Formation of $ZnSe_{1-x}S_x$ quantum dots under Volmer–Weber mode

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$ZnSe_{1-x}S_x$ quantum dots (QDs) grown directly onto GaAs substrates in Volmer–Weber (V–W) mode by low-pressure metallorganic chemical vapor deposition (MOCVD) are investigated. The value of x is determined by the photoluminescence (PL) spectra. The formation of QDs was confirmed by atomic force microscopy (AFM) images. When the growth duration is short, the surface of the substrate is full of pyramid-like dots; while increasing the duration, another kind of dome-like dots with larger size appear. Meanwhile, the density of the dots decreases with increasing growth duration. The above facts are explained systematically taking into account the surface free energy. The PL characteristics of the dots are also assessed. With increasing growth duration, the emission peak of the dots shows an obvious red-shift, which is due to a decrease in quantum confinement effect.

1. Introduction

Numerous attempts have been made to grow semiconductor nanostructures, such as quantum well and quantum dots (QDs). Quantum dots are especially highlighted because they can provide three-dimensional (3D) confinement to electrons and excitons, thus providing lower threshold current density higher gains and higher quantum efficiency compared to 2D quantum wells and 1D quantum wires [1]. Several state-of-the-art methods have been applied to fabricate QD structures, high-resolution lithography combined with dry or wet etching [2, 3] and growth on masked substrates [4] are two cases in point. Unfortunately, such processes inevitably deteriorate the quality of the crystal. Recent reports on the growth under Stranski–Krastanow (S–K) mode offer possibilities for growing high quality QD structures [5–8]. However, growth under S–K mode needs precise control over the growth rate and the film thickness, which is arduous for some growth systems such as vapor phase epitaxy (VPE), hot wall epitaxy (HWE), metallorganic chemical vapor deposition (MOCVD) and so on. Furthermore, growth under S–K mode requires a large lattice mismatch between epilayer and substrate. Therefore, it cannot be applied to grow low sulfur content ZnSeS QDs on GaAs substrates (lattice mismatch between $ZnSe_{0.88}S_{0.12}$ and GaAs $< 0.3\%$). In the present paper, a relatively simple method, Volmer–Weber mode, in which a rough layer was introduced first, and then the QDs were formed on the rough surface, was carried out to fabricate $ZnSe_{1-x}S_x$ QDs by MOCVD. ZnTe and ZnSe QDs structure have been grown successfully under this growth mode [9–11]. However, the formation process was not available at all. In this paper, the formation process of the QDs was also studied preliminarily from the surface morphologies and photoluminescence characteristics.

2. Experimental

The samples were prepared on GaAs (100) substrates in a horizontal low-pressure MOCVD system at 350 °C, and the growth pressure was fixed at 210 mm Hg. The precursors were dimethylzinc (DMZn) hydrogen sulfide (H_2S) and hydrogen selenide (H_2Se), respectively. The growth rate determined by the scanning electron microscopy (SEM) was 13 Å/s for the growth of the ZnSeS layers. The GaAs substrates were chemically polished in $H_2SO_4 : H_2O_2 : H_2O = 3:1:1$ at 40 °C, and then boiled in hydrochloric acid. After being loaded into the reaction chamber, the substrates were annealed at 600 °C in hydrogen ambience for 10 min to avoid the gallium, and arsenic oxide layer. The surface morphologies of our samples were characterized by atomic force microscopy (AFM). The photoluminescence (PL) spectra were excited by the 325 nm line of a He–Cd laser at room temperature and the signals were measured by a Jobin–Yvon-630 micro-Raman spectrograph.

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3. Results and discussion

The PL spectra of $ZnSe_{1-x}S_x$ and ZnSe at room temperature are shown in Fig. 1. The near-band edge emission peaks are located at 2.753 and 2.70 eV, respectively. According to Ebina *et al*. [12]:

$$E_g(x) = E_0 + 0.352x + 0.63x^2 \qquad (1)$$

where E and E_0 are the emission peak positions of $ZnSe_{1-x}S_x$ and ZnSe, respectively. Therefore, we can deduce the following formula:

$$x = -0.279 + \sqrt{0.078 + (E - E_0)/0.63} \qquad (2)$$

Based on the above equations, the x value in our samples is 0.123, which is in good agreement with the value ($x = 0.12$) obtained from X-ray diffraction patterns (not given in this paper).

