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Growth of Self-Organized ZnSe Quantum Dots by MOVPE

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1. Introduction

In recent years, low-dimensional structures such as quantum wires or quantum dots (QDs) based on II-VI and nitride semiconductors, which are expected to be short wavelength light sources, have been actively studied [1~3]. Their structures have attracted much attention through new physical phenomena and for the applications of high efficiency optical devices such as very low-threshold semiconductor lasers. In II-VI semiconductors, excitonic properties are enhanced compared with conventional III-V semiconductors due to the larger exciton binding energies in these materials. Until now, studies of self-organized II-VI QDs have been focused on the relatively narrower gap CdSe and CdTe. Self-organized ZnSe dots, which will show blue emission, was recently studied [2], but the dot size was too large to observe quantization effect.

In this study, the size reduction of the self-organized ZnSe QDs will be demonstrated by lowering the growth temperature using metalorganic vapor phase epitaxy (MOVPE). The blue shift of the luminescence observed from the QD structures is consistent with the average dot size measured with atomic force microscopy (AFM).

2. Experiments

All ZnSe dots were grown by MOVPE in this work. GaAs (100) surfaces were cleaned with the tris-dimethylamino-arsenic (TDMAAs) flow of 10 μmol/min together with the hydrogen carrier gas for 10 mim at 670°C. The TDMAAs flow was stopped at 550°C after the cleaning. The growth temperature (Tg) was set to 350, 400 and 450°C. An about 90-nm-thick ZnS underneath layer was grown on the GaAs surface using the precursors of diethyl-zinc (DEZn) and ditertialybutyl-sulfide (DtBS) with the respective flow rate of 0.28 and 0.84 μmol/min. Because of the large lattice mismatch of 4.5% in the ZnS/GaAs heterostructures, the grown ZnS films were almost fully relaxed with the measurement of X-ray diffraction (XRD). ZnSe of about 5 ML equivalent thickness was deposited on the ZnS subsequently using DEZn and ditertialybutyl-selenide (DtBSe, Tg=350 and 400°C) or tertialybutyl-isopropyl-selenide (tBiPSe, Tg=450°C). The respective flow rates were 0.28 and 0.56 μmol/min when Tg was 350 and 400°C, and 1.5 and 0.75 μmol/min when Tg was 450°C. The sample surface morphology was observed using tapping-mode AFM, and photoluminescence (PL) emission of the ZnSe QDs was investigated using He-Cd laser (325 nm) at 14 K.

3. Results and Discussion

The ZnS surface observed by AFM is shown in Fig. 1(a). Although the ZnS surface shows the remaining undulation, it will be clear that no dot structures were observed. The root-mean-square (rms) value of this ZnS surface roughness was 0.6 nm and was increased from that the GaAs surface underneath because of the strain-induced lattice relaxation in the ZnS film. AFM images where 5 ML-thick ZnSe was deposited on the ZnS surface at 450°C,

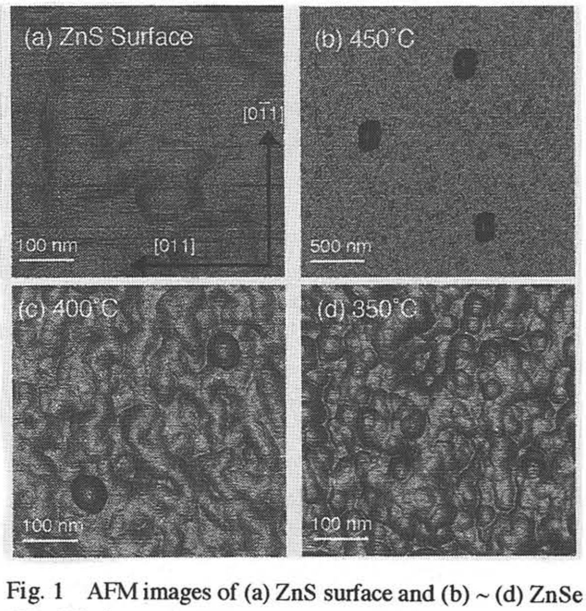

Fig. 1 AFM images of (a) ZnS surface and (b) ~ (d) ZnSe QDs. The image is 500 nm square except for (b).

