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Journal of Crystal Growth 233 (2001) 785–790

JOURNAL OF CRYSTAL GROWTH

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The formation mechanism of self-assembled CdSe quantum dots

Yi Yang[a,*], D.Z. Shen[a], J.Y. Zhang[a], X.W. Fan[a], B.S. Li[a], Y.M. Lu[a], Y.C. Liu[a], Y.N. Liu[b]

[a] *Laboratory of Excited State Processes, Chinese Academy of Science, Changchun Institute of Optics, Fine Mechanics and Physics, 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, Changchun 130022, People's Republic of China*

Received 15 March 2001; accepted 21 July 2001
Communicated by R. James

Abstract

The formation process of CdSe self-assembled quantum dots (SAQDs) was investigated systematically by atomic force microscopy (AFM). Several monolayers (MLs) of CdSe coverage were grown directly on GaAs substrates by metalorganic chemical vapor deposition (MOCVD). AFM images were taken constantly on the same area within several hours after the growth. It revealed that the relaxation of misfit strain is completed by two competing processes. One is the formation of quantum dots assisted by surface diffusion; another is the formation of misfit dislocations.

PACS: 68.65.+g; 81.05.Dz; 81.10.−h; 81.40.Jj

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

1. Introduction

Semiconductor quantum dot structures, with atomic-like discrete energy states, are expected to lead to improvement in optical and electronic device application, due to the three dimensional confinement on the carriers or excitons [1–4]. By the Stranski–Krastanow mode (S–K mode), self-assembled quantum dots (SAQDs) have been fabricated successfully in group-IV (e.g., Ge/Si) and III–V semiconductors [5–8]. Recently, group II–VI semiconductor system, such as CdSe/ZnSe [1,3,9], CdTe/ZnTe [4] and ZnSe/ZnS [10], have been extensively studied from the interest on the wider energy band and the higher exciton binding energy in these materials. However, the formation mechanism of SAQDs is not very clear until now especially for II–VI quantum dots. Moreover, the

*Corresponding author. Tel.: +86-431-5937596; fax: +86-431-5955378.

E-mail address: shen@public.cc.jl.cn (D.Z. Shen).

0022-0248/01/$ - see front matter
PII: S0022-0248(01)01644-X

formation process of SAQDs has attracted our interest not only for fabricating top-quality quantum dots and novel devices but also from the point of view of basic science.

To fully understand the formation mechanism of SAQDs, in situ measurement is needed. Reflection high-energy electron diffraction (RHEED) [11,12] or reflectance anisotropy spectroscopy (RAS) [13] can offer the real-time information during the formation process of quantum dots. With RHEED, we can obtain information about the layer thickness from the intensity oscillations, the surface lattice parameter from the spot position, and the surface morphology and the growth mode from the diffraction pattern. Nevertheless, most of the structure information from the RHEED pattern indirectly reflects the formation process of quantum dots. Atomic force microscopy (AFM) is an effective instrument to get direct information of the surface morphology. However, the processes of releasing strain usually happen only within several minutes or less after the growth of epilayer. The time needed to cool down the sample, take it out of the growth chamber and monitor it under AFM usually requires about an hour. Hence, AFM can usually be used to characterize the morphology or the ripening process of quantum dots. Recently, we reported the formation process of quantum dots by AFM [14]. We found out that the process of surface diffusion can compensate for the time that is needed for measurement and considered that surface diffusion can lead to the formation of quantum dots below the critical thickness. Therefore, it is possible to directly observe the process of releasing strain and obtain the actual information of the formation process of SAQDs.

In this paper, we report the systematic investigation of the formation process of CdSe SAQDs by AFM for the first time. We noticed that the total energy of the system is decreased by elastic deformation and misfit dislocations. It is considered that the minimum of system energy is realized by two competing processes. One is the formation of quantum dots assisted by the surface diffusion and another is the formation of misfit dislocations.

