ELSEVIER

Journal of Crystal Growth 225 (2001) 431–434

JOURNAL OF CRYSTAL GROWTH

www.elsevier.nl/locate/jcrysgro

The effect of diffusion on formation of self-assembled CdSe quantum dots

Yi Yang[a,*], D.Z. Shen[a], J.Y. Zhang[a], X.W. Fan[a], Z.H. Zhen[a], X.W. Zhao[a], D.X. Zhao[a], Y.N. Liu[b]

[a] *Laboratory of Excited State Processes, Chinese Academy of Science, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Science, 1 Yan An Road, Changchun, 130021, People's Republic of China*

[b] *The State Key Laboratory of Applied Optics, Chinese Academy of Science, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Science, Changchun, 130022, People's Republic of China*

Abstract

The effect of diffusion on formation of self-assembled CdSe quantum dots (SAQDs) was studied in this paper. Two kinds of diffusion were observed during the growth of CdSe layer. Surface diffusion was confirmed by atomic force microscopy (AFM). Interdiffusion was verified by the photoluminescence (PL) and X-ray diffraction measurement. The surface diffusion might help to form quantum dots. However, the interdiffusion could prevent the formation of quantum dots. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 81.05.Dz; 81.10.-h; 81.15.Gh

Keywords: A1. Atomic force microscopy; A1. Diffusion; A1. Low dimensional structures; A3. Metalorganic chemical vapor deposition; B1. Cadmium compounds; B2. Semiconducting II–VI materials

1. Introduction

Self-assembled quantum dots (SAQDs) are presently attracting much attention since they can lead to improvements in optical and electronic device applications [1,2]. However, for group II–VI semiconductors, the mechanism of formation is not very clear, even in the case of CdSe on ZnSe (the most widely studied II–VI materials combination). Recently, Ivanov [3] reported the formation of CdSe-enriched islands within a broadened ZnCdSe alloy-like quantum well by interdiffusion, and Schikira [4] demonstrated that interdiffusion is enhanced under Se-rich growth conditions even at temperature of about 300°C.

In this paper, the effect of diffusion on formation of CdSe SAQDs was studied by atomic force microscopy (AFM) and photoluminescence (PL) measurement. Two kinds of diffusion were observed during the growth of the CdSe layer. One was surface diffusion on CdSe surface, while the other was interface interdiffusion between the ZnSe and CdSe layer.

2. Experimental procedure

Samples were grown by low-pressure metal-organic chemical vapor deposition (LP-MOCVD).

---

*Corresponding author.

E-mail address: shen@public.cc.jl.cn (Y. Yang).

PII: S0022-0248(01)00910-1

Dimethyl-selenide (DMSe), Dimethyl-cadmium (DMCd) and Dimethyl-zinc (DMZn) were used as precursors. The growth pressure was kept at 220 Torr. GaAs (1 0 0) substrates were cleaned ultrasonically with a sequence of organic solvents and chemically etched by a $H_2SO_4:H_2O_2:H_2O$ (3 : 1 : 1) and HCl solution, then rinsed in deionized water (18.2 MΩ) and blown dry with N_2. After heating at 600°C for 10 min, the substrates were cooled down to the growth temperature.

For surface analysis, about 2 monolayers (ML) of CdSe coverage were deposited directly on the GaAs (1 0 0) surface at 500°C. Then, this uncapped sample was cooled down to room temperature and taken out of the growth chamber immediately, and then was monitored constantly at the same area of 1 μm^2 by a digital instrument nanoscope IIIa system.

For PL measurement, Samples A and B were grown with ZnSe buffer layer (500 nm), alternating layers of CdSe/ZnSe, and ZnSe cap layer (30 nm). The growth temperature of sample A and B was at 520°C and 550°C, respectively. Sample A contained 10 periods of CdSe well layer (1.1 nm) and ZnSe barrier layer (12 nm). Sample B contained 20 periods of CdSe well layer (1.6 nm) and ZnSe barrier layer (12 nm). X-ray diffraction and PL spectra were used to measure the crystal structure and the luminescence properties of the samples. The K_{α_1} and K_{α_2} of Cu were used as the X-ray resources. The 325-nm line of He–Cd laser was used for PL measurement.

3. Results and discussion

Fig. 1 shows the AFM images and cross-section analysis of the uncapped sample surface. Those AFM images were taken from the same area of the uncapped sample. (a) and (b) were taken about 60 and 80 min after the growth of CdSe layer, respectively. The bottom panel is the cross-section analysis. The cross-section analysis (a) and (b) were exactly taken from the same area of AFM images (a) and (b). From (a) to (b), the surface trended to smooth and many dots were formed. The average height, diameter and density of those dots were 13 nm, 50 nm and 5 dots per μm^2.

