

Raman scattering of ZnSe grown by molecular beam epitaxy

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Abstract. LO phonon frequency of ZnSe thin films on GaAs grown by molecular beam epitaxy (MBE) has been measured from 20 to 300 K by Raman scattering. Frequency shift of the ZnSe LO phonon is estimated in terms of elastic strains due to lattice mismatch and thermal strains due to the difference in thermal expansion coefficients of film and substrate. Strains due to lattice mismatch for thin films are dominant at high temperatures, while thermal strains due to large differences between growth and measurement temperatures are dominant at low temperatures. Temperature dependence of full width at half maximum (FWHM) in LO phonon spectra of ZnSe are discussed in terms of imperfection and phonon contribution.

Keywords. Raman scattering; ZnSe thin films on GaAs; molecular beam epitaxy; LO phonon spectra.

1. Introduction

ZnSe films grown by molecular beam epitaxy (MBE), vapor phase epitaxy (VPE) and metalorganic vapor phase epitaxy (MOVPE) have been investigated because of their potential application in optoelectronic devices such as blue light emitters and lasers. Many studies on ZnSe films grown on GaAs substrates have been reported from the point of view of X-ray diffraction (Mitsuhashi *et al* 1985), photoluminescence (Yao 1986), ellipsometry and Rutherford backscattering (RBS) (Imai *et al* 1988). From these studies it has been shown that strains exist in ZnSe thin films due to accommodation of the lattice mismatch and that they decrease with increasing film thickness. It is well-known that strains in thicker epitaxial films are released by misfit dislocations (Yao 1986; Olego 1987) produced near the heterointerface but thermal strains are introduced by the difference in thermal expansion between ZnSe and GaAs on cooling from growth temperature to room temperature.

Recently electronic Raman scattering due to acceptor impurity (Walsh *et al* 1987) and Brillouin scattering (Lee *et al* 1988) were measured in MBE-ZnSe films. And further film thickness dependence of LO phonons by Raman measurement (Nakashima *et al* 1988) was explained in terms of the conversion of elastic strains to thermal strains. However, this experiment cannot be explained completely by both strains as mentioned below. One reason is that the elastic strains are small as the experiments were carried out on samples of thickness greater than the critical value, where misfit dislocations are present. The other reason is that thermal strains are small because of the experiments being carried out at temperatures higher than 80 K. In this work,

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our aim is to evaluate precisely both strains in MBE-ZnSe films on GaAs from Raman measurements, by enhancement of elastic strains by using thinner films and of thermal strains by larger differences in growth and measurement temperatures.

2. Experimental procedure

ZnSe films were grown on Cr-doped semi-insulating (100) GaAs substrates with Zn and Se vapor pressures of about 3.0×10^{-7} Torr under about 8×10^{-10} Torr at the optimal growth substrate temperature of 300°C (Imai *et al* 1988). Raman spectra were measured by backscattering configuration from the (100) ZnSe surface with an Ar⁺ laser line at 514.5 nm and of about 100 mW. The samples were mounted in a double monochromator (JY U-1000) with variable-temperature optical dewar (LH RW-2).

3. Results and discussion

Figure 1 shows a typical Raman spectrum of a film of thickness 0.45 μm at 20 K. The peaks near 260 and 300 cm^{-1} correspond to LO phonon frequencies of ZnSe and GaAs because TO phonons are forbidden in this configuration and on this surface. The LO phonon frequencies of ZnSe and GaAs are about 5 and 2 cm^{-1} larger than those of both bulk-crystals at 300 K. The peak due to disorder activated phonons was not observed.

Figure 2 shows the Raman shift frequency of LO phonons for 0.45 and 1.2 μm -thick ZnSe films as a function of temperature. The deviation of the shift frequency is about $\pm 1 \text{ cm}^{-1}$ at low temperature and about $\pm 0.8 \text{ cm}^{-1}$ near room temperature. Both frequencies decrease monotonously with increasing temperature. It accrues from the softening of the crystals with increasing temperature. The Raman shift of the

