In-Situ RHEED Study of the Alloying of CdSe/ZnSe Quantum Dot Structure Fabricated by an Alternate Molecular Beam Supply

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(Received 9 September 2009; Accepted 29 March 2010; Published 5 June 2010)

CdSe quantum dots (QDs) were fabricated by using an alternate supply of Se- and Cd-molecular beams on ZnSe (100) films. The reflection high-energy electron diffraction and its specular beam intensity were used to investigate the moment of dot-generation, dot-coalescence and the alloying of the CdSe wetting layer (WL) and QDs due to the Zn beam irradiation. The alloying of CdSe WL under Zn beam irradiation, increased the critical thickness for the CdSe QDs generation, and the composition of the alloy depended on the irradiation period of Zn beam. The alloying speed of CdSe QDs was found to be fairly fast, but the alloying stopped at a certain Zn composition (self-limiting of diffusion). [DOI:10.1380/ejssnt.2010.283]

Keywords: Reflection high-energy electron diffraction; CdSe; Molecular beam epitaxy; Self-assembly; Photoluminescence

I. INTRODUCTION

It is well known that the lattice-mismatched heteroepitaxy give rise to the self-assembled quantum dots (QDs). This self-organization by Stranski-Krastanov (SK) mode is an attractive subject [1-6]. For the in-situ monitoring of dot formation process, the reflection high-energy diffraction (RHEED) is simple and easy method [7,8]. The appearance of spots in RHEED pattern is the direct evidence of existence of three-dimensional (3D) dots. So far, the CdSe/ZnSe dot structures have been fabricated by an MBE mode with using reduced growth rate [9-12]. In this study, CdSe dots were fabricated by using an alternate supply (ALS) of Se- and Cd-molecular beams. The alloying of CdSe wetting layer (WL) and CdSe QDs with ZnSe is a serious issue in the preparation of CdSe/ZnSe QD structure. To examine directly the alloying of the WL and QDs with Zn atom, we intentionally supplied Zn atoms on the growing surface. The alloying speed of CdSe QDs increases the band-gap energy of dot, which leads to the blue shift of PL emission energy. In this study, we investigated the dot formation process, and also the alloying of the WL and the QDs by using the RHEED intensity observation and PL observation.

II. EXPERIMENTAL

CdSe QDs were fabricated by an alternate supply (ALS) of Se- and Cd-molecular beams onto ZnSe surface grown on GaAs (100). Both molecular beams were irradiated for 10 sec, respectively. The typical beam pressures of Zn-, Se- and Cd-beam were on substrate position 3×10⁻⁷, 5×10⁻⁷ and 1.5×10⁻⁷ Torr, respectively. The growth temperature was 350°C through the fabrication of CdSe QDs. To study the initial stage of the QD generation, i.e. the coalescence and alloying of CdSe QDs, the reflection high-energy electron diffraction (RHEED) method was used, especially the specular beam intensity (Isp) was recorded during the growth. The incidence azimuth of electron beam was along [1-10], perpendicular to Se dimer rows. The PL spectra measurement was measured in liquid-He bath (Tm=4.2 K) by the He-Ne laser excitation (λ=325 nm).

III. RESULTS AND DISCUSSION

A. RHEED pattern variation during ALS growth of CdSe

The appearance of spotty RHEED pattern is the indications of 3D CdSe dot generation. Figure 1 shows the RHEED patterns observed at several stages during the ALS growth of CdSe on ZnSe buffer layer. The ALS cycle of CdSe deposition was five cycles. The RHEED pattern, that observed from the surface exposed to Se beam, exhibited ×2 streaks through all ALS cycles. On the other hand, the pattern from the surface exposed to Cd beam exhibited ×1 reconstruction in the initial 2 ALS cycles, and then the pattern varied to ×2 reconstruction during the 4th and 5th ALS cycles. As shown in the next section the critical thickness for the dot generation in CdSe/ZnSe system was 2 ML, and the dot generation was expected on the surface deposited more than 3 ALS. However, it should be emphasized that unclear diffraction spots were observed in the all RHEED patterns. It is well known that the streaky pattern suggests atomically flat surface. Since

[FIG. 1: RHEED patterns observed during the ALS growth of CdSe on ZnSe layer, (a) initial ZnSe surface, (b) 1–3 ALS, (c) 4 ALS, and (d) 5 ALS, respectively.

