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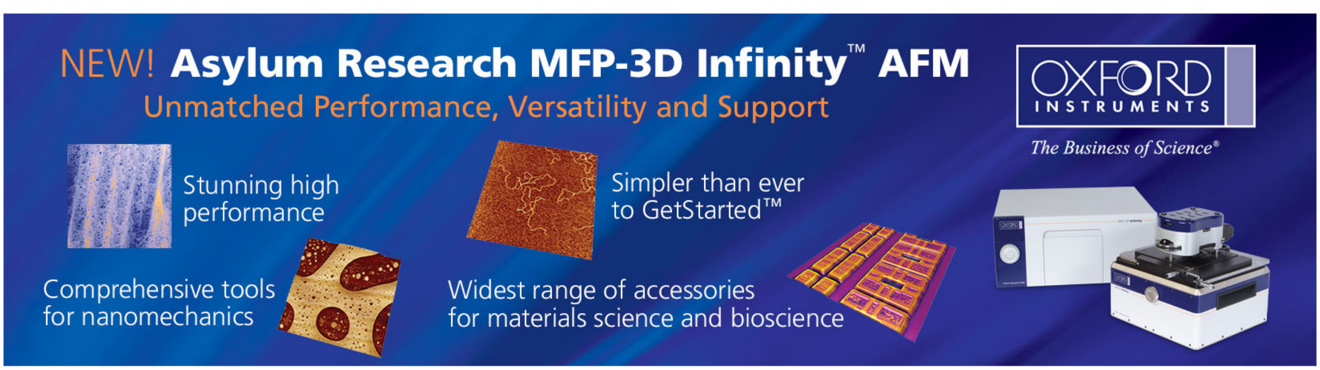

Effect of ZnSe partial capping on the ripening dynamics of CdSe quantum dots

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The ripening dynamics of CdSe quantum dots (QDs) partially capped with ZnSe layer are investigated. Atomic force microscopy (AFM) images show that the ripening of QDs is dramatically accelerated by depositing a ZnSe partial capping layer. The driving force of ripening enhancement is attributed to the increasing strain energy with capping thickness. For a ZnSe partial capping layer of below 3 ML, photoluminescence exhibits a clear redshift with increasing ZnSe monolayers. It is attributed to the size of the CdSe QD increases with ZnSe partial capping, in a manner that is consistent with the results of the AFM study. © *2007 American Institute of Physics*.
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II-VI semiconductor quantum dots (QDs) have attracted great attention due to their fascinating optical properties, interesting growth dynamics, and potential application in light-emitting devices.[1–6] One of the important issues regarding the growth mechanism of self-assembled QDs is the stability of islands after the growth has ended. The equilibrium calculations predict that the island stability depends on the amount of deposited material. A surface coverage window exists in which stable (nonripening) QDs may survive.[7,8] For surface coverage beyond the window, the islands undergo morphological changes with time. A significant change in the size and density of CdSe QDs with time was observed by atomic force microscopy (AFM).[2,9] This behavior is regarded as ripening of QDs. The dynamic of the ripening process was interpreted in terms of Ostwald ripening.[10,11] The ripening phenomenon was also investigated in different systems.[12–14] However, the effects of substrate temperature or capping thickness have not yet been reported.

In this letter, we investigate the ripening dynamics of CdSe QDs covered with several monolayers of the ZnSe capping layers. The final morphology and optical properties depend on the coverage of the ZnSe partial capping. The mechanism of ripening depending on the thickness of the partial capping layer is discussed. Our model indicates that the enhancement factor of ripening is an exponential function of the partial capping thickness.

The CdSe/ZnSe QDs were grown on GaAs (001) substrates at 260 °C by molecular beam epitaxy (MBE).[15] After the growth of QDs, a subsequent interruption of 2 min at 260 °C allowed the ripening of QDs to proceed. Following the 2 min interruption, a thin ZnSe capping layer, which is thinner than the dot height (so-called partial capping), was deposited. Finally, a 2 min annealing process was carried out at the same temperature to proceed the enhanced ripening. Then, the sample was immediately cooled and removed from the MBE chamber. For photoluminescence (PL) measurements, a 50-nm-thick ZnSe layer was deposited on top of the ZnSe partial capping layer. The surface morphology of QDs was investigated using contact mode AFM. The optical characteristics were studied using a TRIX 550 spectrometer with a spectral resolution of 0.2 meV.

Figure 1(a) shows the morphology of a representative CdSe QD from the uncapped sample. The average diameter D=79.5 nm and height H=6.81 nm of the QDs were the average of several scans from different areas. A previous report confirmed this QD formation in ripening (R_2) mode.[15] The size and density of the three-dimensional dots change with time. Figures 1(b)–1(d) show AFM images of the representative CdSe QDs capped with ZnSe layers of various thicknesses from 1 to 3 ML. Notably, the dot size increased from Figs. 1(a)–1(d), and the aspect ratios for the QDs par-

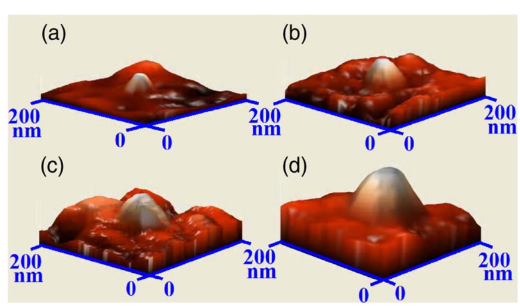

FIG. 1. (Color online) Typical AFM images of CdSe QDs samples capped with ZnSe layers of (a) 0, (b) 1, (c) 2, and (d) 3 ML. The temperature for ZnSe capping was 260 °C.

