Effect of beryllium concentration on the size of self-assembled CdSe quantum dots grown on Zn$_{1-x}$Be$_x$Se by molecular-beam epitaxy

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The effect of Be concentration on the formation of CdSe self-assembled quantum dots grown on Zn$_{1-x}$Be$_x$Se by molecular-beam epitaxy has been investigated using photoluminescence, atomic force microscopy, contactless electroreflectance, and surface photovoltage spectroscopy. Systematic decrease of the quantum dot (QD) size by increasing the Be concentration ($x$) in the Zn$_{1-x}$Be$_x$Se barrier layer has been demonstrated. A 233 meV blueshift in the photoluminescence emission energy was obtained by changing the Be concentration of the barrier layer from $x=0.02$ to $x=0.24$. A corresponding decrease in the size of uncapped QDs was observed. Furthermore, a significant effect of unintentional variation in growth parameters on the size of the QDs was also evident. This suggests that very careful control of the growth conditions is essential in order to utilize this phenomenon for practical applications. © 2005 American Vacuum Society.

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I. INTRODUCTION

The investigation of quantum dot (QD) structures has gained considerable attention in recent years due to their interesting fundamental properties and the potential of being the active region in light-emitting devices. Structures based on II–VI compounds are promising candidates for light emitting devices. The active region in light-emitting devices. Structures based on II–VI compounds are promising candidates for light emitting devices. The investigation of quantum dot structures has gained considerable attention in recent years due to their interesting fundamental properties and the potential of being the active region in light-emitting devices. Structures based on II–VI compounds are promising candidates for light emitting devices.

Though CdSe self-assembled quantum dots (SAQDs) on ZnSe have been well studied, much less work has been done for CdSe QDs on Zn$_{1-x}$Be$_x$Se. We have recently reported the growth and optical studies of CdSe SAQDs on ZnSe and Zn$_{0.97}$Be$_{0.03}$Se by molecular-beam epitaxy (MBE). Atomic force microscopy (AFM) measurements on uncapped QD structures of these materials as well as optical studies on capped QD structures show that the size of CdSe QDs on Zn$_{0.97}$Be$_{0.03}$Se is significantly smaller than that on ZnSe.

In this article we report a study of the effect of Be concentration on the size of self-assembled CdSe QDs grown on Zn$_{1-x}$Be$_x$Se. Varying the Be concentration in the Zn$_{1-x}$Be$_x$Se barrier layer was accomplished by changing either the Zn cell temperature or the Be cell temperature, or both. We show that higher Be concentration in the Zn$_{1-x}$Be$_x$Se layer results in higher QD photoluminescence (PL) emission energy produced by a reduction on the QD size. The smaller size was also observed on uncapped QDs by AFM measurements. We also used contactless electroreflectance (CER) and surface photovoltage spectroscopy (SPS) to characterize the capped QDs. Our experiments indicate a strong dependence of the QD size on other unintentionally varying growth parameters that must be carefully controlled in order to use the Be effect to control QD size for practical applications.

II. EXPERIMENTAL DETAILS

The samples were grown by MBE on GaAs (001) substrates in a dual chamber Riber 2300 system, which has a III–V growth chamber and a II–VI growth chamber connected by ultrahigh vacuum (UHV) channels. A 200 nm GaAs buffer layer was first grown at 580 °C in the III–V chamber after the deoxidation of GaAs substrate under an As flux. Then the substrate with a III–V buffer layer was transferred into the II–VI chamber under UHV. Prior to the growth of the II–VI epilayers, a Be–Zn coirradiation of the GaAs surface was performed at 170 °C to get Zn$_{1-x}$Be$_x$Se

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with better quality and to avoid the formation of Ga2As3, which is related to the formation of stacking faults. Then the substrate temperature was increased to 250 °C and a ZnSe buffer layer was grown for 5 min. After this, Zn1−xBexSe epilayers grown by 10 min, which are nearly pseudomorphic to GaAs, were grown at 270 °C. CdSe QDs were formed by depositing 2.5 MLs of CdSe on Zn1−xBexSe surface at a substrate temperature of 320 °C and with a growth interruption of 30 s. For optical measurements, a Zn1−xBexSe top barrier was grown by 10 min to confine the carriers in the QDs. All the samples were grown with the same Se and Cd cell temperatures.

