

Raman study of disorder and strain in epitaxial $\text{ZnS}_x\text{Se}_{1-x}$ films on a GaAs substrate

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Quantitative characterization of disorder and strain in $\text{ZnS}_x\text{Se}_{1-x}/\text{GaAs}$ lattice-mismatched semiconductor heterostructures was successfully done by means of Raman spectroscopy. The alloy disorder and the phonon coherence length in epitaxial $\text{ZnS}_x\text{Se}_{1-x}$ films were estimated from the Raman linewidth of the ZnSe-like LO phonon by using a spatial correlation model. The strain due to the lattice mismatch near the interface between $\text{ZnS}_x\text{Se}_{1-x}$ and GaAs was deduced from the linewidth of the GaAs LO phonon.

Recently, there is much interest in wide band-gap ternary II-VI semiconductor alloys for their potential applications in optoelectronic devices in the blue spectral region.¹ The ternary semiconductor (e.g., $\text{ZnS}_x\text{Se}_{1-x}$) have many advantages over binary compounds (e.g., ZnSe) because the lattice constant and optical properties can be varied by changing the composition. The epitaxial thin films of ternary II-VI semiconductors have been usually grown on GaAs substrates with slightly different lattice constants. The alloy disorder (alloy potential fluctuations)² of ternary semiconductors and the strain due to the lattice mismatch between the epitaxial films and the substrate^{3,4} play a major role in determining electrical and optical properties of epitaxial films. That is why the quantitative characterization of alloy disorder and strain is an important issue in the epitaxial growth and device applications of II-VI ternary semiconductors. In this work, we tried to evaluate quantitatively disorder and strain in $\text{ZnS}_x\text{Se}_{1-x}/\text{GaAs}$ heterostructures by means of Raman spectroscopy.

$\text{ZnS}_x\text{Se}_{1-x}$ films were grown by atmospheric pressure metalorganic chemical vapor deposition (MOCVD) on the (100) GaAs substrate at 500 °C using dimethylzinc, dimethylselenide, and diethylsulfide. The S composition ranging from $x=0$ to 0.13 was controlled by the flow rate of diethylsulfide. The film thickness of all samples was about 1.3 μm . The lattice constants of epitaxial films were measured by x-ray diffraction. We found that the lattice constant of a $\text{ZnS}_x\text{Se}_{1-x}$ film at $x=0.07$ was nearly equal to that of the GaAs substrate.

Raman scattering measurements were performed at room temperature in two backscattering configurations: (1) The incident laser direction is normal to the growth plane (configuration I). Raman spectra were obtained by using 488- or 514.5-nm Ar^+ laser light and a double monochromator (Spex 1403). (2) The heterostructure samples were cleaved and the cleavage plane was microprobed (configuration II). Microprobed spectra were obtained by using 514.5-nm laser light and a Raman micro-

probe measurement system (Japan Spectroscopic Co. Ltd., R-MPS-11) consisting of a 25-cm filter monochromator and a 1-m monochromator. The diameter of the focused beam was about 1 μm . These configurations are illustrated in the insets of Fig. 1.

Figure 1 shows the Raman spectra of the $\text{ZnS}_{0.07}\text{Se}_{0.93}/\text{GaAs}$ heterostructure ranging from 160 to 320 cm^{-1} in two different configurations. We used the (100) plane in configuration I [Fig. 1(a)] and the (110) plane in configuration II [Fig. 1(b)]. The selection rule for zinc-blende crystal structures shows that only LO modes are allowed in configuration I. On the other hand, LO modes are forbidden and TO modes are allowed in configuration II. In Fig. 1(a), GaAs LO and ZnSe-like LO modes and also a weak forbidden ZnSe-like TO mode were observed. In Fig. 1(b), a ZnSe-like TO and weak forbidden ZnSe-like LO modes were observed. If the strain due to the lattice mismatch between $\text{ZnS}_x\text{Se}_{1-x}$ and GaAs is very high in the $\text{ZnS}_x\text{Se}_{1-x}$ film, the shift of the Raman peak frequency due to high misfit strains³ and/or the splitting of phonon modes due to biaxial stress⁵ may be observed in configuration II. However, over all of the composition range from 0 to 0.13, we were not able to observe a significant difference in the peak frequency between the two configurations.