2. Experimental procedure

A CdSe layer was deposited directly on GaAs (1 0 0) substrates by low-pressure metalorganic chemical vapor deposition (LP-MOCVD). In comparison to the combination of CdSe on ZnSe, the lattice mismatch of CdSe/GaAs is 7.5%, and it is close to that of CdSe/ZnSe, which is 7.2%. Therefore, the strain-induced quantum dots should be similar in both cases [15]. In addition, without the disturbance of the ZnSe buffer layer, the actual information will be obtained. Dimethylselenium (DMSe) and dimethyl-cadmium (DMCd) were used as precursors. The growth pressure was kept at 220 Torr and the growth temperature was 480°C. After being chemically etched and heated at 600°C in H_2 ambient, the substrate was cooled down to the growth temperature. A CdSe layer with a thickness ranging from 0.6 to 1.8 nm was deposited directly on the GaAs substrate. After being cooled down to a set temperature, samples were taken out of the growth chamber immediately and exposed to the atmosphere. The uncapped samples were examined by a Digital Instrument Nanoscope IIIa system constantly at the same region to observe the formation process of CdSe quantum dots.

3. Results and discussion

Fig. 1 shows AFM images and cross-section analysis of the formation process of a CdSe quantum dot. The first image (a) gives the results of measurement within 47 min after the growth for a CdSe coverage of 0.6 nm. From Fig. 1(a) to (k), the time interval of every image is 4 min. The process of strain release to form quantum dot can be seen clearly in the cross-section analysis. We divided the figure of cross-section analysis into five parts. Parts A and E are irrelevant to part C in which the quantum dot was formed. From (a) to (k), parts B and D are sunken, and part C is taller to form a quantum dot.

In our previous work [14], the formation of quantum dots below a critical thickness was attributed to the influence of surface diffusion. The surface of concave areas possesses lower

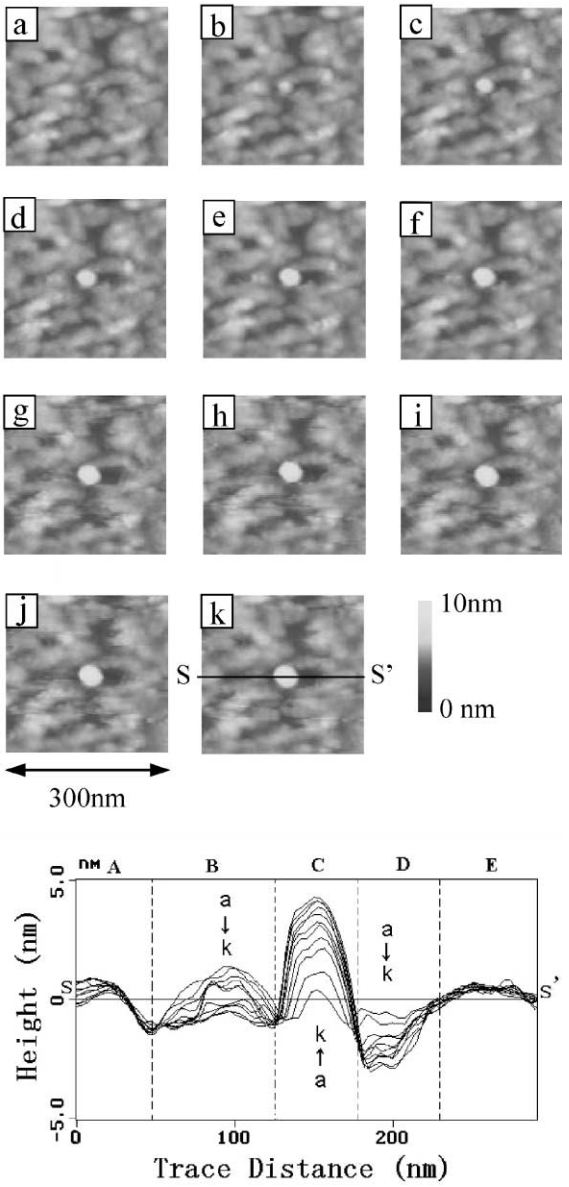

Fig. 1. AFM images and cross-section analysis of the formation process of a CdSe quantum dot. The first image (a) was taken 47 min after the growth of CdSe coverage (0.6 nm), and the time interval of every image was 4 min from (a) to (k).

surface vapor pressures (higher surface binding energies), and the surface of convex areas 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 [14,16,17]. Consequently, the concave areas will continually receive atoms or molecules from the convex areas. The thickness of concave areas will tend to be thicker than the initial growth thickness over time, even reach or exceed the critical thickness, or nucleate at the concave areas. Strain release leads to the formation of SAQDs at those areas. The nuclei leading strain release can be seen in the cross-section analysis of Fig. 1. In the first curve (a), part C have bigger curvity (smaller curve radius) than parts B and D. In another words, part C has higher surface vapor pressure than part B and part D. Without the existence of strain, surface diffusion would lead part C disappear, instead of forming a quantum dot.

