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Raman scattering in $ZnSe_xTe_{1-x}$ thin films: a probe for alloy disorder

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Abstract

Raman spectra of $ZnSe_xTe_{1-x}$ ternary thin film alloys have been reported in the range $0 \leqslant x \leqslant 1$. Raman studies show that the lattice phonons obey one-mode behaviour over the entire alloy range. Phonon energies vary with composition and show asymmetric broadening. The spatial correlation model with cluster distribution described by a gaussian correlation function has been applied to explain asymmetric broadening and used to estimate the cluster sizes of the thin film alloys.

Keywords: Raman scattering; Thin films; Alloy disorders

1. Introduction

In recent years, there has been intense interest in wide-band-gap ternary II–VI semiconductor alloys (AB_xC_{1-x}) for their potential application in optoelectronic devices in the visible region (see for example [1]), wide tunability of their gap [2,3] apart from their fundamental properties as disordered systems [3–5]. The added advantage of thin film alloys is that the particle size of the compounds can be varied by controlling the sample preparation method. One can thus tailor the particle size for a particular application while maintaining a required band gap.

The further development of these technologically important ternary systems depends on our ability to characterize the crystallites fully. Since Raman scattering yields valuable information about the nature of the solids on a scale of the order of nanometres (a few lattice constants), it can be used to characterize the structure and disorder of the system. Raman scattering has been used to determine the composition of thin films by comparing the Raman peak position of thin film samples with those of bulk samples [6,7]. Apart from the studies on phonon frequencies, the relationship between the alloy disorder and Raman line shape has been revealed in some articles [3–5]. Asymmetric broadening of Raman lines induced by substitutional disorder can be quantitatively explained by the "spatial correlation" model [4] similar to that used by Richter et al. [8] for the investigation of Raman scattering in microcrystalline silicon. In this article, we discuss the asymmetric line shapes of $ZnSe_xTe_{1-x}$ ternary thin film alloys in the framework of the "spatial correlation" model.

2. Experimental details

$ZnSe_xTe_{1-x}$ films ($0 \leqslant x \leqslant 1$) were prepared by co-evaporating ZnSe and ZnTe powders from a vertical two-zone evaporator, the details of which has been described elsewhere [9]. Two distinct temperature zones at 1100 and 900 K were located for simultaneous evaporation of ZnSe and ZnTe powders. The films were deposited onto glass substrates kept at 520 K at a pressure of about 10^{-4} Pa.

The 514.5 nm line of an Ar^+ laser (Spectra Physics) was focused on the sample at grazing incidence for Raman measurements. The scattered light was analysed with a double monochromator (Spex model 1403) and detected with a charge-coupled device detection system. A long integration time was used to achieve a good signal-to-noise ratio.

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3. Results and discussion

The behaviour of phonons of ternary alloy semiconductors generally falls into one of two classes [10]. The class of ternary semiconductors displaying a "two-mode" behaviour, e.g. $Al_xGa_{1-x}As$ [6], exhibits GaAs-like longitudinal optical (LO) and transverse optical (TO) modes and simultaneously AlAs-like LO and TO modes. The strength and position of each mode show some dependence on the alloy composition. Such "two-mode" behaviour has also been observed for ZnS_xSe_{1-x} alloy thin films [5]. $ZnSe_xTe_{1-x}$, on the contrary, exhibits "one-mode" behaviour as shown in Fig. 1. In this case, only one set of LO and TO modes is observed over the entire range of alloy compositions. As the composition is varied, their frequencies shift monotonically from the optical mode energy of one end component (ZnTe) to that of the other end component (ZnSe), as shown in Fig. 2. The single-mode behaviour of $ZnSe_xTe_{1-x}$ has been supported by the calculation of Lucovsky et al. [11] who described the local mode as the "in-band" mode. The extension of the linear diatomic chain model predicted that the crystal will exhibit one-mode behaviour. Our data in Fig. 2 confirm this prediction. The zone-centre phonon frequency data of our thin films are also in agreement with published Raman studies of bulk samples [12] and of laser-deposited thin films [13]. Pure binary films of ZnSe exhibit very strong LO scattering compared with ZnTe films. The TO lines are in general weak but still well defined in end-component films and they are less prominent in the alloys. Finally, the Raman lines in the alloys are broader and asymmetric compared with those in pure binary materials.