Figure 2 shows the Raman peak frequency ω and the linewidth Γ_{ZnSe} (full width at half maximum) of the ZnSe-like LO phonon obtained in configuration I as a function of the S composition. With increasing S composition, the peak frequency decreases and the linewidth increases. The composition dependence of Raman spectra in ZnSSe films is considered to be determined by both alloy disorder of the film and the misfit strain. If the strain dominates Raman spectra of the ZnSe-like LO phonon, the composition dependence of Γ_{ZnSe} and ω at $x < 0.07$ differs from those at $x > 0.07$, because the compressive and tensile stresses due to the lattice mismatch should exist in $\text{ZnS}_x\text{Se}_{1-x}$ films at $x < 0.07$ and $x > 0.07$, respectively. However, Γ_{ZnSe} increases monotonically with increasing x . Moreover, the

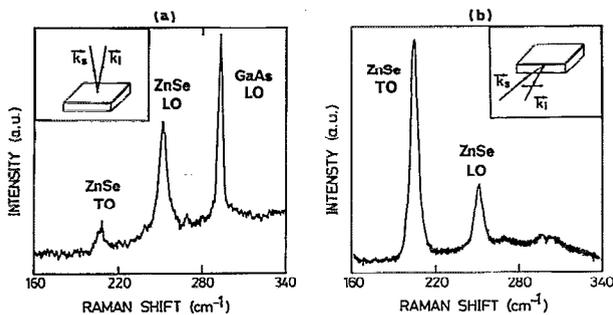


FIG. 1. Raman spectra of the $\text{ZnS}_x\text{Se}_{1-x}$ ($x=0.07$) films at room temperature in two different configurations. The insets indicate the geometrical configuration: (a) configuration I and (b) configuration II.

composition dependence of Raman peak frequencies of the ZnSe-like LO and TO phonons in epitaxial films agrees very well with that observed in the bulk mixed crystals.⁶

Therefore, the geometrical and composition dependencies of Raman spectra show that the strain in thin films do not play an important role in the composition dependence of Raman spectra.

We have more evidence to deny the strain effect. A small TO phonon peak was observed in configuration I, although it is forbidden by a selection rule in this geometry. Figure 3 shows the composition dependence of the intensity ratio of the forbidden TO to the allowed LO phonons. The intensity ratio increases monotonically with increasing S composition. Monotonical composition dependence of Γ_{ZnSe} and $I_{\text{TO}}/I_{\text{LO}}$ clearly shows that disorder

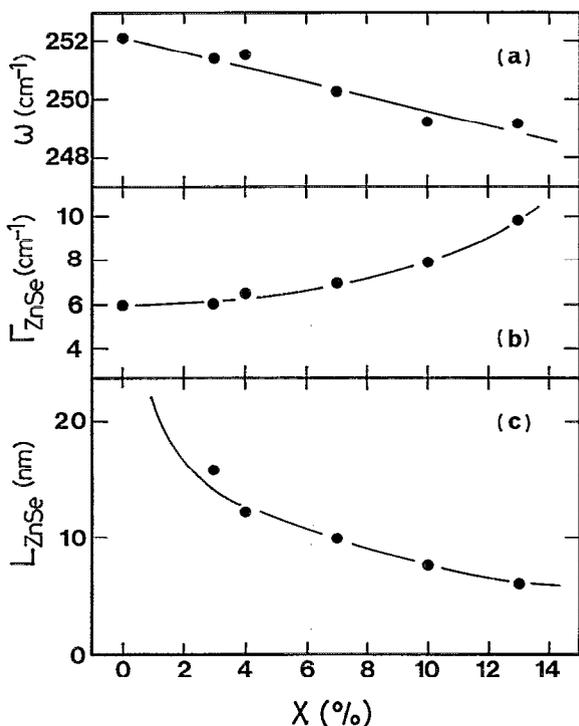


FIG. 2. Peak Raman frequency ω , Raman linewidth Γ_{ZnSe} , and the correlation length L_{ZnSe} of the ZnSe-like LO phonon as a function of molar fraction x in $\text{ZnS}_x\text{Se}_{1-x}$. L_{ZnSe} is estimated by using the spatial correlation model with the Gaussian correlation function.

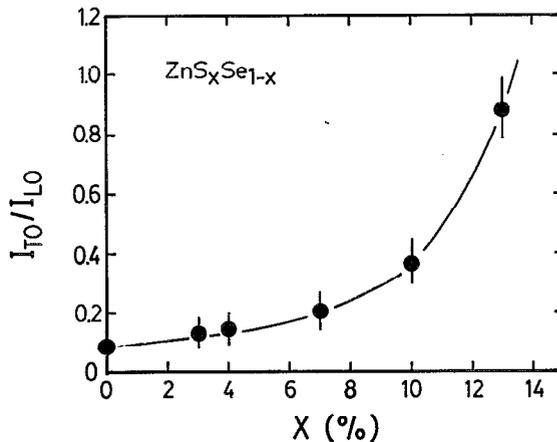


FIG. 3. Intensity ratio of the forbidden TO signal to the allowed LO signal obtained in configuration I as a function of molar fraction x in $\text{ZnS}_x\text{Se}_{1-x}$.

rather than misfit strain determines Raman spectra of ZnSSe films on the GaAs substrate.