Fig. 2 shows the AFM images of $ZnSe_{0.88}S_{0.12}$ grown directly on GaAs (1 0 0) substrates. The growth rate is fixed at 13 Å/s, and the growth durations of samples A, B, C, and D are 0, 2, 3, and 4 s, respectively (Fig. 2). The root mean square (RMS) roughness values are 0.6, 0.43, 0.75, and 0.88 nm, respectively. This indicates that when the growth time is short, namely the coverage of the substrate is small, the epilayer mainly fills in the fluctuations of the substrate's surface and the QDs are formed there [13], but when the substrate coverage is large, islands are mainly formed by coalescence of the ZnSeS epilayer [14]. Consequently, the RMS of the samples decreases slightly at first, and then increases with the increase of the growth duration. Also from the AFM images, we can see that when the growth duration is 2 s, the surface is full of high-density, small-sized acicular dots. When the growth duration is 3 s, another kind of dot with relatively larger size appears. On further increasing the growth duration to 4 s, the dots grow bigger, and the density becomes lesser, which agrees well with what has been seen in InAs and InGaAs systems [15, 16], though no explanation was given. Here, we think the above phenomena can be interpreted in the following way.

Suppose there are two kinds of islands on the surface of the substrate, and for simplicity, they are spherical. Their radii are r_1 and r_2, respectively, so they have a surface free energy of $G_S = 4\pi r_i^2$, $(i = 1, 2)$. The number

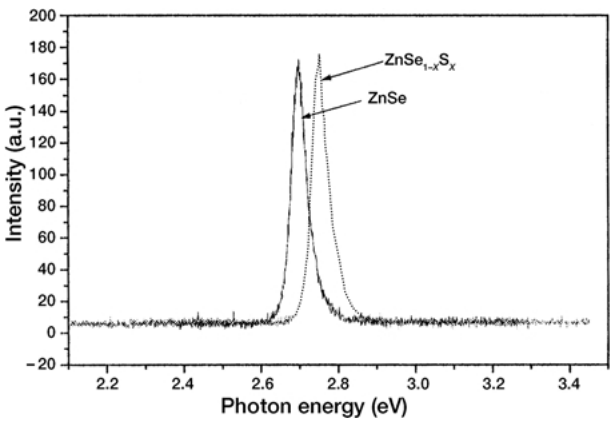

Figure 1 Typical PL spectra of $ZnSe_{1-x}S_x$ and ZnSe epilayers grown on GaAs substrate at room temperature.

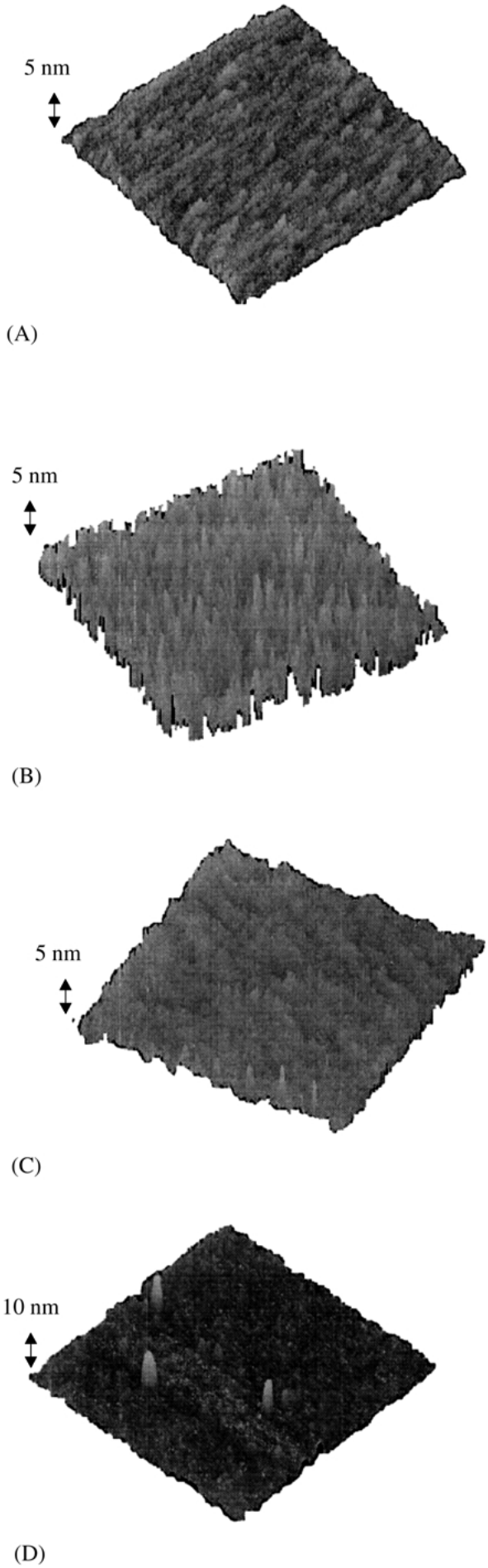

Figure 2 2 × 2 μm surface morphologies of the $ZnSe_{0.88}S_{0.12}$ QDs with growth duration: (A) 0 s, (B) 2 s, (C) 3 s, (D) 4 s assessed by AFM (note that the vertical scale of D is different from the others).

