Photoluminescence from ultrathin ZnSe/CdSe quantum wells

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Self-limiting monolayer epitaxy has been used to prepare ZnSe/CdSe quantum well structures containing 1–5 monolayers (Å) of CdSe quantum wells. Photoluminescence spectra of these structures show bright excitonic lines with a blue shift of maximum 870 meV for the 1 monolayer wide quantum well. Calculations for the energetic positions of the photoluminescence peaks are in good agreement with the experimental data. The full width at half maximum of the photoluminescence lines increases from about 25 meV for the 1 ML quantum well to about 75 meV for the 3 ML quantum wells.

Wide gap II-VI multilayer structures containing quantum wells are of major technological and scientific interest because of the lasing action in the blue-green spectral range that has been demonstrated for ZnSe/(Zn,Cd)Se quantum wells and multiple quantum well structures. There has been an increasing number of investigations of the optical properties of wide gap II-VI quantum wells such as ZnSe/(Zn,Cd)Se, ZnTe/CdTe, and ZnS/ZnSe. Recently we have reported the growth of ZnSe/CdSe short period superlattices using a novel technique for epitaxial crystal growth, the self-limiting monolayer epitaxy (SME). Photoluminescence (PL) investigations have shown the excellent quality of these structures.

In this letter we report the preparation of extremely narrow CdSe quantum wells (QWs) embedded in ZnSe using the SME technique. These structures exhibit bright excitonic photoluminescence emission, with blue shifts as high as 870 meV for a quantum well of 1 ML thickness. The full width at half maximum (FWHM) of the 1 ML QWs is about 25 meV and increases with increasing well width. We compare the experimental data with calculations of the transition energy based on the effective mass approximation. A good agreement was found, although for such narrow QWs the effective mass approximation definitely breaks down. For a qualitative understanding of an extreme case of a 1 ML quantum well we estimated the transition energy describing the QW by the δ-function perturbation. The effective width of a δ-perturbation was found to be close to the atomic size of Cd.

The epilayer growth was performed in a vertical molecular beam epitaxy (MBE) system equipped with a reflected high energy electron diffraction (RHEED) system, seven elemental solid source effusion cells and fast magnetically coupled shutter. The effusion cells of Cd and Zn contain two separately controllable heaters, while the Se source is equipped with an additional cracking furnace.

All the quantum well structures were grown by SME on top of the 1 μm thick ZnSe buffer layers, which themselves were grown by MBE on (100) GaAs substrates. During the QW growth the substrate temperature was 300 °C. Two different kinds of structures were prepared: (a) single quantum wells (SQWs) with a well width of 1, 2, and 3 MLs and (b) one sample containing a series of QWs of 1, 2, 3, 4, and 5 monolayers thickness each of them separated by 300 Å ZnSe barriers. These barriers are sufficiently wide to decouple the QWs. In the following this latter structure will be denoted as multiquantum well (MQW) for simplicity.

SME can be described as a sequence of short MBE-like growth processes that are interrupted after the deposition of more than one but less than 2 MLs of the intended compound, e.g., ZnSe or CdSe. During a short intermission a permanent flux of the more volatile species, which is Se in our case, is incident on the sample surface to stabilize the full monolayer coverage. Only the material in excess to the completed monolayer, which is more loosely bound to the surface, is allowed to reevaporate. This gives rise to a two-dimensional growth process with an excellent thickness control on an atomic scale. The details of the SME growth process are discussed elsewhere.

The deposition times of ZnSe and CdSe and also the intermissions were 1 s. At the interfaces between ZnSe and CdSe the growth was interrupted for additional 30 s. The thickness of the CdSe wells is derived from growth rate calibrations obtained with ZnSe/CdSe superlattices grown by SME. The periods of these superlattices showed a deviation of less than 5% from the designed period lengths, i.e., the SL period which is expected assuming the growth of one ML at each shutter cycle. Therefore it is justified to assume that the thickness of our quantum wells can be controlled to the same degree of accuracy. In the following we shall denote the quantum well width in integer multiples of monolayers according to the number of shutter cycles performed during their growth.