Here, we discuss the disorder in $\text{ZnS}_x\text{Se}_{1-x}$ films using a spatial correlation model.^{2,7} The alloy disorder causes a relaxation of the q -vector selection rule and the spatial correlation function of the phonon becomes finite. A Gaussian spatial correlation function $\exp(-2r^2/L^2)$ has been used to account for q -vector relaxation related to the alloy disorder, where L is the correlation length. The Raman intensity $I(\omega)$ at a frequency ω can be expressed as^{2,8}

$$I(\omega) \propto \int_0^1 \exp(-q^2 L^2/4) / \{[\omega - \omega(q)]^2 + (\Gamma_0/2)^2\} d^3q, \quad (1)$$

where q is expressed in units of $2\pi/a$, a is the lattice constant, and Γ_0 is the linewidth of the ZnSe LO phonon in the pure ZnSe film. We take the dispersion $\omega(q)$ of the LO phonon based on a one-dimensional chain model:

$$\omega^2(q) = A + \{A^2 - B[1 - \cos(\pi q)]\}^{1/2}, \quad (2)$$

where $A = 3.2 \times 10^4 \text{ cm}^{-2}$ and $B = 4.5 \times 10^8 \text{ cm}^{-4}$ for ZnSe.⁹ These parameters were determined for Eq. (2) to describe well the neutron scattering data.⁹ By using Eqs. (1) and (2), we can calculate the line shape of the Raman signal as a function of L . We compared the experimental linewidth of the ZnSe-like LO phonon with the calculated one. In this way, the correlation length of the ZnSe-like LO phonon, L_{ZnSe} , was deduced from Γ_{ZnSe} .

Figure 2(c) shows L_{ZnSe} plotted as a function of S composition. In the two-mode behavior alloys such as $\text{ZnS}_x\text{Se}_{1-x}$,^{6,10} we can consider that the ZnSe- and ZnS-like phonon modes are localized in the ZnSe and the ZnS regions, respectively. L_{ZnSe} means the average size of the localized region of ZnSe-like phonons. The phonon coherence length L_{ZnSe} decreases with increasing S composition; the phonon extended region becomes very small. This is caused by the alloy disorder. The intensity ratio of TO to LO phonons in Fig. 3 increases with decreasing L_{ZnSe} and this can be also interpreted by the disorder-induced Raman

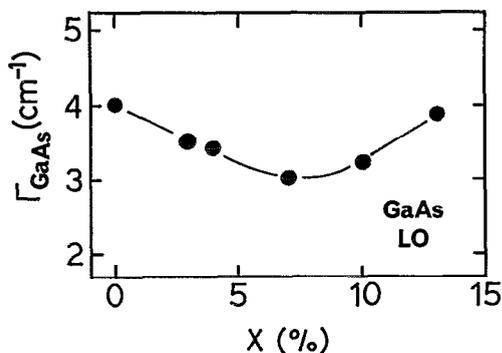


FIG. 4. Raman linewidth Γ_{GaAs} of the GaAs LO phonon as a function of S composition in $\text{ZnS}_x\text{Se}_{1-x}$.

scattering. Therefore, the correlation length L_{ZnSe} becomes a quantitative parameter reflecting disorder of ZnSSe epitaxial films.

Figure 3 shows that the very weak forbidden ZnSe-TO phonon was observed even in the *pure* ZnSe film. We believe that this is caused by the misfit strain near the interface. Figure 4 shows the Raman linewidth of GaAs LO phonons, Γ_{GaAs} , as a function of S composition of $\text{ZnS}_x\text{Se}_{1-x}$ films. At $x=0.07$, Γ_{GaAs} exhibits a minimum value, although we were not able to observe the peak frequency shift. Since the lattice constant of $\text{ZnS}_x\text{Se}_{1-x}$ at $x=0.07$ is nearly equal to that of GaAs, the composition dependence of Γ_{GaAs} is explained by the strain near the interface due to the lattice mismatch. Figure 4 implies that compressive ($x > 0.07$) or tensile ($x < 0.07$) stress exists in the GaAs substrate near the interface.

If there is homogeneous strain in the penetration depth of the incident laser light (~ 100 nm), the strain ϵ exhibits the maximum value at $x=0$ and 0.13 and is calculated to be about 3×10^{-3} . Here, we used the relationship between Γ_{GaAs} and the strain in GaAs epitaxial films¹¹ for calcula-

tions. However, the strain-induced frequency shift was not clearly observed: It is below our reproducibility limit of about 0.3 cm^{-1} . A phenomenological theory¹² deduces the strain of $\sim 1 \times 10^{-3}$ from a frequency shift of 0.3 cm^{-1} at most. Raman spectroscopy of the GaAs substrate shows that there exists a small misfit strain of the order of 10^{-3} or less near the interface.

In conclusion, we have successfully examined the disorder and strain in lattice-mismatched $\text{ZnS}_x\text{Se}_{1-x}/\text{GaAs}$ heterostructures by means of Raman spectroscopy. The disorder and the phonon coherence length in epitaxial $\text{ZnS}_x\text{Se}_{1-x}$ films were deduced from the linewidth of the ZnSe-like LO phonon. The strain at the interface was evaluated from the linewidth of the GaAs LO phonon. The experimental and analytical procedures demonstrated in this work are expected to be useful for the microscopic characterization of semiconductor heterostructures.

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¹See, for example, Proceedings of the 5th International Conference on II-VI Compounds, Tamano, 1991 (to be published).

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