In order to better understand the effect of surface diffusion on the formation of quantum dots, different thickness of CdSe coverage were investigated. Fig. 2 shows the formation process of quantum dots at different thicknesses of CdSe coverage. The formation of quantum dots in sample 2A, 2B, 2C needed the assistance of surface diffusion, and sample 2D did not. The thickness of the CdSe layer in sample 2D is 1.8 nm, which is beyond the critical thickness of 3 monolayers

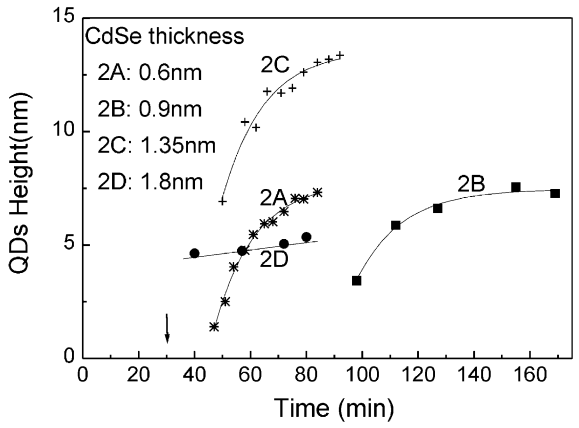

Fig. 2. The dependence of CdSe SAQDs height on time after growth. The origin of X-coordinate represents the time when the growth is stopped. The arrow on the X-coordinate represents the time when samples were taken out of the chamber and exposed to the atmosphere.

(MLs) (about 0.91 nm) [18]. Hence it could release strain to form quantum dots directly. It's worth notice that the CdSe thickness of sample 2C was 1.35 nm, which is also beyond the critical thickness. However, it still needed the assistance of surface diffusion to form quantum dots. We considered that the critical thickness in the actual case is thicker than the value based on theoretical calculation. For nucleation of SAQDs, the total system energy needs to exceed an activated barrier. However, in the real growth condition, the total system energy can't reach the activated barrier due to the influence of surface roughness and misfit dislocations, even if the epilayer reaches or exceeds the critical thickness. Then, it can't nucleate by releasing strain to form quantum dots directly and needs the assistance of surface diffusion.

Recently, some researchers consider that a thin layer of SeO_2 in atmosphere is formed by the initial oxidation of the ZnSe or CdSe at the surface [16,19]. The SeO_2 molecules coalescence via surface migration and can form surface clusters. To understand the vole of the oxide, an experiment was conducted with different oxide condition. In Fig. 3, the growth condition of sample 3A is the same as that of sample 3B. The thickness of CdSe was 0.6 nm in both cases. Sample 3A was taken out of the chamber immediately after deposition and sample 3B was kept in the chamber for an additional hour. The results indicated that quantum dots can be formed in sample 3A, but not in sample 3B. Moreover, the surface of sample 3B becomes rougher than sample 3A. We considered that the action of surface oxidation can enhance the surface diffusion and ease nucleation. Then, the misfit strain would release via those nuclei, although the total system energy didn't reach the activated barrier and could not release strain to form a quantum dot by itself. For sample 3B, which is kept in the chamber for an hour, the strain had been released via formation of misfit dislocations. The surface roughness allows a partial relaxation of the strain by purely elastic deformation of the epilayer and substrate [20–22]. Moreover, the roughness can allow easy nucleation of dislocations [23]. The formation of misfit dislocations also can minimize the total system energy. Hence, although the process of oxidation and surface diffusion still happened when sample 3B was exposed to the atmosphere later, the quantum dots could not form on the surface, because the total system energy had been lowered by misfit dislocations. Thus, we consider the effect of oxidation as a means to enhance or promote the nucleation of SAQDs.

