Photoluminescence properties of MgS/CdSe quantum wells and quantum dots

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The optical properties of MgS/CdSe quantum structures grown by molecular beam epitaxy are characterized by photoluminescence (PL) spectroscopy. The increase in the CdSe thickness from 1 to beyond 3 ML results in the formation of, at first, quantum wells (QWs) and then quantum dots (QDs) by Stranski–Krastanov growth. The PL temperature dependence measurements reveal that, in the QWs, excitons localized by potential fluctuations principally govern the PL properties, which is in strong contrast to the QD PL properties. © *2002 American Institute of Physics.*
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Zincblende (ZB) MgS is an excellent barrier material for wide-gap II–VI quantum structures due to the large band gap of about 4.8 eV and because the lattice parameter is close to GaAs and ZnSe.[1,2] Although the stable MgS crystal structure is rocksalt, we have recently established a molecular beam epitaxy (MBE) technique that enables the growth of ZB–MgS on lattice-matched GaAs substrates.[1] This technique has allowed us to fabricate MgS-based quantum structures on GaAs and the excitonic properties of high quality MgS/ZnSe quantum wells (QWs) have already been reported.[1] In this study, we explore the quantum structure MgS/CdSe where the growth development from the monolayers to quantum dots can be observed clearly.

Since ZB–MgS is nearly lattice matched to ZnSe, strain in the MgS/CdSe system is almost identical to that in ZnSe/CdSe and so the growth behavior of CdSe on MgS should be similar to that on ZnSe. For example, a transition from two-dimensional to three-dimensional growth with increasing CdSe thickness [Stranski–Krastanov (SK) growth] resulting in self-formation of quantum dots (QDs) is expected, as reported many times for ZnSe/CdSe.[2–5] However, MgS/CdSe is not a simple replica of ZnSe/CdSe because of the much larger exciton confinement. On the basis of linear combination of atomic orbital theory,[6] the conduction and valence band offsets at the MgS/CdSe interface were evaluated to be 2.16 and 0.87 eV, respectively, which are much larger than those in the ZnSe/CdSe system (0.84 and 0.23 eV). Using these band offsets, we have calculated the QW exciton binding energies and found that the decrease of the binding energy due to tunneling effects observed in ZnSe/CdSe QWs which are narrower than 3 ML does not occur even in a 1 ML MgS/CdSe QW (1 ML=0.33 nm, if CdSe is coherently grown). Furthermore, it is interesting to note that interface fluctuations, particularly in narrow QWs, produce localization states for excitons and that such localization states act like QD.[7] Since the confinement potential in MgS/CdSe is very large, interface fluctuations are expected to provide significantly deep localization states in QWs. Thus localization of excitons in either QDs or potential minima in QWs governs the optical properties of the MgS/CdSe quantum structures.

In this study the optical properties of a series of samples with different CdSe nominal thicknesses (both thicker and thinner than the critical thickness for SK growth) are characterized by photoluminescence (PL) spectroscopy. The samples were grown on GaAs(001) substrates by MBE and have the structure GaAs (substrate)/ZnSe (50 nm, buffer)/MgS (20 nm)/CdSe/MgS (10–20 nm)/Zn(Mg)(S)Se (5 nm, protective cap). The MgS growth method has been described previously.[1] CdSe layers were deposited at 240 °C using either MBE or migration enhanced epitaxy (MEE). However, there was no discernible difference in the PL properties due to the growth methods. CdSe layers grown by MBE were deposited with a low growth rate of 50 nm/h, and subsequently annealed at 280 °C for approximately 5 min.[8] The MEE layers were also annealed at 280 °C. Layer morphology was monitored during growth using reflection high-energy electron diffraction (RHEED) while sample structural quality and the thicknesses of the CdSe layers were obtained after growth using x-ray double crystal diffraction.