The PL measurements were made using the 325 nm output of a He–Cd laser as the excitation source and a double spectrometer and photomultiplier tube as a detector. The measurements at 77 K were performed using a liquid nitrogen continuous flow cryostat. AFM measurements in the contact mode were done right after growth as the characterization of the surface morphology for the uncapped CdSe QD structures. To determine the different transitions in our structures we have used CER and SPS. CER measures the changes in the optical reflectance of the material with respect to a modulating electric field, giving rise to sharp, derivative-like spectra in the region of the transitions. CER utilizes a condenser-like system consisting of a front wire grid electrode with a second metal electrode separated from the first electrode by insulating spacers, which are ~0.1 mm larger than the sample dimension. We placed the sample between these two capacitor plates. Thus, there is nothing in direct contact with the front surface of the sample. The probe beam is incident through the front grid wire. Electromodulation is achieved by applying an ac voltage of 1.2 kV, 200 Hz across the electrodes. In the SPS technique, the contact potential difference between the sample and a reference grid electrode is measured in a capacitive manner as a function of the photon energy of the probe beam. This was accomplished by holding the grid fixed and chopping the probe beam. We used the same grid-back metal plate configuration as CER except that the incident probe radiation is chopped; and there was no applied high voltage between the grid-back plate but rather the surface photovoltage (SPV) is introduced directly into the lock-in amplifier.

### III. RESULTS AND DISCUSSION

Shown in Fig. 1 is the PL peak energy at 77 K for QD structures with different Be concentration in the Zn1−xBexSe barrier layer obtained by changing the Zn cell temperature while keeping the Be cell temperature constant at 950 °C. In these, the growth of the QD structures is computer controlled to avoid unintentional variations of the deposition time of CdSe. The x-ray diffraction measurements on reference samples give Be concentration obtained with these two Zn cell temperatures to be 2.0% and 5.3%, respectively. Two sets of Mo blocks were used in these experiments. One set had been used for a prolonged period of time and had been subjected to repeated etching and cleaning steps. The other set was newer and had been subjected to the etching and cleaning process only a few times. The triangles and the squares represent the QD structures grown on “new” and “used” Mo blocks, respectively. The lines connect the QD structures having different Be concentration in the barrier layer grown on the same day and are a guide for the eye. The two QD structures represented by the open triangles and the two by the open squares were grown on the same day with two types of blocks.

![Fig. 1. PL peak emission at 77 K for the CdSe QD structures on Zn1−xBexSe with different Be concentration obtained by changing the Be cell temperature while keeping the Zn cell temperature constant. The dashed line is drawn to aid the eye.](image1)

![Fig. 2. PL peak emission at 77 K for the CdSe QD structure on Zn1−xBexSe with different Be concentrations obtained by changing the Zn cell temperature while keeping the Be cell temperature constant. The two QD structures represented by the open triangles and the two by the open squares were grown on the same day with two types of blocks.](image2)
and the squares represent the QD structures grown with the “new” and “used” Mo blocks, respectively. Full lines are used to connect the results of QD structures grown on the same day, and are a guide to the eye. Clearly all the sets of samples in which only one type of Mo blocks was used to exhibit a similar trend, with similar slope, although there is a large variation in the absolute value of the emission between samples grown on different days. A blueshift of the PL peak energy of about 90 meV was observed in all sets of samples grown using the two types of Mo blocks. The results of the two QD structures represented by open squares and the two represented by open triangles were all grown on the same day but with two types of Mo blocks.

In order to better characterize this phenomenon we have performed room temperature (RT) CER and SPS measurements on some samples. The solid lines in Fig. 3 are the 77 K PL spectrum (a), amplified (10×) RT measured CER spectrum (b), RT measured CER spectrum (c), and the first derivative of the SPV spectrum (d) for the sample with 77 K PL peak energy of 2.553 eV ([Be] ~ 5.3%) shown in Fig. 2. For spectra (b) and (c), the dash-dot lines are the fitting obtained by using the first derivative of a Gaussian line shape due to their bound origin. Four peaks at 2.529, 2.7098, 2.8157, and 2.9479 eV were obtained and attributed to the emission from QDs, ZnSe, Zn$_{0.952}$Be$_{0.048}$Se, and the excitonic transition $E_1$–$R_1$ of GaAs, respectively. The identification of these peaks was done by comparison with the PL emission (2.553 eV at 77 K), and considering the reported values for $E_0$(ZnSe) = 2.700 eV, $E_0$(BeSe) = 5.1 eV, and $E_1$–$R_1$(GaAs) = 2.97 eV. Comparing the two peaks (2.50 and 2.816 eV) in the DSPV spectrum are very useful to identify the emissions from the QDs and the Zn$_{1-x}$Be$_x$Se barrier layer simultaneously. Shown in Fig. 4 is the measured RT DSPV spectra for the four samples represented by the open symbols in Fig. 2. The spectra (from top to bottom) correspond to the open symbols (from left to right). The top two spectra correspond to those grown with the “new” blocks, meanwhile the bottom two correspond to the “used” blocks. Figure 4 indicates that the change in the band gap of the barriers of the structures grown on the “new” blocks (top two spectra) due to the increased Be content is 8 meV, while the quantum dot transition is blueshifted by 52 meV. Numerical calculations indicate that an increase in the band gap barrier by 8 meV will shift the QD energy transition by only 5 meV. Similarly, for the samples grown on the “used” blocks (bottom ones) an increase in the band gap energy of the barrier by 44 meV corresponds to a blueshift of 12 meV in the QD transition if the same size is assumed, however the observed shift is 30 meV. This indicates that the main contribution to this shift is the QD size reduction. It follows that the effect of the Be incorporation is not only the increase of the barrier energy but also the formation of smaller QDs. The data on Fig. 4 also show that the discontinuity in the emission energy of the four samples shown in open symbols in Fig. 2 is not due to lack of control of the Be content in the samples, which is seen to vary monotonically as expected, but rather is due to another unintentional variation in the
growth parameters that affects the size of the QDs. As previously stated, we suggest that substrate temperature may be the unintentional variable introduced by changing the blocks.

