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The formation process of self-assembled CdSe quantum dots below critical thickness

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Abstract

The formation process of CdSe self-assembled quantum dots (SAQDs) below the critical thickness was observed by atomic force microscopy (AFM) for the first time. Two monolayers (MLs) of CdSe coverage were grown directly on GaAs (1 0 0) surfaces by metalorganic chemical vapor deposition (MOCVD). AFM images were taken constantly of the same area of $1\,\mu m^2$ within several hours after the growth. It revealed that the formation of CdSe SAQDs under critical thickness was due to the effect of surface diffusion and strain release. Our results make it possible to directly observe the process of release strain and to obtain the actual information on the formation process of self-assembled quantum dots.

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Keywords: CdSe; MOCVD; Self-assembled quantum dots; Surface diffusion; Strain release

1. Introduction

Semiconductor quantum dots are known to have atomic-like discrete energy states, which are expected to lead to improvement in optical and electronic device applications. So, in recent years, a great deal of research has been devoted to fabrication of high-quality quantum dots [1–4]. Compared to lithographic methods, the Stranski–Krastanow mode (S–K mode) is a promising method, which does not need complicated fabrication techniques and which achieves high optical quality due to low interface defects. Such self-assembled quantum dot formation is now well established in group-IV (e.g., Ge/Si) and III–V semiconductors [5–8]. Group II–VI semiconductors, CdSe/ZnSe [1,3,9], CdTe/ZnTe [4] and ZnSe/ZnS [10] have also been widely researched. However, the formation mechanism of II–VI

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self-assembled quantum dots is currently under extensive debate. Even in the case of CdSe on ZnSe (the most widely studied II–VI materials combination), the mechanism by which the dots form remains even less understood. Some issues remain unresolved. For example, the critical thickness of CdSe/ZnSe is usually considered to be 3 ML [11]. The thickness of the CdSe layer needs to reach or go beyond 3 ML, then it can release strain to form the self-assembled CdSe quantum dots. Recently, some researches [9,12] showed that the quantum dots can form far below the critical thickness. For CdSe/ZnSe system [12], even 1.1 ML coverage of CdSe can form quantum dots. More recently, Smathers [13] reported nanometer-scale surface clusters on ZnSe/GaAs. They considered that the vacuum-grown ZnSe epilayer produced SeO_2 clusters on a stable Zn related oxide surface, then thought that the formation of CdSe quantum dots on ZnSe was much more complicated. In this paper, we investigated the formation of self-assembled CdSe quantum dots directly on GaAs (1 0 0) surfaces below the critical thickness, and observed the formation process by AFM for the first time. In comparison to the combination of 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-assembled dots should be similar in both cases [14]. In addition, without the disturbance of the ZnSe buffer layer, the actual formation of self-assembled CdSe quantum dots will be observed.

2. Experimental procedure

The sample was grown on GaAs (1 0 0) surfaces by low-pressure MOCVD. Dimethyl-selenium (DMSe) and dimethyl-cadmium (DMCd) were used as precursors. The growth pressure was kept at 220 Torr and the growth temperature was 500°C. Before loading into the growth chamber, the GaAs substrate was etched by $H_2SO_4:H_2O_2:H_2O$ (3:1:1) and HCl. After being heated at 600°C in H_2 ambient for 10 min, the substrate was cooled down to the growth temperature of 500°C. Approximately, two monolayers (2 ML) of CdSe film were grown directly on the GaAs (1 0 0) surfaces. The uncapped sample was cooled down to room temperature immediately after the growth, and then was monitored constantly on the same area of 1 μm^2 by a Digital Instrument Nanoscope IIIa system.

3. Results and discussion

Fig. 1 showed the AFM images that were taken as a function of time after the growth. Those images were from the same area of the uncapped sample surface. The top panel (a) was taken about 60 min after the growth. The middle panel (b) was 80 min and the bottom panel (c) was 100 min after the growth. Two kinds of dots were observed on the sample surface. One kind was low dot with high density. The size varied from 30 to 200 nm for different orientations. The average height and density were about 2–3 nm and 100 μm^{-2}, respectively.

