Exciton line broadening in $Cd_{x}Zn_{1-x}Te/ZnTe$ multiple quantum wells

R. P. Stanley and J. Hegarty
Department of Pure and Applied Physics, Trinity College Dublin, D2, Ireland
R. D. Feldman and R. F. Austin
AT&T Bell Laboratories, Holmdel, New Jersey 07733

(Received 2 May 1988; accepted for publication 3 August 1988)

We have investigated $Cd_{x}Zn_{1-x}Te/ZnTe$ multiple quantum wells using absorption techniques. We have observed sharp excitonic features at low temperatures which strongly broaden at room temperature. The strength of the exciton-phonon coupling is determined from linewidth analysis. The large measured coupling explains the lack of well defined exciton resonances at room temperature, an important consequence for their use as optoelectronic devices.

Epitaxial growth of II-VI semiconducting materials has led to high quality thin films and multiple quantum well structures (MQW's). The ability to tailor the band gap to cover the visible to the UV region of the spectrum opens up the possibility of semiconductor lasers and a variety of devices based on band-edge excitons in this new wavelength region. In III-V materials it is known that quantum well and superlattice structures enhance lasing properties and increase excitonic effects. Many of the bulk properties of II-VI semiconductors have already been well studied and by comparison to III-V materials they are more polar, have larger exciton binding energies, and have greater electron-phonon coupling. The greater exciton binding energy is favorable for room-temperature operation of devices based on excitons but the effect of the electron-phonon coupling which homogeneously broadens the exciton resonances has not yet been determined. Photoluminescence excitation (PLE) has previously been used to study excitonic features in these materials at low temperatures. This technique, however, becomes less useful at higher temperatures due to the decrease in luminescence efficiency and the increase in line broadening. In this letter we study excitons directly by absorption up to room temperature and we measure the strength and nature of the thermal (homogeneous) broadening.

Although epitaxial growth has been achieved with II-VI materials there are few lattice-matched compounds available and most II-VI heterojunctions are intrinsically strained. Strain effects complicate the band structure of the crystal, particularly the valence band, by shifting the band-edge energy as well as lifting the degeneracy present at the zone center. Lattice mismatches as great as 7% exist in CdTe/ZnTe and in ZnTe/ZnSe MQW's, both of which have been investigated recently. We have studied $Cd_{x}Zn_{1-x}Te/ZnTe$ alloy quantum wells with $x = 0.13$ which are less strained than the binary ZnTe/CdTe MQW's. The lattice mismatch is of the order of 1%.

The quantum well structures were grown by molecular beam epitaxy on GaAs substrates, with a 2 µm buffer layer of ZnTe to reduce dislocations. The structures consisted of $Cd_{0.13}Zn_{0.87}Te$ alloy wells sandwiched between layers of ZnTe which acted as barriers. Sample 1 consisted of 50 Å wells and 50 Å barriers repeated for 15 periods, while sample 2 had 10 periods of 100 Å wells and barriers. The growth direction was (100) in all cases. The GaAs substrate was removed by etching to allow absorption measurements. This was achieved by mounting them well side down on glass cover slips with a transparent glue. The GaAs substrate was selectively etched with a mixture of NH$_4$OH and H$_2$O$_2$ following recognized procedures. It was found that the samples would shatter during the etching process if they were not affixed with a strong adhesive. We attribute the shattering to stress relief in the ZnTe buffer layer after the substrate is removed. The glue leads to additional strain when the sample is cooled, but the effect of this strain on the wells is negligible in comparison to the effect of the 1% lattice mismatch between the ZnTe and the $Cd_{0.13}Zn_{0.87}Te$ layers. Absorption spectra were taken with a tungsten lamp and the sample temperature was varied from 10 to 300 K in a closed cycle He gas refrigerator.