Variation of the low-temperature (5 K) PL spectra due to the CdSe thickness is shown in Fig. 1, where the CdSe nominal thickness increases from top to bottom. The ZnSe heavy hole (HH) emission is from the buffer layer. The CdSe emission energy ranges between 2.2 and 3.8 eV, depending on the CdSe thickness. The highest emission peak energy observed so far is 3.70 eV, as shown in spectrum (a) where it should be noted that a sharp emission at 3.70 eV (emission A^s) overlaps a broad emission A^b about 200 meV wide. Emission A^s was observed also from QWs with thicker CdSe as a shoulder [spectra (b) and (c)]. These results can be understood by considering that we are observing layer-by-layer growth and that the sharp emission (A^s) is from CdSe regions 1 ML high which are large in terms of the exciton Bohr radius (4.8 nm for bulk CdSe) while the broadband (A^b) corresponds to the changes in energy for size fluctuations away from 1 ML QW. The size fluctuations can occur both in the growth direction and in the in-plane (lateral) direction by interface roughness and CdSe ML islands formation, for example. As the CdSe thickness is increased, emissions are detected at 3.05 eV (B^s and B^b) and at 2.74 eV (C^s) in addition to emissions A^s and A^b, as shown in spectrum (c). We attributed these to 2 and 3
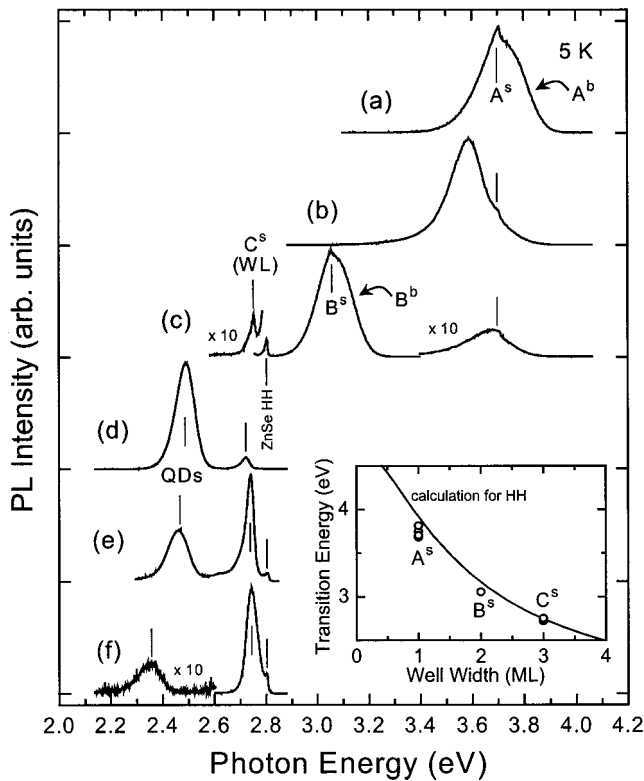
FIG. 1. Low-temperature (5 K) PL spectra from MgS/CdSe quantum structures showing the formation of the QDs as the CdSe nominal thickness becomes thicker from top to bottom. The ZnSe heavy hole (HH) emission is from the buffer layer. In the inset, the PL emission energies of A^s (1 ML), B^s (2 ML), and C^s (3 ML) emissions are compared with the calculated transition energy for $1s$ HH excitons in ML-QWs (solid line).

FIG. 2. Temperature dependence of (a) the PL peak energy and (b) the integrated intensity from the QW sample with the PL (B^s+B^b) spectrum at 5 K shown in Fig. 1(c). The broken line in (a) is the band gap of CdSe shifted to a higher energy for comparison with the data. The solid line in (b) is a fit to the data.

ML QWs, respectively. Our assignments of A^s (1 ML), B^s (2 ML), and C^s (3 ML) are verified by the inset, where the PL emission energies agree well with the calculated transition energy of the $1s$ HH excitons in ML-QWs. Note that, in this calculation, the MgS band gap and the valence-band offset were assumed to be 4.8 and 0.87 eV, respectively. For the broad emissions, the linewidth at the half maximum remains approximately the same at $\sim$200 meV and this characteristic is very different from the ZnSe/CdSe system, where a narrower ML-QW exhibits a narrower emission[9,10] due to interfacial alloy formation.[10] Clearly in the present case there is no significant interdiffusion between Mg and Cd. Increasing the CdSe thickness beyond 3 ML [see spectra (d) to (f)] causes the appearance of an emission with a broad linewidth due to QDs formation by SK growth and a wetting layer (WL) emission corresponding to the 3 ML QW (C^s) energy. In spectrum (f), the SK QDs emission is weakened probably by the introduction of misfit dislocations.

