency LO (LO_1) and the TO modes in cubic $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ are close to, but

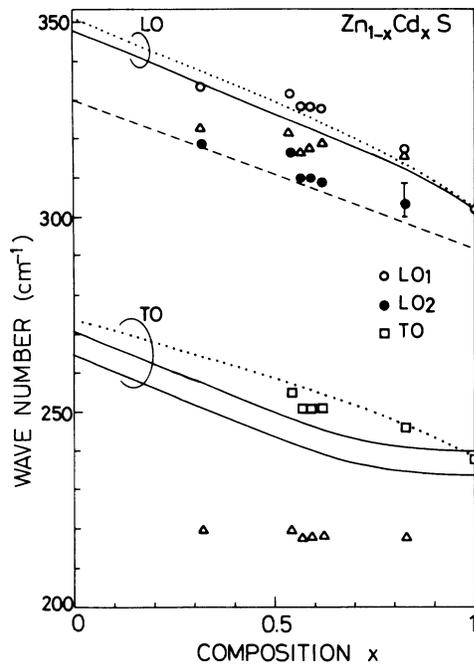


FIG. 3. Composition dependence of the peak frequencies for $Zn_{1-x}Cd_xS$. Circles: LO modes. Squares: TO mode. Triangles: modes tentatively assigned to the disorder-activated modes. The solid and broken lines indicate the dominant and secondary modes in hexagonal $Zn_{1-x}Cd_xS$, respectively (Ref. 5). The dotted lines show LO and TO frequencies calculated on the basis of the MREI model (Ref. 4).

slightly higher than, those of the corresponding modes in hexagonal $Zn_{1-x}Cd_xS$, while the lower-frequency LO (LO_2) in cubic $Zn_{1-x}Cd_xS$ and the secondary mode in hexagonal $Zn_{1-x}Cd_xS$ have almost the same frequency.

The dotted lines represent results of calculation based on the modified random-element isodisplacement (MREI) model of Genzel, Martin, and Perry.⁴ The difference of the crystal structure is not taken into account in the MREI model, and thus the results are the same for both the cubic and hexagonal phases. The calculation predicts the one-mode behavior for $Zn_{1-x}Cd_xS$. The measured frequencies of the LO_1 and TO modes agree well with the calculated values of the dominant LO and TO modes, respectively. The calculated frequency of the secondary mode is lower than 200 cm^{-1} , and thus the behavior of the LO_2 mode is not reproduced in the calculation.

IV. DISCUSSION

A. Zone-center optical phonons

We observed three zone-center optical modes. Two of them (LO_1 and LO_2) have the character of LO and the other has the TO character. Since the two LO peaks have comparable intensity, one might suppose that cubic $Zn_{1-x}Cd_xS$ exhibits a two-mode behavior and that the LO_1 (LO_2) corresponds to the ZnS-like (CdS-like) mode. However, the composition dependence of the spectra

does not support this assignment.

(1) The frequency of the LO_1 mode in the alloy extrapolates to those of the LO modes of the constituent compounds in the limits of $x \rightarrow 1$ and $x \rightarrow 0$. This behavior is typical of the one-mode type.

(2) If the LO_1 and LO_2 modes correspond to the ZnS- and CdS-like modes, respectively, then the relative intensity of the LO_1 mode to the LO_2 mode would decrease with Cd content x . However, this is not the case. (Compare Figs. 1 and 2.)

(3) If LO_1 is the ZnS-like mode, its peak width would increase with x (with decrease of Zn content) because of the damping.³ Such a tendency has been observed for $ZnS_{1-x}Se_x$,⁹ which exhibits a typical two-mode behavior. In cubic $Zn_{1-x}Cd_xS$, however, the LO_2 mode rather than the LO_1 mode broadens significantly in the Cd-rich alloy.

Thus, the main features of the LO modes observed in this study are of the one-mode type. On the other hand, the behavior of the TO mode is obviously the one-mode behavior: only one dominant mode is observed, and its frequency varies smoothly with composition from the TO frequency in ZnS to that in CdS. Therefore, the present results indicate that the optical phonons in cubic $Zn_{1-x}Cd_xS$ show the one-mode behavior.