Figures 1(a) and 1(b) show low-temperature absorption spectra for both samples. Clearly visible are two sharp lines, which we have attributed to light ($|m_f| = 1$) and heavy ($|m_f| = 2$) hole excitons in the quantum well. This interpretation is confirmed by polarization measurements in which transitions involving the $|m_f| = 2$ state are unfavorable for polarizations perpendicular to the plane of the wells. Both the light and heavy hole exciton lines move to higher energies as the well width decreases from 100 to 50 Å. However, the separation between the lines also decreases, which is opposite to that expected from quantum confinement in a type I MQW. Work on ZnTe/CdTe MQW's, both experimental and theoretical, suggests that the valence-band offset is too small to cause the observed light hole, heavy hole splitting. The large splitting implies that strain due to the inherent lattice mismatch plays an important role. This will be discussed elsewhere.

Secondary features can be seen on the high-energy side of the exciton lines in the 100 Å sample. The energies of these features suggest that they are longitudinal optical phonon (LO phonon) replicas of the exciton lines. Strong absorption features were also seen above 2.36 eV which were bulk ZnTe effects mainly due to the ZnTe buffer layer. These features included a broad exciton line centered at 2.375 eV and band-edge absorption at 2.385 eV.

At low temperatures the exciton lines in the quantum wells are inhomogeneously broadened with heavy hole linewidths of 7.8 meV and 7.6 meV for the 100 and 50 Å
samples, respectively. The inhomogeneous broadening is due to granularities in the alloy, which smear out the band-edge energies, and due to well width fluctuations which broaden the confined energy states. The contribution of statistical fluctuations in the alloy to the exciton linewidth has been studied using high quality Cd$_x$Zn$_{1-x}$Te alloys. From those results the alloy contribution to the broadening for $x = 0.13$ is expected to be $\sim 6$ meV. The broadening arising from well width fluctuations was calculated on the basis of a simple Kronig-Penny type model. Assuming fluctuations of the order of one monolayer, the broadening is calculated to be 1.6 meV for the 100 Å sample and 4.5 meV for the 50 Å sample. The calculated alloy width is close to the measured width in both samples. This, combined with the fact that the measured widths are very similar for both thicknesses, indicates that the contribution from well width fluctuations is very small.

As the sample temperature is increased the excitonic features broaden considerably as shown in Fig. 2. At 200 K the light and heavy hole peaks are resolvable, while at room temperature only an absorption edge is seen. This situation is significantly different from the strong exciton resonances observed in III-V MQW's GaAs/AlGaAs and GaInAs/AlInAs at room temperature. The measured line shape is a convolution of an inhomogeneous part of full width half-maximum (FWHM), $\Gamma_f$, and a temperature-de-
binding energy and is resolved from the light hole exciton by a combination of quantum confinement and strain splitting. The large measured value for $\Gamma_{ph}$ indicates that the exciton-phonon coupling is quite strong. In contrast, $\Gamma_{ph} = 10$ meV in GaAs/AlGaAs MQW's.\(^4\) Possible phonon replicas seen in one of the samples [Fig. 1(b)] are consistent with this coupling strength. Since the LO phonon energy is close to the thermal energy at room temperature and because of the strength of the exciton-phonon coupling, the exciton lines broaden rapidly as room temperature is approached. At room temperature, the exciton features are not distinct, and are seen only as broad shoulders.

The operation of certain devices based on excitons must take into account the strong broadening. The homogeneous linewidth implies an ionization time of the order of 60 fs for the excitons at room temperature. Accordingly devices based on exciton lifetimes could be exceedingly fast. Despite the broadening, the excitons show two-dimensional character, as seen by the shift of the exciton energies with a change in well thickness, which may enhance excitonic effects from the device viewpoint. The dimensionality of these structures is complicated by the strain effects on the valence band. The details of the competing effects and their influence on the excitonic properties are not clear at present and will be discussed elsewhere.

In conclusion, we have seen confined excitons in Cd$_{0.12}$Zn$_{0.17}$Te/ZnTe MQW's directly by absorption. Sharp exciton lines observed at low temperature indicate high material quality. These lines broaden with temperature and are not resolved from the band edge at room temperature. We explain this on the basis of a strong coupling between LO phonons and the excitons which are scattered by the LO phonons. The strength of this exciton-phonon coupling, determined from linewidth analysis, is large. The broadening of the exciton lines must be considered in any device design based on excitons.

\(^2\) For recent reviews, see IEEE Quantum Electron QE-20, August (1986).