The temperature dependences of the PL were investigated in detail for both the QW and the SK QD samples. For these experiments, the samples were excited by the 351 nm line (3.53 eV) of an Ar^+ laser to ensure that the MgS barrier layer is not excited. Typical results for the QWs are summarized in Fig. 2 for the 2 ML (B^s+B^b) emission in the sample with the PL spectrum shown in Fig. 1(c). First, it should be emphasized that the integrated intensity at room temperature is still one-third of the intensity at 5 K, indicating a high internal quantum efficiency due to the large confinement potential; the strong confinement of excitons in the narrow well
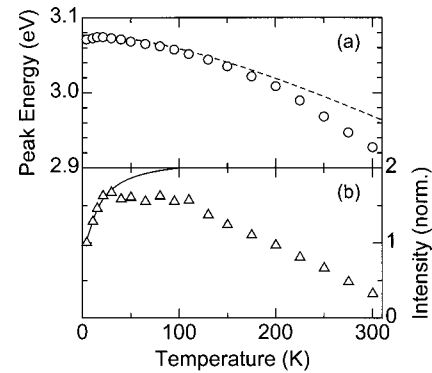
region makes the exciton binding energy large enough to stabilize excitons even at room temperature. When the temperature is increased up to 65 K, the emission energy is blueshifted [Fig. 2(a)], which can be recognized by comparing the emission energy with the broken line representing the temperature dependence for the CdSe band gap.[11] Also, the integrated intensity increases [Fig. 2(b)]. With a further increase in temperature above 65 K, the emission energy is redshifted and the integrated intensity decreases. These temperature dependences are quite anomalous in comparison with the data published on other QWs but the results are understandable in terms of excitons localized by potential fluctuations as illustrated schematically in Fig. 3(a). Such potential fluctuations can be realized, for example, by CdSe ML islands with size fluctuations as shown in Fig. 3(b), where sets of type I and II islands grow on either an extended CdSe ML or the MgS barrier layer (III). The broad PL linewidth indicates that there are many islands with different dimensions, that is, with different potential energies, though only two of both the type I and II islands are drawn in Fig. 3 for simplicity.

The temperature dependence below 65 K is explained well by exciton thermalization from localized states I in Fig. 3 to relatively free states II, because, as demonstrated by Sugawara, the lifetime of free excitons in a QW is shorter than that of localized excitons.[12] We have performed a model calculation in order to see the effects of thermalization between two levels assuming that some of the excitons in the lower energy state (state I) are thermalized into the higher energy state (state II) with a Boltzmann distribution, and so
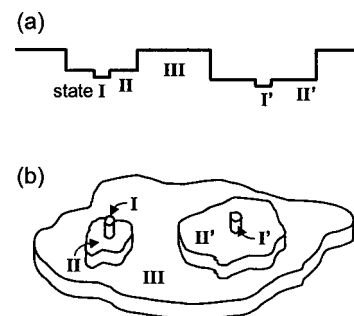

FIG. 3. (a) Schematic of potential fluctuations used for the explanation of the PL temperature dependence shown in Fig. 2. (b) An example of the layer growth that could realize the potential fluctuations in (a), where I and II are CdSe islands and III is either a CdSe ML layer or the MgS barrier layer.
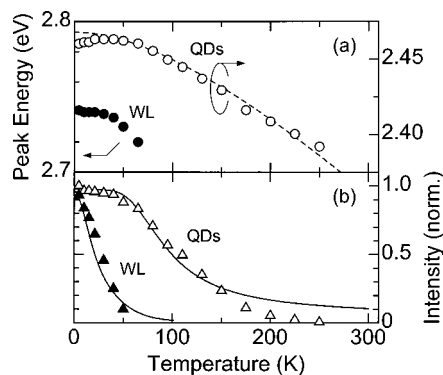
FIG. 4. Summary of the temperature dependence measurement for the QD sample with the PL spectrum at 5 K shown in Fig. 1(e). The closed and open symbols stand for WL and QDs, respectively. The broken line in (a) is the shifted band gap of CdSe. The solid lines in (b) are the result of the simulations based on the rate equations.

