Anomalous temperature behavior of the excitonic emission of a 3 ML ultra-thin quantum well of CdSe

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Abstract

We present a study of the photoluminescence of a subnanometric three monolayers CdSe ultra-thin quantum well (UTQW), grown by atomic layer epitaxy (ALE), as a function of temperature. The sample exhibited quite intense green excitonic emission \( \sim 2.40 \) eV at 14 K and \( \sim 2.34 \) eV at room temperature, still very intense to the nude eye even under low power excitation. The peak energy of the emission presented an anomalous (S-shaped) behavior; initially a \( \sim 6.5 \) meV red shift in the range from 65 to 105 K and then a \( \sim 10.5 \) meV blue shift between 105 and 180 K, following afterwards the expected Varshni relation. Since the UTQW does not present emission related to thickness fluctuations we explain this evolution of the peak energy with temperature in terms of changes in the relative exciton population of regions with slightly different composition produced by \( \pm 1\% \) fluctuations of Cd. These fluctuations are induced by the substitution of Cd atoms by Zn atoms in the QW/barrier interfaces.

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1. Introduction

Ultra-thin quantum wells (UTQWs) based on CdTe and CdSe present intense and well defined excitonic emission which covers the red-blue spectral range [1]. Deposition by atomic layer epitaxy under the appropriate growth conditions produces 2D layers under the critical thickness without noticeable thickness fluctuations. The growth conditions are selected in such a way that the formation of quantum dots or any other type of islands and structural imperfections are avoided or minimized. In spite of the reduced thickness, a single UTQW, few monolayers (ML) thick, is able to produce very intense photoluminescence under low power excitation. This feature makes these nanostructures very attractive for light emitting devices such as LEDs and diode lasers employing binary compounds for the active region instead of Zn\(_{1-x}\)Cd\(_x\)Se or Zn\(_{1-x}\)Cd\(_x\)Te of ternary alloys. One of the typical characterization techniques employed to study the optical properties of semiconductor QWs is photoluminescence spectroscopy as a function of temperature. Our investigations of the 3 ML CdSe UTQW indicate an anomalous behavior of the PL peak as a function of temperature, a noticeable S-shaped curve with red and blue shifts with increasing temperature. This type of behavior has been observed in a large variety of quantum wells and quantum dots, sometimes containing only the blue shift. The departure from a monotonic decrease of the peak emission with increasing temperature has been attributed to potential fluctuations within the quantum systems caused by inhomogeneous distributions of islands with varying composition, thickness, lateral sizes and shapes, see for example, Ref. [2–4]. Since the UTQW studied in this work does not present thickness fluctuations, we explain the S-shaped behavior of the peak energy of the excitonic emission in terms of confinement potential fluctuations due to small deviations in the Cd content of the quantum well.

2. Experimental details

A GaAs(001) substrate was deoxidized by thermal annealing around 560 °C in ultra-high vacuum and afterwards a ZnSe buffer layer of \( \sim 1 \) μm was grown on top of the substrate by molecular beam epitaxy (MBE) in a Riber
32P system with a basis pressure of $5 \times 10^{-11}$ Torr. The buffer layer was smoothed by a few ML thick ZnSe film grown by atomic layer epitaxy (ALE), then the 3 ML CdSe UTQW by the same technique. The single UTQW was covered with a 50 nm thick barrier layer of ZnSe. The sample growth was monitored by reflection high energy electron diffraction (RHEED). since the critical thickness of CdSe in ZnSe by ALE is $\approx 4.5$ ML [1], the film grows fully strained. The structure was grown at 275 °C. More details of the growth can be found in [1]. The PL spectra were measured in the range from 14 to 300 K employing a standard setup equipped with a 0.5 monochromator, the optical excitation was provided by a chopped HeCd 441.6 nm laser. The PL signal was detected by a photomultiplier employing a lock-in amplifier; the sample was placed in the cold finger of a closed circuit He refrigerator.

3. Results and discussion

In Fig. 1, we present the PL spectrum of the 3 ML UTQW measured at low temperature with photons of 2.807 eV energy from a HeCd laser. This energy is above the 1e→1hh (electron to heavy hole) transition of the UTQW but very close to the ZnSe (barrier) energy gap. Due to the high crystalline quality of the ZnSe barriers the electron-hole pairs generated in the ZnSe reach the UTQW without producing any significant emission in the ZnSe barrier (cap layer). We observe a very strong excitonic emission at 14 K with a low level excitation of $\approx 3$ mW/ mm$^2$. The spectrum does not show any other detectable transition in the 2.3–2.7 eV, where we could expect emission from regions of the UTQW presenting thickness fluctuations of at least $\pm 1$ ML (1 ML $= a/2$, where $a$ is the lattice constant) [1], that is, the quantum well does not present any detectable emission from different regions caused by thickness fluctuations. This is true for the whole sample of $\approx 5$ cm$^2$, indicating the very high quality of the quantum well. The full width at half maximum (FWHM) of the peak is in Fig. 1 $\approx 40$ meV and considering the low temperature of the measurement it must be very close to the inhomogeneous broadening caused by composition fluctuations at the second QW/barrier interface (closer to the sample surface). We are confident that the first QW-barrier interface must be very abrupt. This argument is based on the fact that there is a Zn–Cd interaction that conduces to the substitution of Cd atoms by arriving Zn atoms and then the desorption of those Cd atoms [5–9]. The deposition of Cd atoms does not affect the Zn atoms of the underlying surface region and then we consider negligible the commutation of Zn–Cd atoms at the first interface. The efficiency of Cd substitution by Zn increases with temperature and this effect has been applied to tune the emission of the UTQWs [1] and to produce ternary alloys with varying Zn$_1-x$Cd$_x$(Se, Te) composition [5,6]. As the temperature increases the intensity of the PL is reduced but it is still very intense. At room temperature the peak height has decreased to $\approx 1/500$ of the low temperature value, but the emission is still very intense to be seen with nude eye, quantitative measurements are underway. Fig. 2 illustrates the evolution of the PL spectrum with temperature and the inset presents the change of integrated intensity versus temperature. A strong decrease in intensity is observed in the 15–135 K range, however, as said before, the PL signal is still very intense after 135 K. As a function of temperature, to a very good approximation, the PL excitonic peak energy from