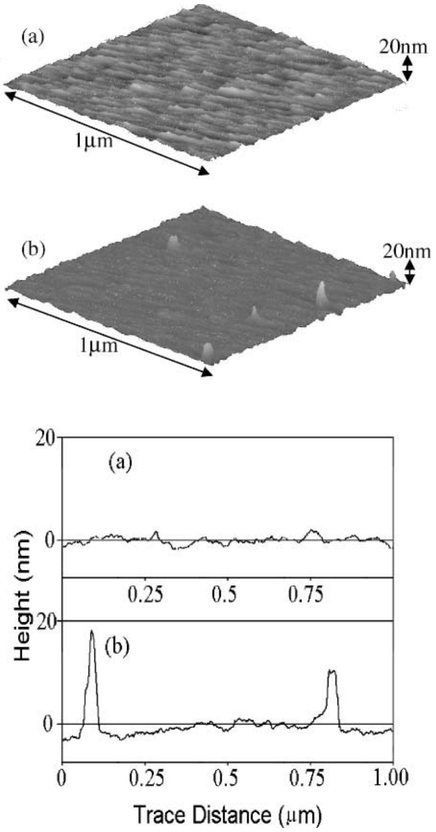

Fig. 1. AFM images and cross-section analysis of the uncapped sample surface. Those AFM images were taken from the same area of the uncapped sample. (a) and (b) were taken about 60 and 80 min after the growth of CdSe layer, respectively.

Fig. 2 shows the PL spectra of samples A and B at 77 K. Sample A had two peaks. The peak value of AP_1 and AP_2 were 495.7 and 547.9 nm. Sample B also had two peaks. The peak value of BP_1 and BP_2 were 520.1 and 609 nm.

Fig. 3 shows the X-ray diffraction patterns of sample B. Four peaks could be seen clearly. The peak value of P_1, P_2, P_3 and P_4 were 66.311, 66.127, 65.944 and 65.702°, respectively.

Comparison with CdSe on ZnSe, the lattice mismatch of CdSe/GaAs is 7.5%, and is close to that of CdSe/ZnSe that is 7.2%. Therefore the strain-induced self-assembling should be similar in both cases. In addition, without the disturbance of ZnSe buffer layer, the actual information of self-assembled CdSe quantum dots will be observed.

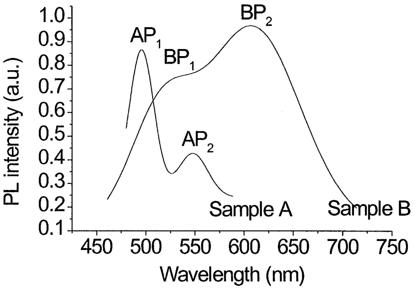

Fig. 2. The PL spectra of the sample A and B at 77 K.

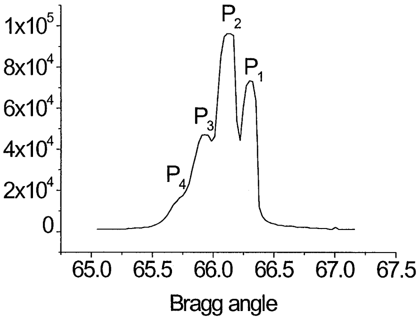

Fig. 3. The X-ray diffraction patterns of the sample B.

Then, for the surface analysis, CdSe coverage was grown directly on the GaAs surface.

In Fig. 1, the surface tending to smoothing could be interpreted as the effect of surface diffusion. According to the theory of crystal growth, the surface of a concave area possesses lower surface vapor pressures (higher surface binding energies), and the surface of a convex area possesses higher surface vapor pressures (lower surface binding energies). Therefore, individual atoms or molecules continually migrate from the parts with higher surface vapor pressures to the parts with lower surface vapor pressures [5,6]. Consequently, the concave areas will continually receive atoms or molecules from the convex areas. Then, the thickness of the concave area will tend to be thicker than the initial growth thickness and the surface will tend to smooth out as time passes.