To enhance the effect of Be concentration on the QD size, we designed an experiment with a much larger change in Be concentration of the barrier layer. This was done by growing two samples using the two “new” blocks, on the same day, with two sets of cell temperatures:

$$T_1(Zn) = 190 \degree C,$$
$$T_2(Zn) = 160 \degree C,$$
$$T_1(Be) = 950 \degree C,$$
$$T_2(Be) = 1010 \degree C.$$  

The Be concentration measured by x-ray rocking curves on reference samples is about 2.0% and 24%, respectively. Figure 5 shows the PL emission at 77 K for these two structures. The PL peak energy for the sample with Zn$_{0.76}$Be$_{0.24}$Se barrier layer is about 233 meV higher than the one with the Zn$_{0.98}$Be$_{0.02}$Se barrier layer. The PL linewidth for the QD structure with higher Be concentration is slightly broader. Also a weak deep level emission at $\sim$2.30 eV is observed in this sample. Two other structures with uncapped QDs were also grown under the same conditions. The AFM measurements on these two uncapped structures are shown in Fig. 6. The AFM scans clearly indicate that the QDs are much smaller in the case of the higher Be concentration sample, which is consistent with the SPS results previously discussed. Profile measurements of the AFM scan show that the height of the QD for the structures with Zn$_{0.98}$Be$_{0.02}$Se and Zn$_{0.76}$Be$_{0.24}$Se barrier layers, are about 20.0 and 3.9 nm, respectively. The AFM images also clearly indicate a large reduction in the QD diameter. The smaller dot size is consistent with the PL blueshift observed in the capped samples. A rougher surface for the Zn$_{0.76}$Be$_{0.24}$Se sample compared to the Zn$_{0.98}$Be$_{0.02}$Se sample is clearly evident in the AFM scans. We attribute the broader PL linewidth for the capped sample with higher Be concentration in the barrier to the increased surface roughness in the Zn$_{0.76}$Be$_{0.24}$Se barrier layer. The reduced crystalline quality of the barrier layer is also evident from the weak deep level emission observed in the PL.

Our results demonstrate that the increased Be concentrations in the barrier layer result in smaller QDs. In this study, the size reduction of the QDs is not expected to be due to an increase in lattice mismatch, since the Zn$_{1-x}$Be$_x$Se layers grown are very thin and thus nearly pseudomorphic so that the in-plane lattice constant is the same as that of the GaAs substrate in all the samples. We suggest that the observed size reduction by the presence of Be is due to differences in the surface energy and/or the chemical properties of the Zn$_{1-x}$Be$_x$Se surface due to the presence of Be. Chemical effects on the QD size have been observed in other systems such as CdSe/ZnCdMgSe$^{19}$ and CdSe/ZnMnSe. $^{20}$

In summary, the effect of Be on the formation of the CdSe QDs grown on Zn$_{1-x}$Be$_x$Se has been studied. The reduction of the QD size by increasing the Be concentration in the Zn$_{1-x}$Be$_x$Se barrier layer has been demonstrated under controlled growth conditions. We have shown that SPS can be a very useful tool to investigate the properties of SAQDs. Our results indicate a very high sensitivity of the QD size to other growth parameters, sometimes difficult to control, such as a variation in the substrate temperature. Very careful control of
the conditions during growth is essential in order to take advantage of the Be concentration effect on SAQD size in practical applications.

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18 For simplicity, we assume no intermixing in the QDs.