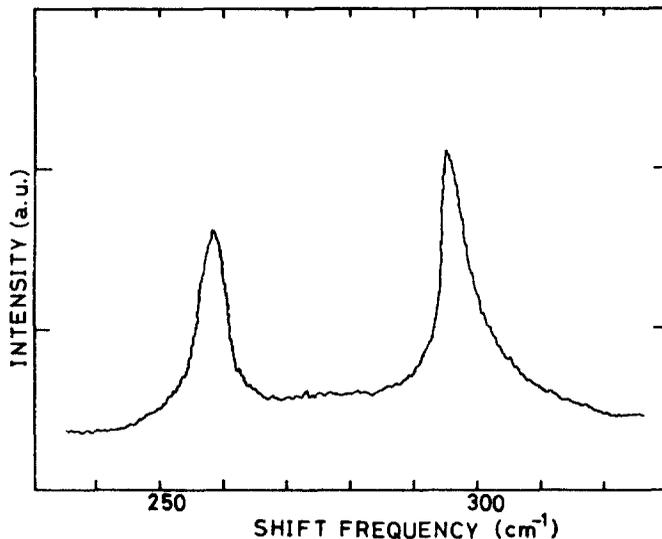


Figure 1. Raman spectrum of MBE-ZnSe film on GaAs substrate with a thickness of 0.45 μm at 20 K.

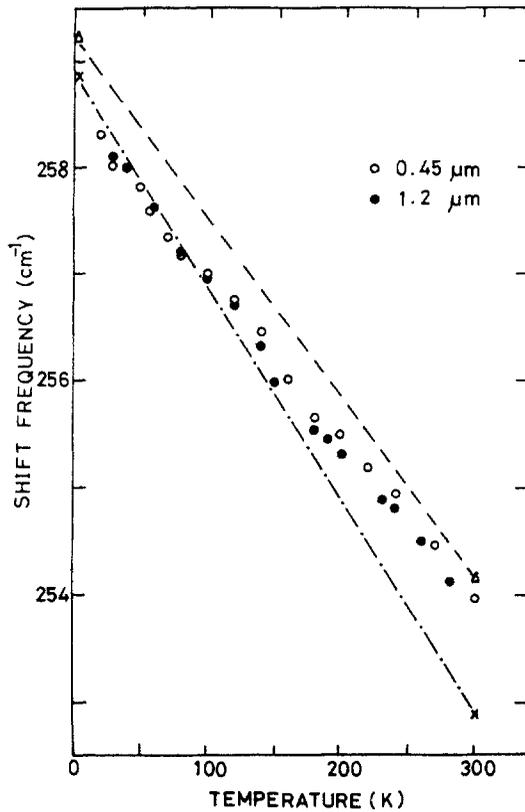


Figure 2. Raman shift frequency of MBE-ZnSe films with 0.45 and 1.2 μm thickness as a function of temperature. The dashed line denotes the Raman shift frequency due to elastic strains and the triangles are calculated values. The dashed and dotted line shows the Raman shift due to thermal strains and crosses denote calculated values.

1.2 μm -sample appears to be larger slightly below 50 K as compared to that of the 0.45 μm one.

The strains in the films are similar to those of the bulk crystals under pressure. The stress-induced shift (Cerdeira *et al* 1972) of the LO phonon is calculated as

$$\Delta\omega = \frac{(p+2q)}{3\omega_0}(S_{11} + 2S_{12})X - \frac{(p-q)}{3\omega_0}(S_{11} - S_{12})X, \quad (1)$$

where ω_0 is the zero strain frequency of LO phonons, p and q are the parameters related to the third elastic coefficients, S_{11} and S_{12} are the elastic compliances and X is the stress. The stress X for thin films is given by the following equations:

$$a''(1 + e_{xx}) = a(\text{GaAs}), \quad (2)$$

$$e_{xx} = (S_{11} + S_{12})X, \quad (3)$$

$$a^\perp = (1 + e_{zz})a(\text{ZnSe}) \quad (4)$$

$$e_{zz} = 2S_{12}X, \quad (5)$$

where a'' and a^\perp are the lattice constants parallel and normal to the epitaxial layer and e_{ij} is the strain tensor. The non-zero components of the strain tensor in thin layers coherently grown on lattice-mismatched (100) substrates are $e_{xx} = e_{yy} = e$ and $e_{zz} = [2S_{12}/(S_{11} + S_{12})]e$. Therefore we obtain the difference, $\Delta\omega$, between LO phonon frequencies of strained and strain-free layers from (1) to (5) and the physical values of ZnSe: at 300 K $\omega_0 = 253 \text{ cm}^{-1}$ (Landolt-Börnstein 1982), $S_{11} = 2.237 \times 10^{-12}$ and $S_{12} = -0.8623 \times 10^{-12} \text{ dyn}^{-1} \text{ cm}^2$ calculated by elastic constants (Lee *et al* 1988), $p = -4.10 \times 10^{27}$ and $q = -5.94 \times 10^{27} \text{ s}^{-2}$ (Cerdeira *et al* 1972). The value calculated at 300 K by assuming that the lattice mismatch between ZnSe and GaAs is accommodated only by uniform deformation for thin films is shown by a triangle in figure 2. Because of the lack of low temperature values for the above parameters under pressure, we used the same values in calculation at 0 K. The value of ω_0 is extrapolated by the temperature dependence of the ZnSe-LO phonon (Landolt-Börnstein 1982). We assumed no thickness dependence of physical parameters as in the measurements of elastic constants as a function of film thickness (Lee *et al* 1988). Thus the estimated value at 0 K is denoted by the other triangle. The dashed line is drawn between both points only to visualize the temperature dependence to be expected. The elastic strains calculated agree well with experimental points at high temperatures, while those at low temperatures show a disagreement of about 1 cm^{-1} .

On the other hand, the strains in thick films are relaxed by the misfit dislocations during epitaxial growth, but the strain is introduced on cooling by the difference of the thermal expansion coefficient between the epitaxial film and the substrate. The lattice constant of the films parallel to the layer at room temperature is given by

$$a'' = a(\text{ZnSe}) \left[1 + \int_{\tau}^{T_G} \{ \alpha_{\text{ZnSe}}(T) - \alpha_{\text{GaAs}}(T) \} d\tau \right], \quad (6)$$

where T_G and T are the growth and arbitrary measurement temperatures, $\alpha(T)$ is the thermal expansion coefficient [$8.2 \times 10^{-9} T + 5.1 \times 10^{-6}/\text{K}$ for ZnSe (Feder and Light 1968) and $4.6 \times 10^{-9} T + 4.6 \times 10^{-6}/\text{K}$ for $T < 440 \text{ K}$ for GaAs (Singh and Dayal 1967)]. The frequency differences $\Delta\omega$ calculated from (6) by using lattice parameters at 300 K and that extrapolated to 0 K are also shown in figure 2 by two crosses. Here the strain corresponds to the second term in (6). The dashed and dotted line is drawn by using extrapolated values of the dependence of thermal expansion coefficient on temperature (Feder and Light 1968). We found that thermal strains are very small as compared to elastic strains at high temperature but are dominant at low temperature even for thin samples because of larger differences between growth and measurement temperatures.

We can obtain the lattice parameters normal and parallel to the layer from the above equations. The lattice constants calculated from measured frequency differences $\Delta\omega$ are shown in figure 3. Our constant a^\perp decreases as the thickness increases. The trend in the constant a^\perp showed good agreement with the results of other Raman studies (Nakashima *et al* 1988) but a slight difference between Raman data and results obtained from the X-ray analysis. Raman data seem to be smaller than X-ray ones. This may result from the detection of smaller mean values of the strains by Raman scattering than by X-ray analysis. However, we can find a reasonable trend in a lattice relaxation due to strains with increasing thickness of the films (Mitsuhashi *et al* 1985; Yao *et al* 1987). On the other hand, we can estimate the constant a'' , which to our

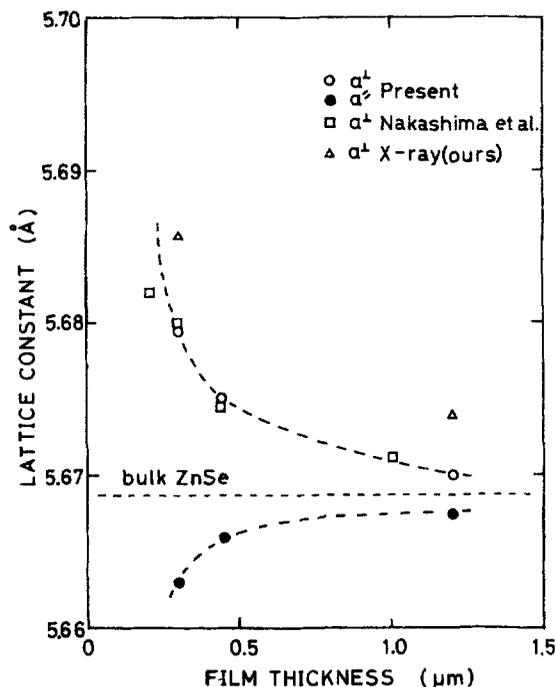


Figure 3. Lattice constants normal and parallel to the epitaxial layer as a function of film thickness at 300 K.

knowledge has not been obtained so far. The results that the values of a'' increase with the thickness is consistent with the fact that the strains in the films are released by the misfit dislocations as seen in the trend for a^\perp .