The photoluminescence spectra were obtained in back-
scattering geometry using excitation by 457 and 488 nm Ar$^+$ laser lines at a power level of 50–100 W/cm$^2$ incident on the sample. Both lines have a quantum energy which is less than the 1.7 K energy gap of ZnSe (2.82 eV). The samples were immersed in a helium bath cryostat pumped to 1.7 K. The photoluminescence was detected with a GaAs photomultiplier through a $f=85$ cm monochromator and registered by a photon counting system.

Figure 1 shows the PL spectra from a series of CdSe SQWs, where the well width was set to 1, 2, and 3 MLs (the structure of the samples is shown in the inset of Fig. 1). These are the first PL data of ZnSe/CdSe single quantum wells. The one-monolayer QW was excited by 457 nm laser radiation. For the 2 and 3 ML QWs the 488 nm laser line was used for excitation, because this line provides a higher intensity than the 457 nm line. The PL spectra of the SQWs consist of a single sharp line, no additional PL emission was observed.

Figure 2 shows the PL spectrum (457 nm excitation) from the ZnSe/CdSe MQW-sample with well widths ranging from 1 to 5 ML (see inset of Fig. 2). For the 2 ML quantum well emission the excitation power dependence was measured. The luminescence intensity of the PL line was found to be proportional to $L^k$, where $L$ is the power of the exciting laser radiation. The coefficient $k$ has been shown to be $1 < k < 2$ for excitonic transitions and $k < 1$ for free-to-bound and donor-acceptor pair transitions. For the 2 ML QW emission line we find $k=1.2$, indicating the excitonic nature of this emission line.

Figure 3 shows the intensity and the FWHM of the PL lines shown in Figs. 2 and 3 as a function of the well width. For an individual layer thickness exceeding 3 MLs (about 9 Å), the PL-intensity of the MQW decreases strongly. The intensities of the PL emission line from the 2 and 3 ML SQWs, however, are almost equal. (The PL intensity from the 1 ML single quantum well cannot be compared to that from the 2 and 3 ML SQW since the laser excitation line was not the same.) A decrease of the PL intensity at a well width of about 3 MLs has also been observed in PL measurements of asymmetric ZnSe/CdSe superlattices and for symmetric ZnSe/CdSe superlattices with individual layer thicknesses ranging from 2 to 6 MLs. The reduction of the PL intensity is attributed to the generation of misfit dislocations when the thickness of the CdSe layers exceeds the critical thickness $L_c=4\pm1$ ML for strained layer growth. From our experimental data we conclude that the 4 and 5 ML QWs in the MQW sample are already partially relaxed by the incorporation of misfit dislocations. The appearing discrepancy in the relative intensities of the PL emission from 2 and 3 ML quantum wells in the SQW and MQW samples, respectively, may be due to (a) an influence of the sample structure, which is different in the MQW and SQW samples, on the critical thickness or (b) a reduction of the intensity of the PL emission from the 3 ML quantum well in the MQW sample due to the dislocations which are generated at the relaxed 4 and 5 ML QWs and propagate towards the QWs underneath.

The FWHM of the photoluminescence line from the SQWs and the quantum wells in the MQW sample with identical well widths are equal within the experimental error. The FWHM of the one-monolayer QWs is about 25 meV and increases to about 75 meV for the 3 ML quantum wells. An increase of the FWHM with increasing well width has also been observed for CdTe/ZnTe QWs for well widths from about 2 to 5 MLs. The increase of the
FIG. 4. Energy of the photoluminescence peak from the SQWs (■) and the MQW structure (□) vs CdSe well width. The solid line shows the transition energies for ZnSe/CdSe quantum wells calculated by an effective mass model.