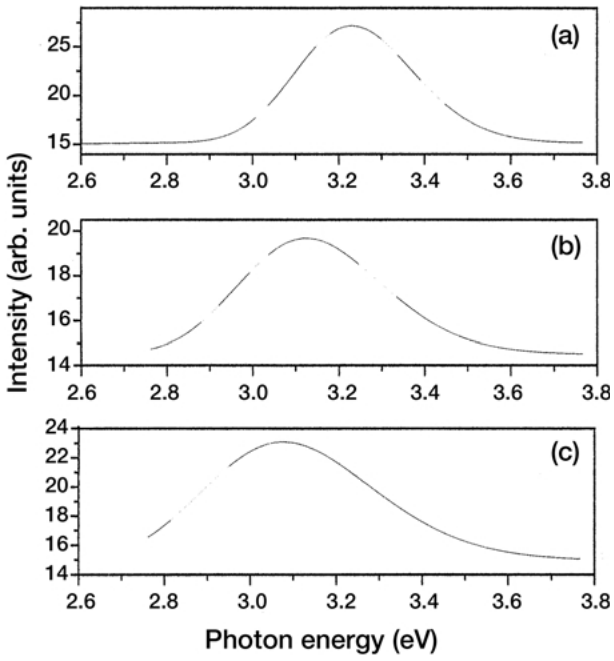

Figure 3 The PL spectra of $ZnSe_{0.88}S_{0.12}$ QDs with different growth durations at room temperature. (a) 2 s, (b) 3 s, (c) 4 s with the growth rate fixed at 13 /s.

of the atoms on the surface of the two islands is $n = 4\pi r_i^3/3\Omega$, where Ω is the volume of an atom. There is an increase in surface free energy when an atom is added to an island:

$$\mu_i = \frac{dG_s}{dn_i} = \frac{2\gamma\Omega}{r_i} \quad (i = 1, 2) \tag{3}$$

where γ is the surface energy per unit area. The free energy of an atom can be rewritten:

$$\mu_i = \mu_0 + kT \ln a_i \tag{4}$$

where μ_0 is the standard free energy and a_i is the activity of the two kinds of islands. Based on Equations (3) and (4), the activity of the atoms in r_i can be written in the following form:

$$a_i = a_\infty e^{\frac{2\Omega\gamma}{r_i kT}} \tag{5}$$

where a_∞ is the activity of the atoms in an infinitely large island. We can see from the formula that the smaller the islands, the larger the activity, thus, they have a higher equilibrium evaporation pressure. Therefore when two islands with different sizes are in neighborhood, the smaller one has the tendency to self-evaporate because of its higher equilibrium evaporation pressure. Being in the supersaturated surroundings, the larger one with lower evaporation pressure will absorb the evaporated atoms and becomes larger, while the smaller island will disappear gradually. When the growth duration is short, 2 s for example, the coverage of the substrate is low, the islands are so sparse that they have little possibility to interact with others. When the growth duration is long, the density of the island becomes smaller, and the islands with larger size will annex the smaller ones according to the theory described above. Also from the above theory, we can understand why the shape of the dots changes from pyramid-like to dome-like. The results obtained from the AFM images is also verified by the PL spectra which we shall now describe.

The typical PL spectra of $ZnSe_{0.88}S_{0.12}$ dots with different growth durations are shown in Fig. 3. As can be seen, the peak positions of samples with 2 s, 3 s, and 4 s growth duration are 3.23 3.12, and 3.08 eV, respectively. The full width at half maxim (FWHM) of the spectra are 273, 326, and 382 meV, respectively. The blue-shift with the decrease of the growth duration can be explained by the effect of quantum confinement effect [11]. Shorter ZnSeS growth duration results in dot size reduction, the reduction in dot size, in turn, enhances the quantum confinement effect, and increases the blue-shift accordingly. As for the large FWHM, we believed it mainly derives from the broad size distribution of the dots. Other parameters such as fluctuations in the sulfur composition, or coherent strain relaxation can also contribute to the broadness of the spectra [17].

4. Conclusions

$ZnSe_{1-x}S_x$ QDs have been grown successfully in Volmer–Weber mode by MOCVD. The value of x obtained from the PL spectrum agrees well with the one determined from XRD. The AFM images were used to illustrate the formation of the QDs. While on increasing the growth duration, the size of the dots becomes larger and the density decreases, which is explained by virtue of the surface free energy. The PL spectra taken by a micro-Raman spectrograph was also used to access the dots. The PL spectra shift significantly to the lower energy side with an increase in the growth duration, which is assigned to a decrease in the quantum confinement effect.

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