![Fig. 1. Low temperature excitonic emission of a 3 ML CdSe ultra-thin quantum well. No emission from thickness fluctuations of $\pm 1$ ML or larger are observed in the PL spectrum.](image1)

![Fig. 2. Evolution of the excitonic emission of the 3 ML CdSe UTQW with temperature in the 14–300 K range. The height of each spectrum was arbitrarily chosen for the sake of clarity. The inset presents the change of the integrated intensity of the luminescence peak with temperature.](image2)
a quantum well is expected to follow the relation
\[
h\nu_{PL}(T) = E_g(T) + E_{1e} + E_{1hh} - E_{1s},
\]  
where \( E_g(T) \) is the band gap of the semiconductor of the quantum well, \( E_{1s} \) and \( E_{1hh} \) are the ground states for electrons and heavy holes in their respective quantum wells and \( E_{1s} \) is the binding energy of the excitons. The effects of strain must be considered in all the terms of the right-hand side of Eq. (1), however, the only term that presents an important dependence with temperature is \( E_g(T) \) and it is given by the Varshni relation [10]
\[
E_g(T) = E_g(0) - \frac{\alpha T^2}{\beta + T},
\]
where \( \alpha \) and \( \beta \) are constants that depend on the material.

Instead of a monotonic decrease of the excitonic transition with increasing temperature in the 14–300 K range, the behavior of the peak energy of the emission indicates a clear departure from Eq. (1), as shown in Fig. 3. An S-shaped curve with red and blue shifts is clearly observed. This is evidence that several transitions, with varying intensity as a function of temperature, are contributing to the spectra of Fig. 2. Initially, in the 14–55 K temperature range, the peak decreases following Eq. (1). Afterwards, between 55 and 95 K we observe a red shift of the peak (\( \sim 6.5 \) meV) and then a blue shift and above \( \sim 180 \) K follows again very closely a Varshni curve that is blue-shifted \( \sim 10.5 \) meV in relation with the initial one. As explained before, the presence of only one peak in the spectrum indicates that the change with temperature of the energy of the excitonic peak cannot be described in terms of exciton migration and localization due to thickness fluctuations. The potential fluctuations that induce the contribution from slightly different exciton levels are surely caused by inhomogeneous composition fluctuations at the second QW/barrier interface, as explained above. The continuous curves in Fig. 3 were plotted employing Eq. (2), they suggest the main contribution of three different levels. The energy separation between the lower and upper levels is \( 17 \) meV, this suggest a variation of \( \sim \pm 1\% \) Cd around the average value which must be very close to the nominal 100\% Cd content. This means that in average we have a variation of \( \pm 1 \) atom of Zn per each 100 cation atoms in the UTQW, this results in a minimum average distance of \( \sim 5 \) nm between the composition fluctuations if they are confined to the second interface. Then, in each region the exciton, with a diameter around 10 nm, feels and average composition of the 3 ML UTQW produced by the small Cd content variations. The width of the PL peak and its energy will depend on the relative abundance and the distribution of the different regions with composition fluctuations. We can assume, to a good approximation, that the relative abundance of each region is described by their partial contributions to the emission at the lowest temperatures, the excitons have low thermal energy and recombine very close to the regions where they were generated. We can expect that excitation of the quantum wells with photon energies closer to the observed transitions will improve this description. After some small increase in temperature the excitons are able to diffuse with in the QW and are trapped in the fluctuations with lower potential (higher Cd content), even if they represent a small fraction of the quantum well. As the temperature continues increasing the lowest energy levels are emptied and the higher potential energy regions (lower Cd content) are populated. Then, we consider that the potential fluctuations that cause the S-shaped curve in Fig. 3 are caused by composition fluctuations of only \( \sim \pm 1\% \) Cd around the average UTQW composition.

4. Conclusions

A single 3 ML thick UTQW of CdSe has been characterized by temperature dependent PL spectroscopy in the 14–300 K range. The subnanometric QW presents a very bright green emission \( \sim 2.4 \) eV that is very intense even at room temperature under low level excitation. Inspection of the PL spectra indicates the absence of emission from thickness fluctuations. The change in the energy peak with increasing temperature presents a S-shaped curve with a red and a blue shift before and after \( \sim 95 \) K, respectively. This anomalous behavior is attributed to confinement potential fluctuations produced by \( \pm 1\% \) Cd variation in the average composition of the UTQW (slightly deviated from the nominal 100\% Cd). The variation in Cd content is attributed to the Zn–Cd chemical interaction that produces the substitution of Cd atoms by Zn atoms during the formation of the second QW/barrier interface.
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