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TABLE I. Size and density of the uncapped and partially capped CdSe QDs observed from AFM images.

Partial capping (ML)	0	1	2	3
Height (nm)	6.8	7.5	8.1	10.0
Diameter (nm)	79.5	88.1	96.8	118.5
Density (10^8 cm^{-2})	9.8	3.5	2.1	1.8

tially capped with different ZnSe coverages were similar. Table I summarizes the average size and density of the partially capped and uncapped dots. The dot height/density increases/declines as the thickness of the ZnSe partial capping layer increases, revealing that a large amount of mass transportation occurs after the ZnSe partial capping was deposited. The dot transformation is very sensitive to the thickness of the partial capping from 1 to 3 ML, indicating that the ripening rate of partially capped dots exceeds that of uncapped dots. Namely, the ripening rate of CdSe QDs was significantly enhanced by the ZnSe partial capping at 260 °C.

In Fig. 2, the dot height (H) was analyzed as a function of the in-chamber annealing time (t) using the theory of Ostwald ripening to elucidate further the dynamics of the observed ripening effect. At $t=0$, the deposition of CdSe QDs was just completed. From $t=0$ to 2 min, the QDs undergo the ripening process. ZnSe partial capping layers of various thicknesses were deposited at $t=2$ min to accelerate ripening. This process took only about 10 s, depending on the thickness of ZnSe partial capping. The sample was maintained at 260 °C for 2 min (from $t=2$ to 4 min) to undergo enhanced ripening before it was cooled to make AFM measurements. The Ostwald ripening predicts that if the limiting factor for mass transfer involves a kinetic surface barrier to the detachment of the atom from the edge of the island, then $H(t) \sim t^{1/3}$.[2,10] For CdSe QDs without in-chamber annealing, the average dot height at $t=0$ is about $H_0=5.4$ nm. Curve A describes the ripening process of CdSe QD without ZnSe capping for $t=0-2$ min. Curve A connects $H(t=0)=H_0=5.4$ nm to $H(t=2)=6.8$ nm. The equation for curve A is

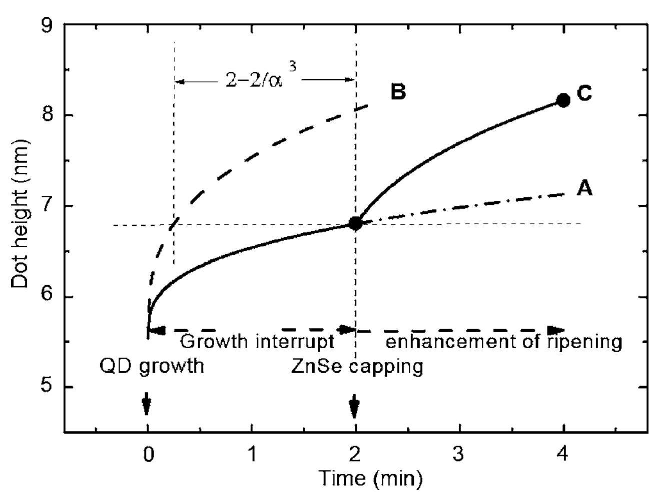

FIG. 2. Dependence of dot height on time. Curve A (dashed dots) expresses Eq. (1). Curve B (dashed line) represents the ripening of a QD which has a faster ripening rate. Curve C (solid line) describes Eq. (3).

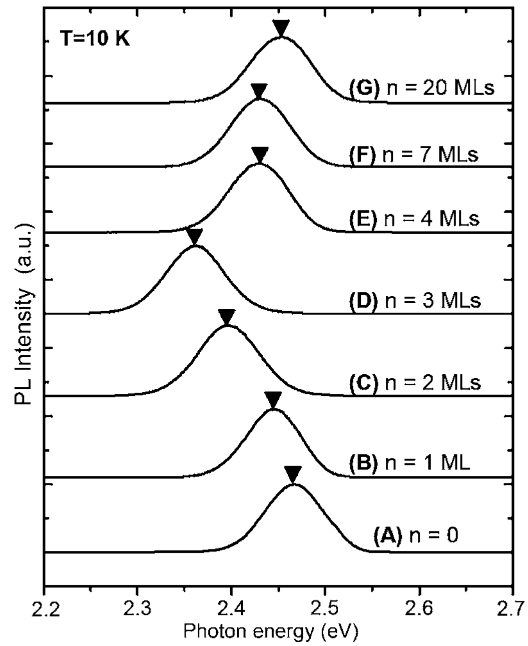

FIG. 3. PL spectra from the CdSe QDs with ZnSe partial capping (n) of samples (A) 0, (B) 1, (C) 2, (D) 3, (E) 4, (F) 7 to (G) 20 ML.

$$H(t) = H_0 + V_0 \times t^{1/3}, \quad (1)$$

where V_0 corresponds to the ripening rate of the uncapped QDs.