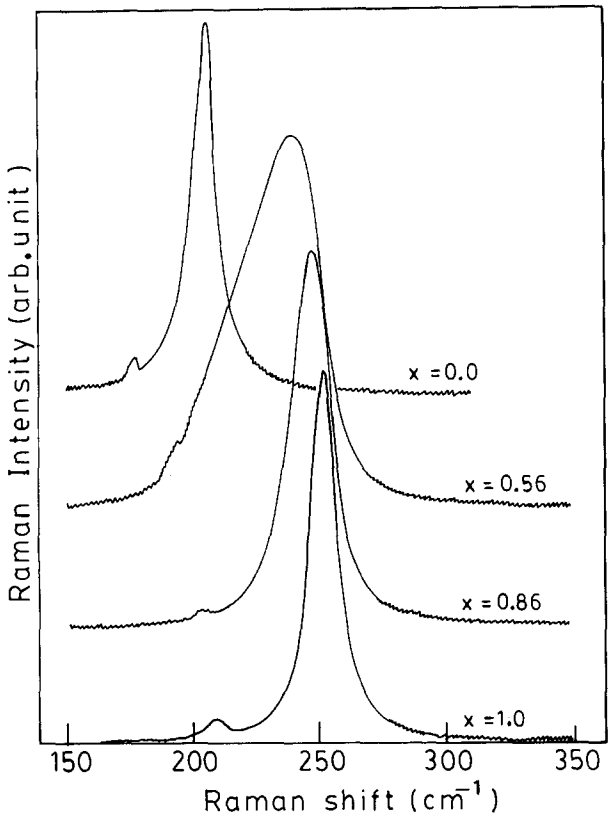

Fig. 1. Raman spectra of $ZnSe_xTe_{1-x}$ thin films with various concentrations x at room temperature.

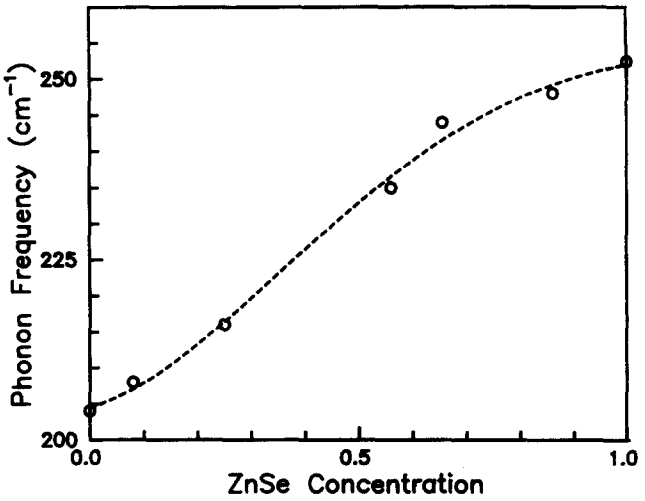

Fig. 2. Variation in LO phonon frequency with alloy composition.

The change in frequency of ZnSe LO phonons from the bulk (252.3 cm^{-1}) to ternary compound (248 cm^{-1} at $x=0.86$) can be explained [14] by considering the lattice strain arising because of modification of the band structure within the multiple-quantum-well region [15]. The "spatial correlation model" [4,8] on the contrary, stresses the spectral feature and asymmetric line shape of Raman bands of ternary systems.

Spectral features of Raman spectra of these ternary compounds are worth discussion. In pure ZnSe, the Raman line shape displays a lorentzian profile and has been assigned to LO phonons of ZnSe and agrees with the published results [12]. The profile becomes more and more asymmetric as the concentration of Te increases in the alloy. Such an asymmetric behaviour in Raman spectra has been reported earlier for $Ga_{1-x}Al_xAs$ [4] and ZnS_xSe_{1-x} [5] alloys. The origin of the compositional dependence of the Raman line broadening and asymmetric line shape, as described by the "spatial correlation" model [4,8], is the breakdown of the q-selection rule due to finite size of the crystal. In an ideal crystal, the spatial correlation function of the phonon is infinite. This leads to the plane-wave phonon eigenstates and the $q=0$ selection rule of Raman scattering. On the contrary, in $ZnSe_xTe_{1-x}$ alloys, the ZnSe-like phonons are "caged" in the ZnSe region and the region over which the ZnSe phonons may extend becomes finite. Moreover, the average size of the ZnSe clusters are not uniform. The ZnSe phonons will therefore be localized in the microscopic clusters of various sizes of ZnSe. The correlation function of the phonon