The comparison with hexagonal $Zn_{1-x}Cd_xS$ also supports this conclusion. The optical phonons of hexagonal $Zn_{1-x}Cd_xS$ exhibit a typical one-mode behavior. As shown in Fig. 3, the LO_2 mode in the cubic phase seems to correspond to the secondary mode in the hexagonal phase.

However, the LO_2 mode has exceptionally strong intensity as a secondary or an incidental mode. The reason for this is not understood. Two LO peaks with comparable intensity are also observed in $Ga_{1-x}In_xP$. Since the masses of Ga, In, and P atoms are nearly equal to those of Zn, Cd, and S atoms, respectively, the similarity between these two alloys seems natural. Lucovsky *et al.* ascribed the one-mode type to $Ga_{1-x}In_xP$.¹⁰ However, Jusserand and Slempek claimed that the optical phonons in $Ga_{1-x}In_xP$ show an intermediate or a modified two-mode behavior and that the lower-frequency LO phonon is the InP-like mode.¹¹ They drew this conclusion from results of Raman measurements of dilute $Ga_{1-x}In_xP$ alloys. We have not measured Raman spectra of dilute alloys. However, if we consider cubic $Zn_{1-x}Cd_xS$ to be the modified two-mode type, it would be difficult to explain the present results, especially the broadening of the LO_2 peak in the Cd-rich alloy.

We can expect similarity between cubic $Zn_{1-x}Cd_xSe$ and $Zn_{1-x}Cd_xS$. Recently, Alonso *et al.* measured Raman spectra of cubic $Zn_{1-x}Cd_xSe$ grown epitaxially on GaAs.¹² Their results show that behavior of optical phonons in cubic $Zn_{1-x}Cd_xSe$ is of the one-mode type according to the classification of Brodsky *et al.*³

B. Disorder-activated modes

We tentatively assigned the two peaks observed in the $z(xx)\bar{z}$ spectra to modes activated by compositional dis-

order in the alloys. The origin of these modes is discussed in this subsection.

The origin of the peak around 220 cm^{-1} is not clear. The zone-edge longitudinal-acoustical (LA) frequency in ZnS is about 210 cm^{-1} ,¹³ close to the frequency of the peak. Thus, we may attribute the peak to the disorder-activated LA (DALA) in the Zn-rich composition region. However, the peak frequency is almost independent of composition. The zone-edge LA frequency in cubic CdS is not known, but it will be considerably lower than that in ZnS; only the heavier atom vibrates in the zone-edge (point X) LA mode, and thus the frequency of LA (X) in CdS is expected to be lower than 170 cm^{-1} considering masses of Zn and Cd atoms. Therefore, if the peak is due to DALA, its frequency should decrease with Cd content. Thus, the peak might be due to the higher-order process and not to DALA in the Cd-rich composition region.

The other peak above 300 cm^{-1} will be due to disorder-activated LO (DALO).¹⁴ In the limit $x \rightarrow 0$, the frequency of the peak extrapolates to about 330 cm^{-1} , which is nearly equal to the zone-edge LO frequency in ZnS.¹³ The theoretical calculation shows that DALO causes Raman scattering of the Γ_1 symmetry, which is allowed in the configuration $z(xx)\bar{z}$.^{14,15} This also supports the assignment of the peak above 300 cm^{-1} to DALO.

A long-range ordering has been recognized in MOVPE $\text{Ga}_{1-x}\text{In}_x\text{P}$.¹⁶ The zone folding accompanying the ordering makes the zone-edge phonon observable in the optical measurements. Gomyo *et al.* observed an additional signal between the frequencies of the two LO modes in ordered $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$.¹⁷ Since the radii as well as the masses of the constituent atoms of $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ are similar to those of $\text{Ga}_{1-x}\text{In}_x\text{P}$, similar ordering may occur in $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ because of local strain. Then, the mode assigned to DALO would correspond to the ordering-induced zone-folded LO mode. At present, however, we cannot determine whether the mode is activated by the disorder or the order.

V. CONCLUSION

We have measured Raman spectra of cubic $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ grown by MOVPE and MOMBE on (001) GaAs substrates. The behavior of the zone-center optical phonons is similar to that of the one-mode type, although the intensity of the peak due to the lower-frequency LO phonon is strong compared with that in hexagonal $\text{Zn}_{1-x}\text{Cd}_x\text{S}$. We have also observed two additional peaks, which are tentatively assigned to DALA and DALO.

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