*This paper was presented at 10th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSM-10), Granada Conference Centre, Spain, 21-25 September, 2009.
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the distinct specular spot was observed through the entire ALS growth, these RHEED patterns show that the surface is atomically flat, i.e., the developed CdSe dot shape after 3 ALS is almost two dimensional (2D) islands. The reason that the reconstruction changes from $\times 2$ to $\times 1$ by Cd exposure, is not known at present. As far as RHEED pattern observation concerned, the CdSe dot growth by ALS mode cannot be confirmed. It is considered that the ALS growth enhances the 2D growth compared with MBE-growth mode, i.e. simultaneous beam supply.

B. Specular beam intensity trace during ALS growth of CdSe QDs.

Since the specular beam intensity (Isp) is affected by an atomically flatness or step density, the Isp variation gives some information on the surface change caused by dot generation. The typical trace of Isp was shown during ALS growth of CdSe QDs in Fig. 2. The used beam shutter program was as follows; 5 ALS cycles with both Se and Cd beams were carried out on Zn-stabilized ZnSe (100) surface, and subsequently Zn-beam exposure for 30 sec. Finally the ZnSe cap was deposited by MBE mode for 60 sec.

The Isp varied during the initial 2 ALS cycles according to the irradiated beam species. By the Se-beam exposure, the Isp decreased abruptly, and also moved to the slow reduction of Isp. By the Cd-beam exposure, on the other hand, the Isp increased steeply and kept high intensity level of Isp. In 3rd ALS during the Cd-beam irradiation cycle, the Isp did not keep constant level, and its intensity drop occurred immediately after Cd-beam irradiation. The sudden increase by Cd-beam irradiation in 3rd ALS cycle means that the 3ML-thick CdSe layer is deposited once on ZnSe films. The Isp drop corresponds to the rapid change of surface state, which is the onset of 2D-3D growth mode transition. The gradual intensity reduction during Cd-beam irradiation is considered as the surface roughening caused by the coalescence of 2D islands. This similar Isp drop was observed in the Cd-beam irradiation in 4th and 5th ALS cycles.

These facts indicate that the 1ML-CdSe layers deposited on 2ML-CdSe WL is metastable and this 1ML-CdSe changes to CdSe dots, and 2ML-CdSe WL is left on the surface after the CdSe dot formation, which acts again as the WL for the dot generation in next ALS cycle.

C. Zn beam irradiation effect on the Isp variation during ALS growth.

To confirm the alloying of CdSe WL and QDs with Zn, the Zn beam was irradiated intentionally at several stages of the ALS growth process, as shown in Fig. 3. Zn beam was irradiated for 10 sec just after Cd-beam irradiation. The surface with CdSe dots was composed of 2ML-CdSe WL and CdSe dots, and their surfaces are terminated with Cd atom, since the CdSe dots originate under Cd beam irradiation. The Zn-beam irradiation on this surface may give rise to the alloying of both CdSe WL and CdSe QDs. Out diffused Cd atoms sublime into vacuum. By the alloying of CdSe WL with Zn, the in-plane lattice constant decreases with increasing of Zn composition. Thus, the lattice mismatch between the alloyed WL and the newly deposited 1ML-CdSe layer became small, responsible for the increase in the critical thickness for SK dot generation.