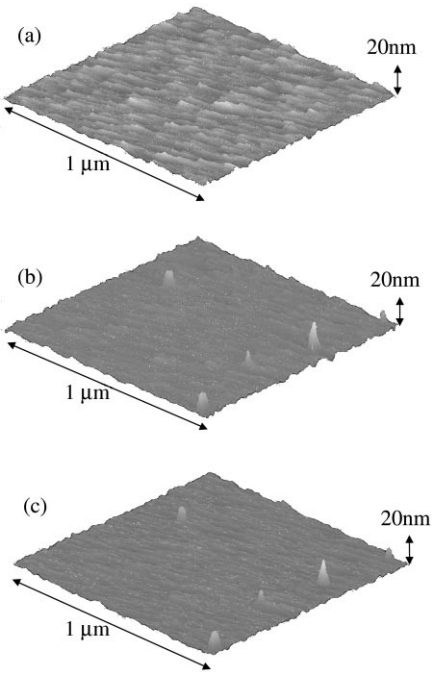

Fig. 1. AFM images taken as a function of time after the growth. CdSe deposition thickness was 2 ML and was grown directly on GaAs (1 0 0) surfaces. Those images are from the same area on the uncapped sample surface. (a), (b) and (c) were taken 60, 80 and 100 min after the growth, respectively.

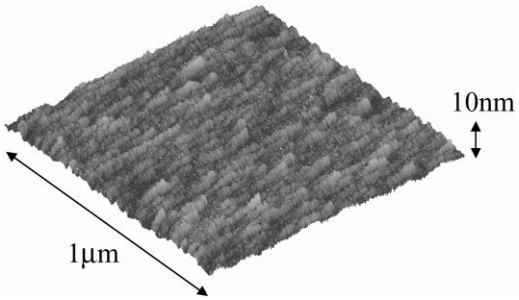

Fig. 2. AFM image of GaAs (1 0 0) surface. GaAs substrate was heated at high temperature of 600°C for 10 min in H_2 ambient.

The low dots could be seen clearly in Fig. 1(a) and disappear gradually in Fig. 1(b) and (c). Another kind was high dot with low density. The average diameter, height and density were 50, 13 nm and 5 dots per μm^2, respectively. Moreover, those high dots appeared only in Fig. 1(b) and (c), which were taken 80 and 100 min after the growth.

The critical thickness of the CdSe layer on GaAs is about 3 ML [11]. In the sample discussed above, only 2 ML of CdSe were deposited on the GaAs surface. Therefore, the thickness of CdSe layer did not reach the critical thickness to form quantum dots by releasing strain. Fig. 2 shows the GaAs surface that was heated at a high temperature of 600°C for 10 min in the H_2 ambient. The roughness observed by AFM was 0.6 nm. Compared with Figs. 1(a) and 2, we considered that the low dots were caused by GaAs surface undulation. However, after 60–80 min, the high dots appeared. The average diameter–height ratio is about 4, very close to the other II–VI quantum dots self-assembled under S–K growth mode [3,9,10,15]. Moreover, the average diameter and height are 50 and 13 nm, respectively. Those results are also very close to the average diameter and height of the other self-assembled quantum dots under S–K mode; such as 40 and 10 nm of CdSe/ZnSe [3]; 47 and 19 nm of CdSe/ZnSe on a ZnSe (1 1 1)A surface [9]; 80 and 20 nm of ZnSe/ZnS on GaP [10]; 47 and 10 nm of CdSe on GaAs (1 1 0) surface [15]. Therefore, we concluded that the high dots were self-assembled under S–K mode.

Why do the S–K mode self-assembled quantum dots form below the critical thickness and need so long time to release strain? For detail information, cross-sectional analysis is shown in Fig. 3, in which (a), (b), and (c) are the actual area as in Fig. 1(a)–(c). In Fig. 3, from (a) to (b), high dots were formed and the areas near the high dots were sunken. There was a trend for the low dots to disappear and the other areas tended to be smooth. From (b) to (c), the high dots did not show evident change. However, the areas near the high dots had risen again and the other areas tended to be smoother.

