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1995 J. Phys.: Condens. Matter 7 1287

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Exciton line broadening in $\text{ZnSe}_x\text{Te}_{1-x}/\text{GaAs}$

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Received 20 July 1994, in final form 31 October 1994

Abstract. Photoreflexion (PR) measurements on $\text{ZnSe}_x\text{Te}_{1-x}$ epilayers were performed in the concentration range $x \leq 0.5$ and $0.9 < x$. The dependence of the E_0 band gap on the composition leads to a bowing parameter of $b = 1.37 \pm 0.03$ eV. Additional photoluminescence (PL) measurements were used to investigate the localization energy of excitons caused by compositional fluctuations. It is shown that the large broadening of excitons in the PR spectra can be explained by localization effects.

1. Introduction

$\text{ZnSe}_x\text{Te}_{1-x}$ is a promising candidate to solve the contact problems of p-ZnSe, which is used in blue light emitting devices. Unfortunately there is a considerable lack of knowledge about the optical parameters of this material. Most of the recent investigations were performed on bulk material by means of absorption and conventional reflectivity [1,2]. The strong broadening of the excitonic transitions has until now prevented a precise determination of the E_0 gap energy. The present measurements reveal a deep bowing of E_0 when plotted versus the composition x . Moreover the magnitude of the bowing derived from bulk material and epilayers differs considerably [3], which suggests that the underlying structural property depends on the growth conditions and temperature. There is enough reason to believe that the observed behaviour of the gap energy cannot be explained within the framework of the usual virtual crystal approximation. This model suggests that the anion sublattice consists of a virtual atom representing a mixture of Se and Te according to the composition instead of a stochastic distribution of Se and Te atoms.

A new approach has therefore been developed, which is based on a spontaneous ordering. Similar models have already successfully been applied to ternary III–V compounds [4]. The results of these recent calculations challenged the experiments and made it necessary to determine the band gap bowing with even higher precision. We report here the first photoreflexance (PR) measurements on $\text{ZnSe}_x\text{Te}_{1-x}/\text{GaAs}$ epilayers in the region of $0 \leq x < 0.5$ and $0.9 < x \leq 1$. This modulation spectroscopic method is more appropriate than for example PL to determine the exciton transition energies since localization shifts the luminescence towards lower energies. Moreover it is much more sensitive than absorption or conventional reflectivity measurements, which would provide the same information.

2. Experimental details

All samples described are about 1 μm thick $\text{ZnSe}_x\text{Te}_{1-x}$ epilayers grown on (001) GaAs substrates by atmospheric pressure metallorganic vapour phase epitaxy (MOVPE) with the

metallorganic sources DMZn:TEN, DiPTe and DTBSe. We evaluated the optimum growth temperature to be 300 °C.

The composition of the samples was determined by high-resolution x-ray diffraction measurements interpolating the relaxed lattice constants between the pure materials (Vegard's law [5]).

For the PR measurements we used an experimental set-up similar to that described by Shen [6]. The light source is a 100 W halogen lamp, which has a line free and relatively smooth spectrum in the visible spectral range. The light passes through a 0.25 m monochromator with a maximal resolution of 1 Å and is then focused onto the sample, which is kept at constant temperature in a continuous flow cryostat. All measurements are performed at 4 K. A 200 W high-pressure Hg lamp serves as modulation source. Essentially only the light of the 366 nm line is used and the lines in the visible suppressed by an appropriate filter. The intensity of the pump beam on the sample surface is of the order of 1 μW. The light reflected from the sample is detected with a bialkali photomultiplier. In conventional PR the pump beam is chopped mechanically whereas in the sweeping PR method the chopper is substituted by a mirror, which undergoes small-amplitude rotatory oscillations at a frequency of 230 Hz. The system is adjusted as follows: during the first half period the pump beam coincides with the probe beam on the sample and modulates the signal, whereas during the second half period the pump beam hits a point on the sample about 100 μm away and leaves the signal unaffected. The angle by which the modulating light beam is moved is so small that the detector sees a DC PL background, which is easily suppressed by the lock in amplifier.

The output of the lock in amplifier $I_0 \Delta R$ is normalized by dividing it by the DC signal $I_0 R$ (reduced by the amount of the DC PL background), so that the incident light intensity I_0 is eliminated.