amplitude can thus be described by a gaussian function $\exp(-2r^2/L^2)$, where L is the correlation length which describes the average size of the clusters. The Raman intensity $I(\omega)$ at a frequency ω can thus be written as [4]

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

where q is expressed in units of $2\pi/a$, a is the lattice constant, Γ_0 is the full width at half-maximum (FWHM) of the Raman line shape in pure binary material. For dispersion $\omega(q)$ of the LO phonon, we take the analytical model relationship based on an one-dimensional linear-chain model:

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

with $A=3.2\times10^4\ \mathrm{cm}^{-2}$ and $B=4.5\times10^8\ \mathrm{cm}^{-4}$ for ZnSe. These parameters have been obtained by fitting the experimental results of neutron scattering [16].

The breaking of q-selection rule will result in $q\neq0$ phonon or phonons with lower energies participating in the Raman spectrum. The additional transitions will thus lead to a broadening and low energy tail in Raman bands. In order to analyse the spectral features, each spectrum can be decomposed in terms of two half-widths: the lower half-width Γ_{low} in the low energy region and the higher half-width Γ_{high} in the high energy region. We have evaluated Γ_{low} and Γ_{high} as functions of correlation length L. In other words, we have calculated the line shape of each Raman signal as a function of correlation length L and compared the experimental linewidth of LO phonons with the calculated value. The relationship between the FWHM and asymmetry as a function of correlation length is shown in Fig. 3. The theoretical curve for the LO phonons is in good agreement with the experimental points.

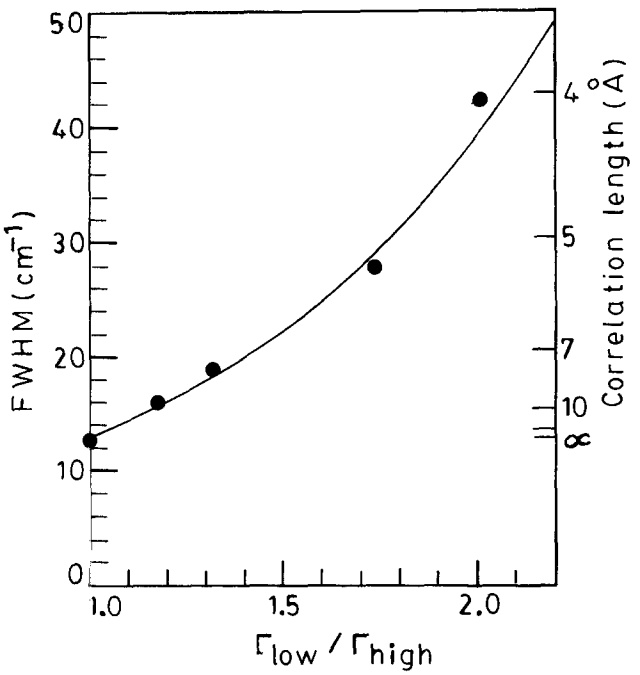

Fig. 3. The relationship between asymmetry $\Gamma_{low}/\Gamma_{high}$ and broadening (FWHM) of the LO phonons as a function of correlation length L. The experimental points are shown to fit the theoretical curve.

In conclusion, on the basis of these results, we have accounted for the compositional dependence of the asymmetric broadening of $ZnSe_xTe_{1-x}$ thin films. The correlation length L is shown to decrease with increasing molar fraction x and is quite reasonable by definition. As the Te concentration increases, the cluster size of the ZnSe in the alloy becomes small. The compositional dependence of half-widths has been explained by the "spatial correlation" model. Moreover, the cluster sizes of the thin film alloys have been estimated as a function of composition.

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