Growth and characterization of MgS/CdSe self-assembled quantum dots

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Abstract

CdSe/MgS quantum dots have been grown successfully by molecular beam epitaxy using a thermally activated reorganization process that occurs during growth interruption. PL measurements show emission from both QDs and the wetting layer, with emission energies ranging between (2.3 and 3.8 eV). AFM topography and \( \mu \)-PL measurements also show evidence of quantum dot structures. Power dependent PL measurements carried out on the dots give a value of 30 meV for the bi-exciton binding energy at 77 K. This value is larger than both the CdSe bulk LO phonon energy and the thermal energy at 300 K. All rights reserved © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Zincblende (ZB) MgS has a very large bandgap of \( \sim 5 \text{ eV} \) and therefore shows excellent potential as a barrier material for wide-gap II–VI quantum structures. Although the stable MgS crystal structure is rocksalt our group has successfully established a novel molecular beam epitaxy (MBE) technique, which utilizes ZnS as a sulfur source, enabling the growth of ZB-MgS lattice matched to GaAs substrates [1,2]. Our ability to grow thick MgS layers with good crystalline quality has enabled us to fabricate and characterize low-dimensional MgS-based quantum structures. The lattice parameter of ZB MgS is similar to that of ZnSe and so strain in MgS/CdSe is almost identical to that in the ZnSe/CdSe system and a similar transition from 2D to 3D growth is expected with increasing CdSe deposition. The benefits of using MgS as a barrier material are however 2-fold. Firstly, the large band discontinuities for both conduction and valence bands, estimated to be 2.1 and 0.9 eV, respectively, provide much stronger carrier confinement. Secondly, as discussed below, interdiffusion of MgS and CdSe is inhibited due to the immiscibility of these two materials. The abrupt interface between the dots and the barrier will enhance the confinement even further.
In this paper, we describe the growth of CdSe quantum dots on MgS, with evidence of dot formation by photoluminescence (PL) spectroscopy and atomic force microscopy (AFM). The excitonic properties of individual quantum dots are investigated by confocal microscope and by using power dependent PL the bi-exciton binding energy for the CdSe/MgS QD system has been recorded.

2. Results and discussion

All structures were grown in a Vacuum Generators V80H MBE system using 6N sources of elemental Zn, Se, Mg and Cd, together with a 6N ZnS source. In order to prevent contamination of the GaAs substrate during the thermal cleanup a liquid nitrogen cooled shutter is placed in front of the ZnS cell [1,2].

The GaAs substrates were etched in H2O2:H2O:H2SO4 solution and then degassed before being transferred to the growth chamber. The substrates were then heated to \( \sim 580^\circ\text{C} \) in order to remove the oxide layer and then cooled to the growth temperature (typically 240–270°C) under a Zn flux [3,4]. In order to protect the substrate from S contamination a 50nm ZnSe buffer layer was deposited prior to deposition of the 20nm MgS barrier, which was grown by our normal method [1,2]. CdSe layers of various thicknesses were then deposited at 240°C using either MBE or atomic layer epitaxy (ALE). The CdSe layers grown by conventional MBE were deposited with a slow growth rate of 50nm/h, then subsequently annealed at 280°C for approximately 5 min before being cooled to the growth temperature under a Se flux. During each ALE cycle both Cd and Se were deposited for 8s followed by a 2s interruption. The structures grown by ALE were annealed in the same way. No discernible difference was noted in the PL properties due to the different growth methods. Structures grown for PL were then capped with a second MgS barrier (10–20 nm) followed by a ZnMgSSe (5 nm) protective (antioxidation) layer. The CdSe layers produced for AFM were capped instead with a thin (3 ML) ZnSe layer which helped protect the material without altering the surface morphology.

During the growth, the layer morphology was monitored using reflection high energy electron diffraction (RHEED), where long streaks were observed during both the growth of the ZnSe and MgS layers. During the growth of the CdSe layers the RHEED became very diffuse but during the annealing of the thicker CdSe layers a transformation from 2D to 3D growth was faintly visible.

Variations in the low temperature (5 K) PL spectra due to increasing CdSe deposition can be observed in Fig. 1(a–f) for samples with nominal layer thicknesses of 0.5, 0.6, 1.7, 3, 3.6 and 4 ML, respectively. These thicknesses were calculated assuming a uniform growth rate of CdSe. As the growth rate of CdSe may be higher in very thin layers, these values are estimates for the thinnest samples [5]. PL emission energies from the CdSe layers decrease from 3.8 to 2.3 eV as the nominal layer thickness increases. The ZnSe HH emission is from the buffer layer. Spectrum (a) shows a sharp
emission ($A^s$) overlapping a broad emission ($A^b$). Emission ($A^s$) is also seen on thicker CdSe layers (b) and (c). These spectral features can be considered to arise from the thickness fluctuations resulting from layer-by-layer growth, where the sharp emission ($A^s$) is from regions 1 ML thick while the broad emission ($A^b$) corresponds to energy changes due to thickness fluctuations away from 1 ML QW. It should be noted that these size fluctuations could occur in both the growth direction and in the in-plane direction due to interface roughness and CdSe ML island formation. Spectrum (c) for example shows further emissions at 3.05 eV ($B^s$ and $B^b$) and at 2.74 eV ($C^s$) corresponding to emissions from 2 to 3 ML QWs, respectively. The assignment of ($A^s$, $B^s$ and $C^s$) as emissions from 1, 2 and 3 ML QWs is confirmed by the inset in Fig. 1, which shows that they agree well with the calculated transition energy of the 1s HH excitons in ML-QWs.

