Engineering the exciton linewidth in II-VI quantum well structures

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Abstract. The excitonic transition in II-VI quantum well materials has recently been used as the basis for optical modulators and also as the lasing transition at low temperatures. The central aspect in the use of the exciton resonance in optical devices is the understanding of the exciton linewidth. We present a detailed study of the interactions that affect the linewidth in II-VI semiconductor quantum well materials. The broadening of the resonance with increasing temperature can be controlled by altering the material parameters of the II-VI structures. In so doing the exciton binding energy can exceed the LO-phonon energy and thereby reduce the homogeneous contribution to the measured linewidth. Efforts to reduce well-width fluctuations in the growth of the II-VI quantum well structures, which are responsible for the inhomogeneous linewidth, must also be made to a limit where the room temperature linewidth is narrow and homogeneously broadened.

Subject terms: II-VI semiconductors; quantum wells; excitons; photoluminescence; linewidth.


1 Introduction

For several decades, excitons have been studied in bulk semiconductor materials. These studies were concerned primarily with the elucidation of exciton dynamics in semiconductors at low temperatures.1 The parallel development of electronic semiconductor devices operating at room temperature was little influenced by this study of exciton dynamics. This is due to the fact that the exciton, which is a weakly bound electron-hole pair, is ionized at room temperature and therefore does not contribute to the electronic properties at room temperature. The advent of molecular beam epitaxy and other thin-film growth techniques means that we can now produce a layer of one semiconducting material with a small bandgap between two layers with high bandgap. Because the layers we can produce are of the size of the exciton Bohr radius, we expect and find in experiments that we have produced real quantum well systems familiar from elementary quantum mechanics. Excitons are observed in these systems at room temperature, and optoelectronic devices based on exciton dynamics have been developed. For the present generation of devices, we have the potential to control exciton dynamics through changes in material composition. A detailed understanding of exciton dynamics in quantum-confined systems is therefore essential so we can provide an engineering-type approach for future device applications. In this paper we look in detail at one aspect of exciton dynamics, the exciton linewidth, and at the interactions that alter the linewidth and our ability to control the linewidth for excitonic applications.

2 Excitons and Quantum Confining Systems

An exciton is an electron-hole pair bound through their mutual Coulomb interaction. In analogy with the hydrogen atom the exciton binding energy in a bulk material is given by:

\[ E_b = \frac{2m_e e^4}{\hbar^2 (8\pi\varepsilon_0)^2}, \]

where \( m_e \) is the reduced mass of the exciton and \( \varepsilon \) is the dielectric constant. The exciton binding energy is dependent on the semiconductor material. If we perform an absorption experiment on a semiconductor material, we expect to find the threshold for absorption at the bandgap energy \( E_g \). In fact, we find for high-quality material such as GaAs, a hydrogenic series of levels below the bandgap corresponding to the exciton series.2 The 1S exciton state occurs at energy \( E_g - E_b \). These lines are sharp as opposed to the broad absorption bands observed above \( E_g \).

When we form quantum well systems of a size comparable to the exciton Bohr radius, confinement effects for the carriers come into play. The electron and hole states become discrete; the confinement increases the overlap of the electron and hole and therefore leads to an increase in the binding energy. In the limit of a square well with infinite barriers, the confined
or 2-D binding energy is four times greater than the bulk or 3-D case. In forming real quantum well materials, we wish to choose structures such that the binding energy is substantially enhanced over the bulk case so that we can use them in optoelectronic devices at room temperature.

By extension of the bulk case, the absorption spectrum of a quantum confined structure will consist of a fundamental bandgap energy $E_g$ above which band absorption occurs and below which we find the hydrogenic exciton series. As a result of the greater exciton binding energy in the confined system, the exciton peak will be shifted by a greater extent from the bandgap than in the bulk material. We show the low-temperature absorption of CdZnTe/ZnTe quantum well materials in Fig. 1 as an illustration. The lowest exciton feature is split into two due to the different masses associated with the light and heavy holes in the valence band.