The set-up for the luminescence measurements essentially consists of a 5 W Ar⁺ laser of which the all line UV emission was used for interband excitation, a 1 m Jarrel Ash double monochromator and a cooled GaAs photomultiplier. The samples were placed in an He bath cryostat to achieve the measurement temperature of 2 K.

3. Results and discussion

In figure 1 the PR spectra of the ZnSe_xTe_{1-x} epilayers are shown for different composition values. The position and the linewidth of the signal was determined by a fit with the usual Aspnes lineshape for excitons [7]:

$$(\Delta R/R)(E) = \text{Re}[C e^{i\varphi} (E - E_0 + i\Gamma)^{-2}]. \quad (1)$$

The parameters E_0 and Γ represent the transition energy and the linewidth. The fit parameters C and φ , which contain interband matrix elements and interference effects, are not of interest in the following considerations.

The intensity of the signal decreases with increasing linewidth. The spectra in figure 1 have been normalized for clarity. An increasing Se content in ZnTe leads to a red shift of the exciton transition energy. The minimum of 2.207 eV is achieved at an Se content of about 35%. Higher concentrations lead to a blue shift of the exciton transition with a simultaneous steep increase of the linewidth. This broadening makes it impossible to obtain PR spectra in the composition range of $0.6 < x < 0.9$.

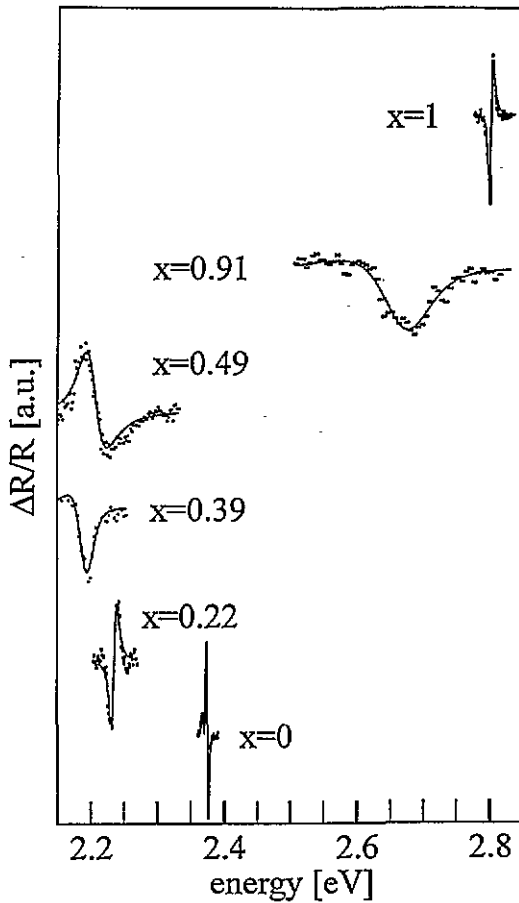


Figure 1. PR spectra of $1 \mu\text{m}$ thick $\text{ZnSe}_x\text{Te}_{1-x}$ epilayers with different compositions x . The solid lines are a fit with the Aspnes lineshape for excitons.

The dependence of the gap energy of the composition (figure 2) can be described by a quadratic polynomial [8]:

$$E(x) = E(\text{ZnSe})x + E(\text{ZnTe})(1 - x) - bx(1 - x). \quad (2)$$

We find the bowing parameter by a least-squares fit to be $b = 1.37 \pm 0.03$ eV. This value is significantly higher than that measured in bulk material ($b = 1.20$ eV) [1, 2]. As already mentioned this may be explained by the tendency of the lattice to form ordered structures during epitaxial growth. Recently an indication of an ordered structure was obtained in our laboratory by the observation of additional peaks in the high-resolution x-ray diffraction pattern [9]. Calculations reported in the same publication have shown that the suggested ordering leads to a red shift of the gap energy with respect to a homogeneously disordered ternary structure.