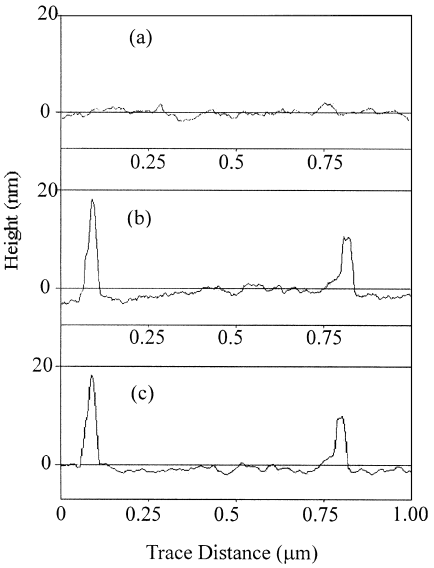

Fig. 3. Cross-section analysis of the AFM images, Panel (a), (b) and (c) were the actual area as in Fig. 1(a), (b) and (c), respectively.

The trend for the low dots to disappear and the sample surface to be smooth could be interpreted as the effect of surface diffusion. We considered that surface diffusion could result in parts of the sample surface to reach or exceed the critical thickness, and then release strain to form the self-assembled quantum dots on these parts of the sample surface. According to the theory of crystal growth, the surface of concave areas possesses lower surface vapor pressures (higher surface binding energies), and the surface of convex areas possess higher surface vapor pressures (lower surface binding energies). Therefore, the parts of higher surface vapor pressures continually migrate individual atoms or

molecules to the parts of lower surface vapor pressures [13,16]. Consequently, the concave area of surface will continually receive the individual atoms or molecules from the convex area. Then, the thickness of the concave area will tend to be thicker than the initial growth thickness and the surface will be smoothened over time. In our experiment, for 2 ML coverage of CdSe, it took 60–80 min for some concave area to reach the critical thickness (3 ML) and then released strain to form quantum dots. The formation of those self-assembled quantum dots required atoms or molecules from the nearby areas, thereby causing these areas to sink. At the same time, the surface diffusion still existed. The sunken area continually received atoms or molecules from the area of higher surface vapor pressures and rose again.

In addition, another sample was grown with 1 ML coverage of CdSe directly on the GaAs (1 0 0) surface by low-pressure MOCVD and was monitored constantly in the same area for several hours by AFM after the growth. Only the phenomena of surface diffusion could be observed. We did not find the formation of self-assembled CdSe quantum dots on this sample surface. We considered that the process of surface diffusion still existed in this sample, but the thickness of the concave area could not reach the critical thickness because the initial growth thickness of 1 ML was too thin. Then the process of releasing strain could not happen.

The formation process of self-assembled quantum dots under S–K mode has not been very clear until now. Most of the information on the formation process has come indirectly from RHEED patterns or theoretical simulation. By using AFM instrumentation, we can get direct information of the surface profile of the quantum dots. However, the process of releasing strain usually needs only several minutes or less and the time needed to take the sample out of the growth chamber and monitor it under AFM usually requires 1 h or more. Hence, we just get the information of quantum dots after they release strain and cannot get the direct information of how the wetting layer release strain to form the S–K mode quantum dots. As shown by our results, the slow process of surface diffusion compensates for the time that is needed for taking the sample out of the growth chamber and observing it under AFM. Therefore, it is possible to observe directly the process of releasing strain and to get the actual information on the formation process of self-assembled quantum dots by AFM.

4. Conclusions

We reported the formation process of self-assembled CdSe quantum dots below the critical thickness and concluded that the formation mechanism of CdSe quantum dots below the critical thickness was due to the effect of surface diffusion and release strain. Our results make it possible to observe directly the process of strain release and to get the actual information on the formation process of self-assembled quantum dots.

Acknowledgements

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