Those dots in Fig. 1b were very similar to SAQDs that had been reported by other researchers [7–10]. However, in our experiment, the thickness of CdSe layer was about 2 MLs, below the critical thickness of 3 MLs [11]. Moreover, those dots appeared about 60–80 min after the growth of CdSe layer. One possible explanation may be the effect of surface diffusion. Surface diffusion could result in parts of the sample surface reaching or exceeding the critical thickness, and then strain releases to form the SAQDs on these parts of sample surface. Nevertheless, the mechanism of formation is rather complicated. Recently, some researchers even thought that those dots might be Se or SeO_2 [5]. Then, the hypothesis of formation of SAQDs by surface diffusion might not be appropriate. However, it is likely that during the formation of those dots, surface diffusion did have an active role.

The thickness of the CdSe well layer in sample A was 1.1 nm, beyond the critical thickness of 3 MLs. Thus, it might release strain and form the quantum dots to lower the total system energy. Then in Fig. 2, we considered that the AP_2 comes from the quantum dots, and the AP_1 come from the wetting layer. However, the growth temperature of sample B was 550°C. It was high enough for Zn and Cd interdiffusion to form ZnCdSe alloy layer. This alloy layer could compensate the high lattice mismatch of CdSe/ZnSe and decrease the actual thickness of CdSe layer. Then, even though the original thickness of CdSe layer in sample B was 1.6 nm, also beyond the critical thickness, we did not observe the PL peak of quantum dots in Fig. 2. We considered that the BP_1 might come from the CdSe ultrathin layer and the BP_2 might come from the ZnCdSe interface or impurity.

The existence of ZnCdSe alloy layer was verified by X-ray diffraction. In Fig. 3, the peak diffraction angle of P_1, P_2, P_3 and P_4 were 66.311, 66.127, 65.944 and 65.702, respectively. The diffraction peak K_{α_1} and K_{α_2} of GaAs (4 0 0) are 66.095 and 66.305. The diffraction peak K_{α_1} of ZnSe (4 0 0) is 65.885 and the K_{α_2} lap over the K_{α_1} of GaAs (4 0 0). Then we can conclude that the P_1, P_2 and P_3 in Fig. 3 belong to the K_{α_2}, K_{α_1} of GaAs (4 0 0) and the K_{α_1} of ZnSe (4 0 0), respectively. However, the P_4 in Fig. 3 does not corresponding to any diffraction peaks of CdSe, ZnSe and GaAs. In addition, we did not observe this peak in the other samples that the growth temperatures were 500°C or 520°C. Hence, we concluded that the P_4 might come from the ZnCdSe alloy layer.

4. Conclusions

As described above, two kinds of diffusion existed during the formation of quantum dots. The surface diffusion might help to form quantum dots. However, the interdiffusion was found to prevent the formation of quantum dots.

Acknowledgements

This work was supported by the National Fundamental and Applied Research Project, the key project of the National Natural Science Foundation of China (69896260), the National Natural Science Foundation of China and the "863" advanced Technology Research Program in China.

References

[1] J.L. Merz, S. Lee, J.K. Furdyna, J. Crystal Growth 184/185 (1998) 228.
[2] F. Flack, N. Samarth, V. Nikitin, P.A. Crowell, J. Shi, J. Levy, D.D. Awschalom, Phys. Rev. B 54 (1996) R17312.
[3] S.V. Ivanov, A.A. Toropov, T.V. Shubina, S.V. Sorokin, A.V. Lebedev, I.V. Sedova, P.S. Kopev, J. Appl. Phys. 83 (1998) 3168.
[4] D. Schikira, S. Schwedhelm, K. Lischka, Abstract Book of the Ninth International Conference on II–VI Compounds, 1999, Japan, Tu-P066.
[5] J.B. Smathers, E. Kneedler, B.R. Bennett, B.T. Jonker, Appl. Phys. Lett. 72 (1998) 1238.
[6] B.R. Pamplin, Crystal Growth, Pergamon, Oxford, 1975, p. 15. [Chapter 2].
[7] S.H. Xin, P.D. Wang, A. Yin, C. Kim, M. Doovrowolska, J.L. Merz, J.K. Furdyna, Appl. Phys. Lett. 69 (1996) 3884.
[8] E. Kurtz, H.D. Jung, T. Hanada, Z. Zhu, T. Sekiguchi, T. Yao, J. Crystal Growth 184/185 (1998) 242.
[9] Z.H. Ma, W.D. Sun, I.K. Sou, G.K.L. Wong, Appl. Phys. Lett. 73 (1998) 1340.
[10] H.C. Ko, D.C. Park, Y. Kawakami, S. Fujita, Appl. Phys. Lett. 70 (1997) 3287.
[11] K. Pinardi, U. Jain, S.C. Jain, H.E. Maes, R. Van Overstraeten, J. Appl. Phys. 83 (1998) 4724.