In figure 2(b) the dependence of the exciton linewidth on the composition is shown. In the samples with $x < 0.15$ there is only a small increase of the linewidth whereas the halfwidth of x-ray rocking curves rises by about a factor of three, which suggests a higher number of structural defects compared to the case of pure ZnSe or ZnTe. Samples with

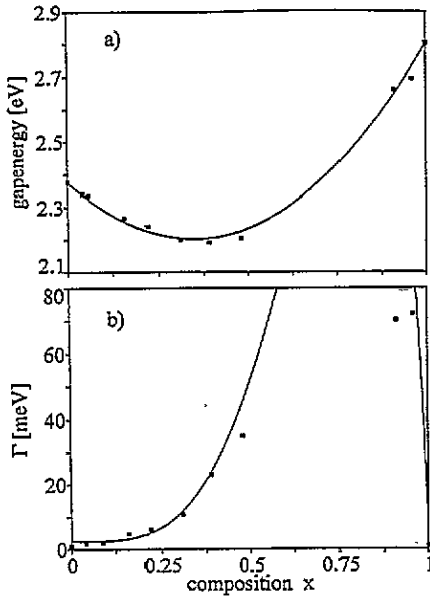


Figure 2. (a) The dependence of the exciton transition energy on the composition x . The solid line indicates a least-squares fit to (2) with the parameters $E(\text{ZnSe}) = 2.803$ eV, $E(\text{ZnTe}) = 2.376$ eV, $b = 1.37$ eV. (b) The dependence of the exciton linewidth on x .

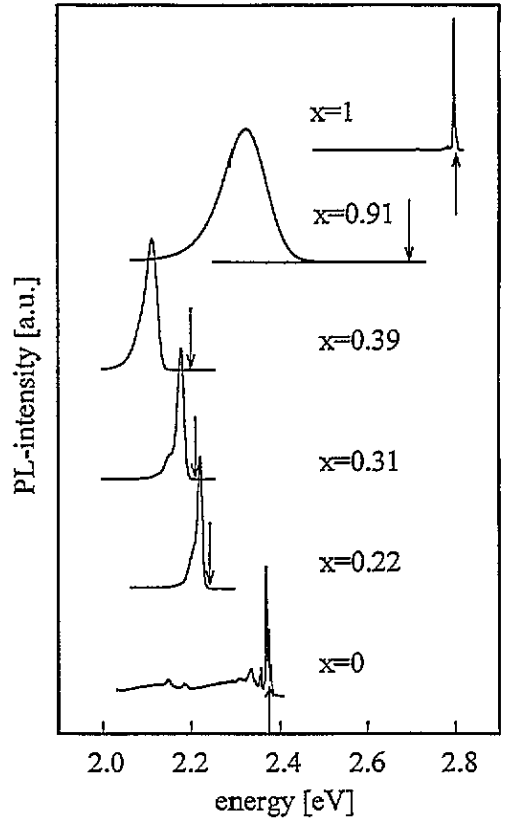


Figure 3. PL spectra of samples with different compositions x . The arrows indicate the free exciton transition evaluated from PR.

an Se content between 20 and 90% show no change in crystal quality. In the composition range $0.2 < x \leq 0.5$ a much weaker increase of the linewidth is found compared to Se rich samples. A small amount of Te added to ZnSe leads to a sharp increase in linewidth from 1 meV in pure ZnSe to about 70 meV in $\text{ZnSe}_{0.91}\text{Te}_{0.09}$. This behaviour is generally predicted by various theories [10, 11] but none of them is able to describe these especially high values. The reason for this disagreement lies in the fact that the theory is limited to cases where the exciton linewidth is smaller than the exciton Rydberg energy. The principal behaviour of the broadening with the composition in our case is the same as in bulk material [1], only deviating by a constant factor.

Parallel to PR, PL also was measured with the same samples. Some of the results are shown in figure 3. As pointed out in a previous publication [3] free exciton luminescence is observed up to a Se concentration of 0.15. The assignment of the luminescence has been confirmed by the coincidence of the high-energy luminescence peaks with the free exciton signals in the PR spectra (note the arrows in figure 3). At higher concentrations only one luminescence band appears together with its phonon replica. The phonon free transition energy is lower than the respective energy of the free exciton transition. The observed

band has therefore been identified as recombination of excitons localized at compositional fluctuations, an assignment supported by the temperature dependence [3]. The band position is determined by the mobility edge of localized excitons. The energy difference between the luminescence peak and the free exciton transition (from PR) can therefore be considered as a localization energy E_{loc} , which measures the quantity of the compositional fluctuations. The principal luminescence in samples with $x > 0.9$ originates from recombination of excitons bound at Te clusters [12], which leads to a very broad band with peak energy about 200 meV below the band gap.