Figure 3(a) depicted the Isp trace introduced 10 sec Zn irradiation period just after Cd-beam irradiation in 2nd ALS cycles. In 2 ALS cycle during 10 sec Cd-beam irradiation, slight Isp decrease was observed, which was due to the degradation of Cd deposited surface. Usually in ALS growth, Isp drop was observed in the 3rd cycle of Cd-beam irradiation. However, the Isp drop was not observed in 3rd ALS cycle (80-90 sec). Instead, the clear Isp decrease was observed in the 4th Cd exposure (100-110 sec).

When the Zn beam was irradiated after 3rd and 4th
ALS cycle (Fig. 3(b), (c)), the Isp drop did not observed in the in 4th and 5th ALS cycle but appeared in 5th and 6th ALS cycles. The cycle delay of Isp drop appearance indicated the lattice mismatch surely decreased by Zn irradiation. This mismatch reduction is the evidence of alloying of WL. Furthermore, during the Zn beam irradiation, the Isp decreased once and increased again, which denoted the surface smoothing by Zn irradiation. Since the CdSe dot shape was 2D island-like as described in Section III A, the alloying of WL and CdSe 2D islands (dots) could not be specified separately by the Isp measurement.

D. Confirmation of dot alloying by PL spectra

Zn beam irradiation on the CdSe dots caused the dot alloying, and that was confirmed by the blue-shift of PL emission peak. Fig. 4 is PL spectra of CdSe dot structures exposed to Zn beam after dot formation, prior to ZnSe cap deposition. The CdSe dots were fabricated by supplying 8 ALS cycles of Se and Cd beam, and then the Zn irradiation period was varied from 5 sec to 180 sec. The PL peaks around 2.8 eV were the band edge emission from ZnSe cap and buffer layer, and the peak at 2.6 eV was Y line due to the exciton annihilation bound to extended dislocation at GaAs-ZnSe interface [13, 14]. The large blue-shift of PL peak was observed in by only the 5 sec Zn irradiation, and then the PL peak energy reached to the constant energy after more than 30 sec Zn irradiation. The similar blue-shift was also observed in the structures deposited 3 and 5 ALS cycles, but not shown in Figures.

Figure 5 depicted the PL peak energy vs. Zn irradiation period for three kinds of CdSe dot structures that were fabricated by supplying 3, 5 and 8 ALS cycles, respectively. By the short Zn radiation of 10 sec, the PL peak energy showed large blue-shift (∼150 meV for 8 ALS cycle dot). This means that the inside of initial CdSe dot is alloyed uniformly by the Zn radiation. Furthermore, each peak reached to constant value, such as 2.475 eV for 8 ALS cycle dot, after more than 30 sec of Zn irradiation. It shows that each peak converges to the different energy depending on initial CdSe dot size. As a result, it indicates the alloying rate of 2D CdSe islands (dots) with Zn is fairly fast, but the Zn diffusion into 2D CdSe islands (dots) stops at a certain Zn composition, which is the result of the self-limiting mechanism of Zn diffusion. The detail mechanism of Zn diffusion is a future subject.

IV. CONCLUSIONS

The alloying of CdSe WL and 2D CdSe islands (dots) during dot fabrication was studied by using RHEED and PL spectra. RHEED patterns during CdSe ALS growth showed streaky reconstruction and specular spot, which means the dot-developed surface is almost atomically flat, i.e., the developed dots have 2D island shape. By the Zn irradiation at several stages of CdSe ALS growth, the alloying of CdSe WL was confirmed by behavior of the specular beam intensity. The alloying of WL was observed as the increase of critical thickness for SK dot formation. This was due to the reduction of in-plane lattice constant of WL. The PL peak energy of Zn irradiated 2D CdSe islands (dots) prior to cap deposition showed the blue shift depending on Zn irradiation period. We found that the alloying rate of 2D CdSe islands (dots) with Zn was fairly fast, but the Zn diffusion into 2D CdSe islands (dots) is automatically limited by a certain Zn composition (self-limiting of Zn diffusion).
Acknowledgments

This work was supported by matching fund subsidy for private universities from MEXT (Ministry of Education, Culture, Sports, Science and Technology).

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