the emission intensity can be expressed as $I_0[1+C\exp(-\Delta E/kT)]$, where I_0 is the intensity at 0 K, C is a constant related to the radiative lifetimes, ΔE is the energy difference between two levels, k is the Boltzmann constant and T is the absolute temperature. The calculated results are shown by the solid line in Fig. 2(b). Very good agreement was found with $\Delta E = 1.3$ meV and this small energy difference suggests strong spatial localization of excitons in state I resulting in weak energy confinement since the subband in states I will be near the top of the wells close to the subbands of states II. It should be noted that the activation energy of 1.3 meV agrees reasonably well with the amount of the blueshift of about 5 meV, estimated from Fig. 2(a).

For the temperature range above 65 K, exciton transfer processes between type II CdSe islands should be considered. At low temperatures CdSe islands are occupied homogeneously by photogenerated excitons, while at higher temperatures excitons thermally escape from a higher energy II state (e.g., smaller CdSe island) and are re-trapped in a lower energy II′ state (larger CdSe island). In Fig. 3(b), this process is recognized as the exciton transfer from II to II′ via state III, which is an extended CdSe QW or the MgS barrier layer. This process involves a redshift of the emission energy, consistent with the experimental results. The PL linewidth exhibits a narrowing between 150 and 250 K, which is also consistent with this model as only a part of CdSe islands ensemble may contribute to the PL as a consequence of the exciton transfer. The decrease of the integrated intensity is probably due to nonradiative recombination. In summary, exciton localization at states I and II due to potential fluctuations and transfer via state III determine the optical properties of MgS/CdSe QWs. Note that, similar results were obtained for other QW samples.

For the SK QD samples, the temperature dependences of the PL from the QDs and the WL are shown in Fig. 4. The differences from the QW samples are very obvious, in particular, for the integrated intensity. To explain the temperature dependence of the intensity, we solved rate equations (see, e.g., Ref. 13) which take into account the photogeneration of excitons, the radiative and nonradiative recombinations, the transfer between QD and the WL, and the thermal activation. We have assumed that in the WL the radiative recombination rates are inversely proportional to the tem-

perature and the nonradiative rates are proportional to the temperature[13] while those in QDs are independent of temperature.[12] These differences are derived from the difference in the electronic structures of QW and QD. The results of fitting the data are shown by the solid lines in Fig. 4(b). Although we have neglected the QD size distribution, agreement is fairly good, indicating that there are indeed two levels (QDs and WL) and that their correlation is described well by the rate equations. From the calculation it was found that the parameter which dominates the thermal quenching of the QD PL is the energy for the thermal activation, which was evaluated to be 28 meV. The origin of this activation energy is uncertain but it is consistent with a phonon process since the CdSe LO phonon energy is 26 meV.

The peak energy changes are shown in Fig. 4(a). For the QDs, the peak energy shows a blueshift below 50 K, though the cause of this is unclear and, at present, cannot be described by the above rate equations. Above 50 K, the peak energy almost follows the temperature dependence of the bulk CdSe band gap, indicating the absence of exciton transfer between QDs either due to uniform QD size or low QD density, which would give a redshift. For the WL, the peak energies should follow the CdSe bulk band gap. However, the data around 50 K are less reliable as the WL emission is on the tail of the QD emission and so no further conclusions can be reached.

In summary, the PL properties of MgS/CdSe quantum structures have been investigated. The transition from QW to SK QDs with increasing the CdSe thickness has been observed in the low-temperature PL and the difference in the optical properties has clearly been demonstrated by PL temperature dependence measurements.

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