It should be noted that the FWHM of the broad emissions remains unchanged at ~200 meV which is in contrast to the ZnSe/CdSe system where the emission width narrows with decreasing well width [6,7] due to alloy formation at the interface [8]. This is consistent with there being little interdiffusion between MgS and CdSe, which is expected by analogy with Mg$_x$Zn$_{1-x}$S$_y$Se$_{1-y}$ where there is a large miscibility gap over a wide range of $x$ and $y$ [7]. Even less miscibility is expected for Mg$_x$Cd$_{1-x}$S$_y$Se$_{1-y}$ alloys, due to the greater differences in heats of formation between Cd and Mg compounds than between the corresponding Zn compounds.

When more than 3 ML of CdSe is deposited (d to f), a broad emission due to QD formation is observed along with emission from the 3 ML thick wetting layer ($C^s$). In spectrum (f), weak emission from the QDs is most probably due to the presence of misfit dislocations.

Preliminary investigations into the surface topography of CdSe QDs on MgS have been carried out. These dots were grown under the same conditions as those reported above and examined by contact mode AFM immediately after they were removed from the machine. The presence of QDs is observed only on layers with more than 3 ML deposited and a typical image from such a
layer is shown in Fig. 2. The QD parameters and surface roughness variations are recorded in Table 1 for a series of samples.

Cross section analysis roughness measurements from a sample with 1.5 ML CdSe indicates ML sized fluctuations on the surface corresponding to the thickness fluctuations predicted from the PL spectra for a sample of similar thickness (see Fig. 1(c)). The AFM scan shown in Fig. 2 is from a 3 ML CdSe layer and uniform, circular dots can be observed, with an average density of $5 \times 10^8 \text{cm}^{-2}$. The section analysis and roughness measurements carried out on this sample indicates an almost atomically flat surface between the dots and corresponds to the narrow 3 ML emission peak observed in spectra (e) shown in Fig. 1. The 5 ML sample shows that the dot density is in the same order of magnitude as the 3 ML thick sample but the dot size has increased. The section analysis and roughness measurements for this scan indicate surface thickness fluctuations of a few monolayers. This increase in the surface roughness would be expected for CdSe growth beyond the critical thickness (approx. 3 ML for CdSe) where a distinct roughening transition is observed by AFM. PL spectra from a sample of similar thickness show a dramatic drop in the intensity (see Fig. 1(f)), indicating the formation of nonradiative centres through dislocation formation.

Further evidence of QD formation has been demonstrated by the presence of local emission centres using a confocal microscope system with a collection spot of 400 nm diameter. Carriers are optically excited into the wetting layer by a GaN single mode laser diode emitting at 405 nm. The PL signal collected by the microscope is then dispersed in a single grating spectrometer with a spectral resolution of 0.2 meV and recorded by a charge coupled device camera (CCD). Sharp emission lines (0.2–0.5 meV) have been observed at 4 K, each corresponding to a single dot as shown in Fig. 3.

Power dependent PL spectra taken at 77 K on an individual CdSe QD are shown in Fig. 4a. At low pump powers only one feature (X) is observed at 2.319 eV which is attributed to single exciton recombination. As the pump energy is increased, an additional feature is observed (XX) at 2.289 eV. The intensity of the XX line ($I_{XX}$) versus the X line ($I_X$) is plotted for different pump powers and shown in Fig. 4b. $I_{XX}$ can be fitted by a quadratic dependence on $I_X$ and so XX is assigned to the

<table>
<thead>
<tr>
<th>CdSe thickness (ML)</th>
<th>~1.5</th>
<th>~3</th>
<th>~5</th>
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<tbody>
<tr>
<td>Dot height (nm)</td>
<td>—</td>
<td>16</td>
<td>22</td>
</tr>
<tr>
<td>Density ($\times 10^8 \text{cm}^{-2}$)</td>
<td>—</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Roughness $R_{\text{ms}}$ (nm)</td>
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<td>0.291</td>
<td>0.863</td>
</tr>
<tr>
<td>Thickness variations (ML)</td>
<td>1</td>
<td>—</td>
<td>2</td>
</tr>
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recombination of one exciton bound in a bi-exciton [9]. The difference in PL energies between the single and biexciton emissions results in a biexciton binding energy of 30 meV, an enhancement of 1.9 times when compared to the bulk CdSe exciton binding energy of 16 meV. To our knowledge this is the largest enhancement observed for a biexciton binding energy in both III–V and II–VI semiconductor quantum structures. This value for the binding energy not only exceeds the thermal energy of 26 meV at room temperature but also the bulk LO phonon energy in CdSe of 26 meV and as a result we expect these features will still be discernible at room temperature. This result is encouraging for the realisation of quantum dot based single photon sources, which have so far only been demonstrated at cryogenic temperatures.

3. Conclusions

CdSe/MgS quantum dot structures have been grown by MBE for the first time. The dots have been characterized by PL spectroscopy and a transition from QW to QDs is observed with increasing CdSe thickness. μPL emission is observed from individual dots and using power dependent PL a bi-exciton binding energy of ~30 meV has been measured for the CdSe/MgS QD system. The presence of QDs is also observed by AFM and roughness measurements taken of the WL for various thicknesses coincide with WL thickness fluctuations observed in the PL.

References