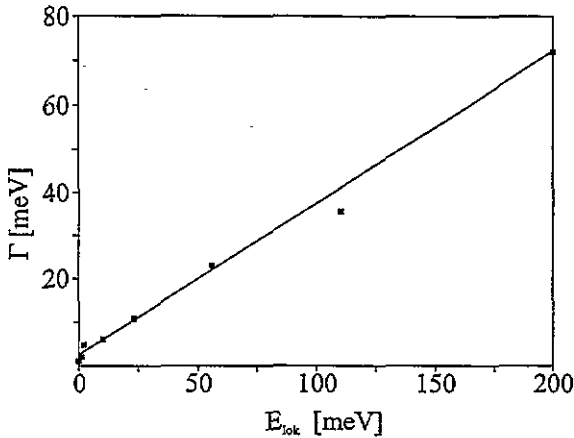


Figure 4. The dependence of the exciton linewidth on the localization energy E_{loc} . The proportionality factor is 0.35.

Figure 4 relates the exciton linewidth Γ to the localization energy E_{loc} . Obviously significant exciton broadening occurs if the compositional fluctuations are strong enough to localize excitons. In this case E_{loc} is directly proportional to Γ by the factor 0.35 ± 0.01 . Furthermore the structural quality of the lattice leads to a constant contribution to the linewidth of 2.5 meV.

In the region $x < 0.15$ where no localized states are formed the excitons behave like free particles that do not feel the variation of gap energy due to compositional fluctuations. There exists therefore only one exciton ground state with the same width as in the binary system.

As soon as localization takes place the fluctuation is also strong enough to affect excitonic states. In this case absorption measurements suggest an exponential decrease of the density of states of the form [13]

$$\delta(E) = \delta_0 \exp(-E/E_0).$$

Γ is then the energy difference between the absorption maximum and the value where $\delta(E) = \delta_0/2$:

$$\Gamma = (\ln 2)E_0. \quad (3)$$

Abdukadyrov *et al* [13] modelled the luminescence assuming that the localization of excitons takes place via tunnelling of holes in states with lower energies and the subsequent formation

of excitons by Coulomb interaction. With the above mentioned density of states an average distance between one state and others with lower energies was calculated and from that an average tunnelling time. The main contribution to the luminescence is thought to originate from that state where the tunnelling time is equal to the exciton lifetime because lower states are practically not reached during the lifetime and higher states are not occupied long enough to recombine. As a result they obtained for the localization energy

$$E_{\text{loc}} = E_0 \ln[(\pi/6)\delta_0 E_0 a^3 \ln^3(\omega_0 \tau_0)]. \quad (4)$$

With the appropriate values for the lifetime τ_0 , the tunnelling frequency ω_0 and the localization radius for holes a they obtained $E_{\text{loc}} = (4.3 \pm 0.8)E_0$. This leads with (3) to the proportionality factor 0.16 ± 0.04 , which is not too far from the value we obtained. The deviation might be caused by the poor knowledge of the input parameter of the model and by the difficulty of determining exactly the gap energy in $\text{ZnSe}_x\text{Te}_{1-x}$ with absorption.

4. Conclusions

The excitonic transitions in ternary $\text{ZnSe}_x\text{Te}_{1-x}$ epilayers were determined over a large composition range by PR measurements. The dependence of the gap energy on composition x is described by a bowing parameter of $b = 1.37$ eV. The localization energy was derived from the energy difference between the PL band, which is due to localized states, and the signal of PR. A linear dependence of free exciton linewidth on localization energy is observed, which supports the interpretation of excitation broadening and the localization as a consequence of compositional fluctuations.

Acknowledgments

The author wishes to thank the Deutsche Physikalische Gesellschaft for supporting this work via the Graduiertenkolleg 'Komplexität in Festkörpern: Phononen, Elektronen und Strukturen'. Special thanks to A Naumov for some fruitful discussions.

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