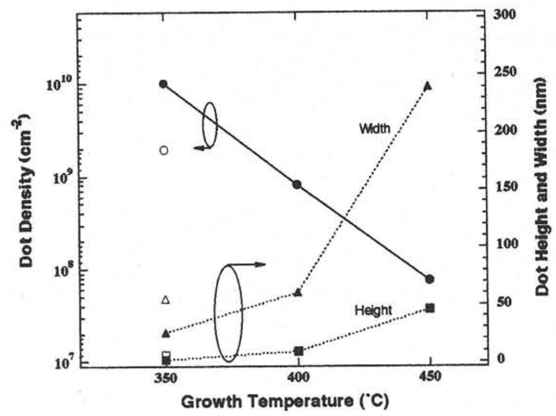

Fig. 2 Dot density and size dependence on the growth temperature. Open symbols indicate "big dot" density and size.

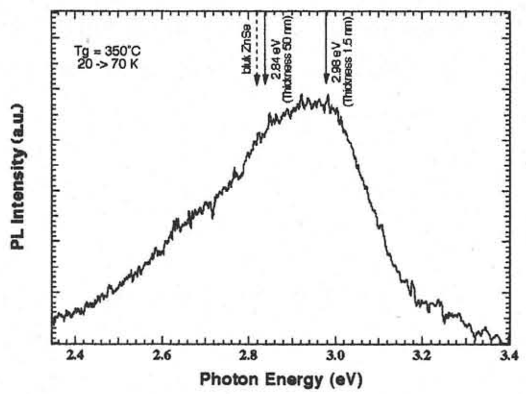

Fig. 3 PL spectrum of the ZnSe QDs grown at 350°C. Arrows show the caluculated peak corresponded with dot height.

400°C, 350°C are shown in Figs. 1(b), (c) and (d), respectively. Scan size of these images are 500 nm square (except for (b)450°C, since the dot density was very low in this case). The formation of ZnSe dots will be evident in these AFM images. The increase of the dot density and the decrease of the dot size will be clear for the lower growth temperature. The dot density and size measured from the AFM images are summarized in Fig. 2. In the sample grown at 350°C, smaller dots with the average 1.5 nm height and the 25 nm width exist together with the bigger ones with the 5 nm height and the 50 nm width (open symbols). The reason why these dots with different sizes coexist at this low temperature of 350°C is still unknown, but big dots may be related to the defects on the ZnS surface. Furthermore the dots grown at 350 and 400°C have the round shape, but the dots grown at 450°C only showed the (111)A and B facets. The dependence of the dot density, size and shape on the growth temperature have been studied on III-V QDs [4~6]. In case of InAs growth on GaAs (211)B, the dot shape changed from circular to hutlike shape for the higher growth temperature as reported by Guo et al [5]. This shows a similar tendency to the present temperature dependence of the ZnSe dot shape.

PL spectrum measured on the ZnSe QDs grown at 350°C is shown in Fig. 3. The sample was not capped and the dots are open to the air. The apparent emission peak was distributed around 2.96 eV and was blue shifted by 140 meV from the free exciton line of bulk ZnSe. In the figure, the solid arrows show the calculated peak of the ZnS/ZnSe/ZnS single quantum well for the well widths corresponding to the average dot heights for the smaller and the larger dots measured by AFM. Considering the additional lateral quantum confinement in the dots, these arrows will correspond to the average minimum transition energies of the dots. These calculations reasonably explain the measured PL spectrum.

4. Conclusions

In conclusion, self-organized QDs of ZnSe grown on (100) ZnS/GaAs were observed. It was demonstrated that the lower growth temperature leads to the higher dot density and the smaller dot size. At the growth temperature of 350°C, the dot density of ~10^{10} cm^{-2} was observed, which was increased by two orders of magnitude from the previous report [2]. The small dot size was 1.5-nm high and 25-nm wide in average, and the PL emission showed the blue shift consistent with the quantization estimated from the average dot size.

Acknowledgments

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