FWHM of ZnSe-LO phonons for the 0.45 and 1.2 μm -samples is illustrated as a function of temperature in figure 4. Our experimental errors in the values of FWHM are about $\pm 1 \text{ cm}^{-1}$ on the surface. The values of FWHM for both samples increase with temperature. A similar tendency in both samples is explained by increase of number of phonons as the temperature increases. We can not see a clear difference in the temperature dependence of both samples.

The line width indicates a kind of measure of spatial inhomogeneity of magnitude and type of stress in depth (Matsumoto *et al* 1987; Nakashima *et al* 1988). We observed a large deviation of the shift frequency of about $\pm 1 \text{ cm}^{-1}$ from point to point on the surface as mentioned above but no lateral direction dependence of photoluminescence. The variation of LO phonons on the surface reflects a variation of the strains and a number of hillocks of a few μm diameter on surface (Matsumoto *et al* 1987; Nakashima *et al* 1988). Thus we have to consider the effect of imperfections due to native defects and of elastic and thermal strains in the FWHM. So we consider a new definition of FWHM as a characterization of crystallinity as follows,

$$\hbar\Gamma = \hbar\Gamma_0 + A \exp(-\hbar\omega_0/kT). \quad (7)$$

Here A is the constant, ω_0 the LO phonon frequency and k the Boltzmann constant. The first term corresponds to FWHM due to imperfections including both strains

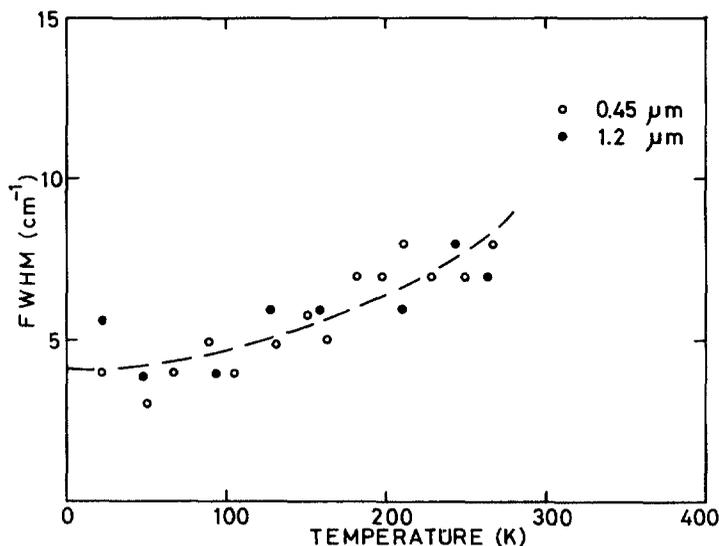


Figure 4. Full width at half maximum (FWHM) of MBE-ZnSe films of 0.45 and 1.2 μm thickness as a function of temperature. The dashed line represents our model.

without temperature dependence and the second is the phonon term with temperature dependence, which is proportional to the reverse of phonon correlation time, namely to the population of phonons. In this term, the energy of acoustic phonons is negligibly small as compared to thermal energy kT . We obtain the values of $\hbar\Gamma_0 = 4.5 \text{ cm}^{-1}$ and $A = 9.5 \text{ cm}^{-1}$ from our data assuming that the main phonons in phonon-phonon interactions are LO phonons only and other optical phonons are neglected. The dashed line in figure 4 is obtained by this procedure. The value of $\hbar\Gamma_0$ on a kind of scale of native lattice defects is small compared to that of the bulk ZnSe or VPE (Matsumoto *et al* 1987).

In conclusion, it is confirmed by Raman scattering that strains due to lattice mismatch for MBE-ZnSe thin films are dominant at high temperatures, while thermal strains due to large differences between growth and measurement temperatures are dominant at low temperatures even if the films are thin. The strains estimated from our Raman scattering are consistent with those obtained from X-ray analysis which are slightly smaller in magnitude. We estimated a term of native lattice defects by measuring the FWHM of Raman spectra. We believe that this constant will be effective for a characterization of crystallinity together with the photoluminescence method.

Acknowledgements

We acknowledge the Private College Promotion Foundation, the Suhara Memorial Foundation the Hokkaido Institute of Technology Special Foundation, and the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan (No. 02805004), for their financial support.

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