The FWHM with increasing well width for ultrathin QWs can qualitatively be explained by a model proposed by Bimberg et al.12 for GaAs/AlGaAs quantum wells. This model predicts an increase in the FWHM for well widths between 1 and approximately 4 MLs, and a subsequent decrease for a well width larger than 4 MLs. It has also been shown in Ref. 12 that the interface roughness has a severe influence on the linewidth of the PL emission from QWs. We thus conclude that the almost identical FWHM of the PL from 1 and 2 ML quantum wells in the SQW and MQW samples indicates that the interface roughness in these samples is identical due to the high reproducibility of the employed growth process.

In Fig. 4 the PL peak positions are plotted versus the CdSe quantum well width. The curve in Fig. 4 shows the transition energy between the lowest electron and hole quantum well states, calculated by an effective mass approximation model. The parameters used in the calculations are \( m_{el} = 0.12m_0 \), \( m_{hh} = 0.5m_0 \), \( E_g = 1.75 \) eV for CdSe and \( m_{el} = 0.15m_0 \), \( m_{hh} = 0.75m_0 \), \( E_g = 2.82 \) eV for ZnSe. The conduction and valence band offsets were assumed to be 650 and 420 meV, respectively. (The results are not very sensitive to this value, as long as the offset is larger in the conduction band than in the valence band.) These material parameters have already been successfully employed to explain the PL spectra from short period ZnSe/CdSe superlattices.9 In our calculation we assume pseudomorphic growth of the CdSe layer. However, no strain effect and no excitonic effects are included in the calculation of the transition energy. The latter would reduce the theoretical values by the exciton binding energy which is about 30–60 meV. In view of the assumptions made in our model the agreement between calculated and measured PL peak energies is deemed to be satisfactory. The difference of the PL peak energies from the quantum wells in the SQW and the MQW samples is not fully understood. We assume that it is due to a difference in the strain distribution in both samples, which is also reflected in the pronounced difference of the PL intensity variation as discussed above.

In spite of an amazing agreement with the experiment, the effective mass model cannot be adequate for such a narrow QW as that of 1 ML thickness. In this case the perturbation corresponds to the substitution of one monolayer of Zn atoms by a monolayer of Cd atoms. For qualitative estimate we take the perturbation for conduction and valence bands as \( V_{\alpha}(x) = aW_{\alpha} \delta(x) \), where the x-axis is along the growth direction (100). \( W_{\alpha} \) are the conduction and valence band offsets and parameters \( a \) the effective width of a perturbation, described by the \( \delta \)-function. For a given perturbation \( V(x) \) the sum of electron and hole binding energies is

\[
e_{e} + e_{hh} = \left(2\hbar^2\right)^{-1}a^2\left(m_eW^2 + m_{hh}W^4\right)
\]

where the effective masses \( m_e \) and \( m_{hh} \) refer to ZnSe. Taking the same values of parameters as listed above, we find \( a \approx 3.5 \) Å, in order to get \( e_e + e_{hh} \) close to the experimental value of about 0.19 eV. This value of \( a \) is only 0.5 Å larger than the atomic diameter of Cd (\( a_{Cd} \approx 3 \) Å), which supports the description of a 1 ML QW as a highly localized perturbation. A quantitative theory of ultranarrow QWs requires numerical calculations of the electronic spectrum, based on a microscopic hamiltonian.

In summary, we have reported the first PL investigations of CdSe single quantum well structures. Two kinds of structures were investigated: (a) single quantum wells of 1, 2, and 3 MLs well width and (b) a sample containing 5 QWs with well widths increasing from 1 to 5 MLs. The PL spectra of these structures exhibit sharp excitonic lines. The energetic positions of these lines and the observed dependence of the linewidth on the width of the QWs can be understood in the framework of an effective mass theory model, although the quantitative theory requires microscopic calculations. Our results show that SME is a highly reproducible growth process suitable to prepare structures with a thickness control on a monolayer scale.

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