Consider the enhancement in the ripening rate due to the presence of the partially capped ZnSe layer. Curve B in Fig. 2 represents the enhanced ripening of CdSe QDs with a 2-ML-thick ZnSe partial capping, given that the ZnSe partial capping was completed at $t=0$. The equation for curve B is

$$H(t) = H_0 + V \times t^{1/3}, \quad (2)$$

where V corresponds to the ripening rate of partially capped QDs. However, in this work, the ZnSe partial capping layer was deposited 2 min after QD formation. Therefore, the equation describing the increase in the dot height after the deposition of ZnSe partial capping ($t=2-4$) should be modified as

$$H(t) = H_0 + V\left[t - \left(2 - \frac{2}{\alpha^3}\right)\right]^{1/3}, \quad (3)$$

where α is an enhancement factor, defined by $\alpha = V/V_0$. The term $(2-(2/\alpha^3))$ denotes the difference between the times required on curves A and B for the dot height from H_0 increases to 6.8 nm. Curve C plots Eq. (3) for $t=2-4$, which was obtained by shifting curve B by $(2-(2/\alpha^3))$. Consequently, the variation of dot height could be completely described by the solid line in Fig. 2. The ripening rates for the samples that were partially capped with ZnSe layer of 1 and 3 ML were $1.5V_0$ and $3.8V_0$, corresponding to the enhancement factors of $\alpha=1.5$ and 3.8, respectively.

Figure 3 displays the PL spectra of samples with ZnSe partial capping coverage of various thicknesses at 10 K. The samples with partial capping with a thickness below 3 ML exhibit a strong redshift, revealing that the dot size increases with the coverage of partial capping. However, when the coverage of partial capping exceeds 4 ML, only a small redshift occurs in the PL peak energy. If the QDs are covered with a thick capping layer, then atomic migration will be

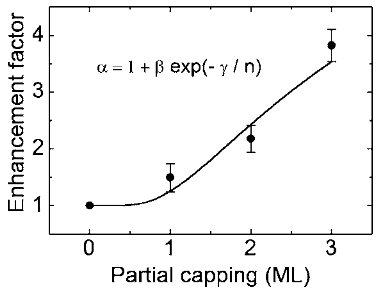

FIG. 4. Dependence of the enhancement factor on the coverage of partial capping. The solid line simulates Eq. (5). The error bars represent the accuracy in the AFM measurements.

significantly suppressed, and the ripening rate is substantially reduced. Therefore, the redshifts in samples E (4 ML) and F (7 ML) are less than that of sample D (3 ML). As the coverage of partial capping further increases to 20 ML (sample G), the ripening process is fully suppressed by the existence of thick capping layer. Hence, the peak energy of sample G is very close to that of the uncapped sample A, as shown in Fig. 3.

The rates of atomic detachment and attachment are governed by the energy barrier at the edge of the ripened quantum dots. Strain lowers the energy barrier for atomic diffusion.[8] As a result, the increasing thickness of partial capping raises the strain energy and accelerates the ripening. Therefore, the ripening rate of QDs can be artificially controlled by tuning the strain energy through thickness manipulation of capping layer. The strain energy (ε) can be related to the coverage of capping layer (n) by

$$\varepsilon(n) = \varepsilon_i + (\varepsilon_f - \varepsilon_i)\exp\left(\frac{-k}{n}\right), \tag{4}$$

where k is a fitting parameter which corresponds to the degree of dependence of ε on n. Without ZnSe partial capping (n=0), the strain energy of QDs is ε_i. The strain energy increases with the coverage of the capping layer. However, it converges to a limiting value ε_f at high coverage of partial capping. An exponential function that is similar to Eq. (4) is applied to fit the dependence of the enhancement factor on the coverage of partial capping, as shown in Fig. 4. The results could be fitted very well by

$$\alpha(n) = 1 + \beta\exp\left(\frac{-\gamma}{n}\right), \tag{5}$$

where β and γ are the fitting parameters. Equation (5) describes a strong increase in the enhancement factor α at low partial capping coverage and agrees nicely with the presented results. However, for partial capping that exceeds a thickness of 4 ML, atomic migration for the ripening process is significantly suppressed, making ripening more complicated that is out of our assumption and discussion.

In conclusion, we performed AFM and PL studies of a series of CdSe QDs with partially capped ZnSe layers of various coverages. The AFM images offer clear evidence that the coverage of partial capping is important to ripening. The enhancement factor of ripening is an exponential function of the partial capping coverage. Furthermore, the PL measurement corroborates the AFM study. These results strongly support the fact that ZnSe partial capping enhances the ripening of CdSe quantum dots.

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