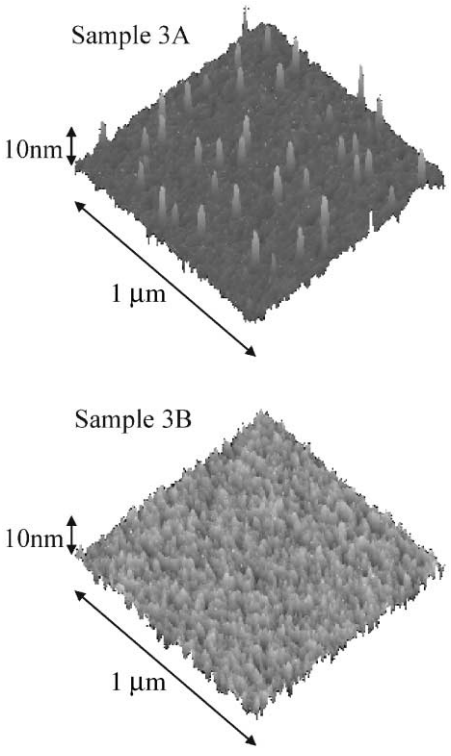

Fig. 3. AFM images of sample 3A and sample 3B with the same thickness of CdSe layer. Sample 3A was taken out of the chamber immediately after CdSe deposition and cooled down to room temperature. Sample 3B was kept in the chamber for an hour.

Based on our experiment and the literature [24], the formation mechanism of CdSe SAQDs is better understood. The basic question is how to release the strain-induced by the misfit between the quantum dot material and substrate to minimize the total energy of this system. As shown in Fig. 4, the accumulated elastic strain energy $E(\mathrm{el})$ (curve I) increases linearly with the deposited volume: $E(\mathrm{el}) = Cm^2At$, where C is the elastic coefficient, m is the misfit, A is the area and t is the thickness of

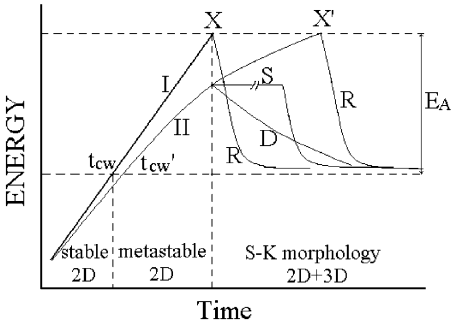

Fig. 4. Schematics of the formation mechanism of the CdSe SAQDs. Curve I shows the accumulated elastic strain energy E(el). Curve II shows the total system energy E. E_A represents the transition barrier. R is the process of releasing strain to form S–K quantum dots. S is the process of releasing strain assisted by the surface diffusion. D is the process of the formation of misfit dislocations.

the epilayer. At the point of t_{cw} (the critical wetting thickness), the system leaves the stable 2D growth and begins metastable 2D growth. The extension of the range of metastable 2D growth depends primarily on the height of the transition barrier E_A. A pure strain-induced 2D–3D transition becomes possible at point X. The strain will be released to form SAQDs under S–K mode (process R). However, at real growth condition, the elastic deformation and misfit dislocations can minimize the total energy of the system. Hence, the total energy of system (curve II) should be, $E = E(\text{el}) - E(d)$, where $E(d)$ is the energy that be consumed by elastic deformation and misfit dislocations. If the thickness of the epilayer is large enough, the total energy E will reach the point of X'. Then it can release strain directly to form SAQDs (just like sample 2D in Fig. 2). If the thickness is not enough, the total energy E is between the point of t'_{cw} and X'. The strain will be released via a competing mode (process S and D). Process S is the process of strain release assisted by surface diffusion (just like sample 2A, 2B and 2C in Fig. 2, and sample 3A in Fig. 3). Process D is the formation of misfit dislocations (just like sample 3B in Fig. 3). The surface oxidation will enhance the process S, leading to the formation of SAQDs. The surface roughness contributes to the formation of misfit dislocations.

4. Conclusions

In conclusion, we used AFM to systematically investigate the formation process of CdSe SAQDs. Two competing processes were observed during the process of releasing strain. The surface oxidation can enhance the process of surface diffusion and cause the strain released to form quantum dots. Surface roughness can allow easier nucleation of misfit dislocations.

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.

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