At 10 K the excitonic features in Fig. 1 have a linewidth of about 5 meV, which broadens with temperature. To optimize these devices, we need to know the mechanisms behind the broadening of the exciton feature and from there to suggest ways to control the broadening.

### 3 A Simple Electro-Optic Device

If we apply an electric field to a semiconductor sample, we effectively reduce its bandgap and therefore the exciton resonance moves to lower energy. If light of energy $E_{pk}$ corresponding to the peak of the exciton resonance is shone onto a sample, the light is strongly absorbed. To make an effective modulator, we need to have as large an on/off ratio for the device as possible. In our case this corresponds to a large change in the absorption of light in the quantum well sample. We can achieve this by applying an electric field to the sample shifting the exciton peak to lower energy. This phenomenon is known as the quantum-confined-Stark effect. Light of energy $E_{pk}$ is no longer strongly absorbed by the sample. Ideally, we could change from a large absorption feature to zero absorption, giving a large modulation depth for the device.

For real quantum well samples, we find that the exciton resonance broadens as well as shifts when we apply an electric field. The application of an electric field has the effect of polarizing the exciton. The barrier walls prevent the dissociation of the exciton and thereby allow us to observe excitonic features to much higher electric field strengths in quantum well compared with bulk systems. The exciton feature is broadened due to the well-width fluctuations that occur during the growth process and that alter the "local" potential well of the exciton. Our goal therefore is to produce an exciton feature with a very small linewidth so that the application of an electric field shifts the resonance sufficiently to make a good modulator but does not appreciably broaden the exciton resonance. Therefore need to know the factors that govern the linewidth of the exciton resonance in quantum well systems.

### 4 The Exciton Linewidth

As with all experimentally measured optical linewidths, the measured exciton linewidth $\Gamma_m$ is composed of an inhomogeneous $\Gamma_i$ and a homogeneous part $\Gamma_h$, which when convoluted together give the measured linewidth $\Gamma_m$. We consider the two parts separately.

#### 4.1 Inhomogeneous Broadening

The inhomogeneous broadening of the exciton linewidth occurs due to variations in the sample parameters. For quantum well materials this is normally due to well-width fluctuations $\Delta L_w$ between the well and barrier materials. The exciton resonance is sensitive to the "local" well width and therefore the exciton acquires a width $\Delta E$ due to these fluctuations. Well-width fluctuations arise during the growth process and tremendous efforts have been made to reduce the inhomogeneous broadening in quantum well systems. For presently available high-quality III-V GaAs-based quantum well systems, linewidths of the order of 0.5 meV at low temperatures are now commonly available. We are now approaching the linewidth of exciton features observed in bulk semiconductors, which is probably a realistic limit for future quantum well materials. For materials with an alloy well material, there is an additional broadening of the exciton due to potential fluctuations occurring due to the random ordering of atoms in the lattice.

#### 4.2 Homogeneous Broadening

The two contributions to the homogeneous linewidth are (1) broadening due to the finite lifetime of the excitons and (2) broadening due to scattering events in the semiconductor material. In the limit of low exciton densities the main scat-

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Fig. 1 Absorption spectrum for CdZnTe/ZnTe multiple quantum well samples with well widths of 50 and 100 Å. The main absorption peaks at low energy are due to heavy-hole and light-hole exciton transitions, and $E_b$ corresponds to the energy gap of the ZnTe buffer layer in the sample.
tering events are due to the exciton-phonon interaction, known as the Fröhlich interaction. Because the population of phonons is temperature dependent, we expect that the homogeneous contribution to the broadening is also temperature dependent. Acoustic and optic phonons both participate in these interactions. The interaction with the high-energy LO phonons is by far the strongest scattering event for excitons. This is due to the distortion of the unit cell, which produces an electric field with which the exciton can interact. The homogeneous exciton-linewidth is given by:

$$\Gamma_h = \frac{\Gamma_{ph}}{\exp(hv/kT) - 1},$$

where $hv$ is the LO-phonon energy and $\Gamma_{ph}$ is the phonon interaction parameter and describes the strength of the exciton-phonon interaction. Our aim is to reduce $\Gamma_{ph}$ by engineering the quantum well structure; $\Gamma_{ph}$ is determined by the Fröhlich interaction and the number of final states into which the exciton can be scattered. The Fröhlich interaction is basically determined by the material, be it GaAs or ZnSe, but not by quantum confinement in these materials. On the other hand, the number of final states for scattering can be altered by adjusting the quantum well material. This is most easily achieved by varying the well width in the structure. In Fig. 2 we show the exciton dispersion curve for a narrow ($n$) and a wide ($w$) well. Also indicated are the corresponding exciton binding energies $X_{BE,n}$ and $X_{BE,w}$ and the LO-phonon energy $E_{LO}$. When the exciton binding energy $X_{BE}$ is smaller than $E_{LO}$, the zone center excitons can be scattered into the continuum states as well as exciton bound states away from the zone center. As the exciton binding increases, the range of wave vector states available decreases (range of $K_r$ less than range of $K_c$ in Fig. 2). If $X_{BE}$ exceeds $E_{LO}$, scattering to continuum states is no longer possible. This process should lead to a strong reduction in broadening with temperature and therefore to a smaller observed linewidth at room temperature.

For III-V materials such as GaAs, $X_{BE}$ is about 8 meV and $E_{LO}$ is about 36 meV. On the other hand, II-VI materials have a much greater $X_{BE}$ for ZnSe. $X_{BE}$ is 20 meV, whereas for $E_{LO}$ it is 30 meV. Quantum confining excitons in II-VI structures should allow us to fulfill the condition $X_{BE} > E_{LO}$ and thereby reduce $\Gamma_{ph}$. Evidence to support this framework has been found for the CdZnSe/ZnSe and CdZnTe/ZnTe systems.8,9

To provide a method to control the exciton linewidth, we need to do the following:

1. Measure the linewidth as a function of temperature for a series of samples with varying well widths.
2. Determine the inhomogeneous contribution $\Gamma_i$ to the linewidth.
3. Deconvolute the inhomogeneous contribution.
4. Fit the resulting homogeneous contribution $\Gamma_h$ to Eq. (1) in order to determine $\Gamma_{ph}$.
5. Define the material parameters for which $\Gamma_{ph}$ and $\Gamma_i$ are simultaneously minimized.

### 5 The Measured Exciton Linewidth

The inhomogeneous contribution to the measured exciton linewidth is due to the material fluctuations that have a Gaussian-shaped distribution. The exciton scattering and recombination events are responsible for the homogeneous contribution to the measured linewidth and have a Lorentzian-shaped distribution. The measured linewidth will contain both homogeneous and inhomogeneous contributions and the measured linewidth will be a convolution of a Lorentzian and a Gaussian distribution, known as a Voigt distribution. In Fig. 3 we show the results of our studies of the exciton linewidth in a 70-Å CdZnTe/ZnTe single quantum well sample. We note the following results:

1. The low-temperature lineshape is a Gaussian and the measured low-temperature linewidth is taken to be the inhomogeneous linewidth $\Gamma_i$. At low temperatures (10...
K) the phonon population is negligible and so only the lifetime contributes to the homogeneous linewidth. For CdZnTe/ZnTe quantum wells, the lifetime is about 100 ps at 10K corresponding to a linewidth of 45 μeV. The measured 10-K linewidth is about 3 to 4 meV for these materials and so we are dominated by the inhomogeneous linewidth at low temperature.

2. As the temperature is raised the exciton linewidth increases and concomitantly the lineshape gradually changes from a Gaussian to a Voigt. The inhomogeneous linewidth \( \Gamma_i \) is independent of temperature, whereas the homogeneous contribution depends on the phonon population and is strongly temperature dependent.

3. To determine the homogeneous linewidth \( \Gamma_h \), we must deconvolve the inhomogeneous contribution \( \Gamma_i \). To obtain the true \( \Gamma_h \), we must numerically deconvolve \( \Gamma_i \) from the measured \( \Gamma_m \).

In the literature we find that the inhomogeneous lineshape is approximated as a Lorentzian, then because the homogeneous contribution is also a Lorentzian, the deconvolution is achieved simply by subtracting the two linewidths. This has been used extensively in the literature on GaAs materials. In Fig. 3 we show the results of our numerical deconvolution and that produced using the approximation of two Lorentzian lines for the 70-Å CdZnTe sample. We see immediately that \( \Gamma_{ph} \) is much smaller using the approximation method. To compare different materials where the inhomogeneous and homogeneous contributions can be widely different, the numerical procedure described earlier must be used. A detailed analysis of the deconvolution procedure will be published elsewhere. For our present purposes, we wish to point out the need for proper deconvolution so that meaningful comparisons between materials can be made.

The inset in Fig. 3 shows the variation of \( \Gamma_{ph} \) for three CdZnTe/ZnTe wells. We see that \( \Gamma_{ph} \) is smallest for the 40-Å well in accordance with the model given earlier. For this well the exciton binding energy is approximately equal to the LO-phonon energy with the result that the scattering is strongly reduced. This characteristic is unique to II-VI semiconductors and has also been observed in the CdZnSe/ZnSe systems. For III-V materials the opposite trend is observed, i.e., the broadening is strongest in the narrower wells. This is due to the much greater LO-phonon energy in these materials with the result that the inequality \( X_{BE} > E_{LO} \) cannot be achieved.

6 Materials Engineering of the Exciton Linewidth

To achieve our goal of minimum exciton linewidth at low temperature, we need to reduce simultaneously the inhomogeneous and homogeneous contributions to the observed linewidth. For II-VI materials, with which we are chiefly concerned here, we need to use narrow quantum well samples to achieve as small a broadening factor \( \Gamma_{ph} \) as possible. However, as the wells are narrowed the inhomogeneous contribution increases. This is due to the stronger interaction with the well-width fluctuations, which are an inevitable part of the growth procedure. Therefore, there is a trade-off between what we can achieve with decreasing \( \Gamma_{ph} \) and therefore \( \Gamma_h \) and increasing \( \Gamma_i \) due to the well-width fluctuations. Our approach must then be as follows:

1. We must define the material parameters for which \( X_{BE} > E_{LO} \) for each II-VI system studied. The value of \( X_{BE} \) depends principally on well width and confinement energy and so a range for both these quantities needs to be specified. Note also that, for very narrow wells, the exciton wave function penetrates strongly into the barrier with a concomitant reduction in the exciton binding energy. A recent study of the newly developed ZnSe/ZnMgSSe wide-bandgap system suggests that a confinement energy greater than 600 meV combined with a well width in the range of 20 to 40 Å should induce the relationship \( X_{BE} > E_{LO} \). The ZnSe/ZnMgSSe material has produced the first room-temperature diode laser operating in the blue region.

2. Continuing efforts will be necessary to ensure that the inhomogeneous linewidth \( \Gamma_i \) can be further reduced. Of course, there is a limit to what can be achieved in reducing well-width fluctuations in thin-film growth techniques such as MBE. Also because our devices are intended for room-temperature use if the homogeneous width \( \Gamma_h \) dominates at room temperature, further efforts to reduce \( \Gamma_i \) will not produce a measurable reduction in the measured linewidth \( \Gamma_m \).

7 Conclusions

The exciton resonance in quantum well structures has been used as the basis for an optical modulator. The contrast ratio of the modulator depends strongly on the width of the exciton resonance. We have looked at the contributions to the exciton linewidth observed in quantum well systems in an effort to find ways to engineer the linewidth for excitonic device applications. For II-VI materials, we have the unique possibility to reduce the broadening of the exciton resonance with temperature when the exciton binding energy exceeds the LO-phonon energy. For each II-VI system, a range of material parameters can be specified to reduce the temperature broadening of the exciton. For II-VI materials, efforts to reduce well-width fluctuation in thin-film growth techniques such as MBE should also continue to a limit where the room-temperature linewidth is homogeneously broadened. Recently, evidence for an excitonic contribution to lasing in the CdZnSe/ZnSe system has been obtained. Use of the engineering approach in designing further II-VI structures should help to produce reliable data on excitonic effects in semiconductor diode laser structures.

References

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John Hegarty: Biography and photograph appear with the special section guest editorial in this issue.