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Mechanism for coarsening of P-mediated Ge quantum dots during in-situ annealing

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Abstract

The coarsening of phosphorus-mediated Ge quantum dots (QDs) on Si(0 0 1) during in-situ annealing at 550 °C is studied. In-situ annealing makes the as-grown sample morphology be remarkably changed: the larger dots are formed and the dot density is greatly reduced. The results of chemical etching and Raman spectra reveal that the incorporation of Ge atoms which originate from the diminishing dots, rather than substrate Si atom incorporation is responsible for the dot coarsening at the incipient stage of in-situ annealing. Besides, Raman spectra suggest that the larger dots formed during in-situ annealing are dislocated, which was confirmed by cross-sectional high-resolution electron microscopy observation. Through the generation of dislocations, the strain in the dots is relaxed by about 50%.

Keywords: Molecular beam epitaxy (MBE); Quantum dots; Coarsening; Silicon–germanium

1. Introduction

Self-assembled Ge quantum dots (QDs) have attracted great interest in the past decades because of their potential applications in optoelectronic and few-electron devices [1]. However, quantum-sized QDs with high density and high size uniformity are remarkably desired but still difficult to obtain. Adding a third species, such as C, B, Sb and P, during deposition may change dot morphology and structure [2–6]. Thermal treatment after deposition can further modify these properties [7,8]. In our last work [6] we have reported the formation of small-size, highly uniform self-assembled Ge QDs with an area density of $1.4\times10^{11}\,\mathrm{cm}^{-2}$ in the presence of 0.1 ML pre-deposited P atoms. In this paper, the coarsening of phosphorus-mediated Ge QD during in-situ annealing is studied. We found that the rapid dot coarsening at the beginning of in-situ annealing is mainly due to the lateral mass transport of Ge atoms. During in-situ annealing, the misfit dislocations are generated in some larger dots, which further favors the growing up of these dots from a strain energy point of view.

2. Experimental

The samples were prepared in a Riber EVA-32 molecular beam epitaxy (MBE) system with two electron beam evaporators for Si and Ge, respectively. A GaP decomposition cell was used as the P source, which has a specially designed Ga-capture cap to separate the parasitic Ga atoms from P_2 beam [9]. The base pressure of the system was lower than 5×10^{-10} Torr. p-type Si(0 0 1) wafers with resistivity of 1–10 Ω cm were used as substrates and chemically cleaned by the Shiraki method [10]. After the thin protective oxide layer being desorbed at 1000 °C, a sharp 2×1 surface reconstruction was observed by the in-situ reflection high-energy electron diffraction (RHEED). Then a 50-nm-thick Si buffer layer was grown at 650 °C, followed

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by the deposition of 0.1 ML P atoms at 500 °C. Finally 1.7 nm Ge was deposited at 550 °C. The growth rates of Si and Ge were 0.08 and 0.015 nm/s, respectively. For as-grown sample, the sample temperature was immediately cooled down to room temperature after finishing Ge deposition in order to limit physical processes such as atomic surface diffusion. For in-situ annealed samples, the sample temperature was kept at the Ge growth temperature of 550 °C for 2, 10 and 20 min, respectively before cooling down to room temperature.

Sample morphology was analyzed by atomic force microscopy (AFM) using the contact mode in air. Ge composition was determined by Raman spectra in $00\bar{1}(100, 010)00\bar{1}$ back scattering geometry with an excitation of 514.5 nm line of Ar^+ laser. The second-order transverse acoustics phonon mode of Si at 303 cm^{-1} from Si substrate is suppressed in this scattering geometry [11]. Dot microstructure was further inspected by cross-sectional high-resolution electron microscopy (HREM), which was carried out using a 400-keV JEOL-4010 transmission electron microscope (TEM).

3. Results and discussion

Fig. 1 shows AFM images of the as-grown and in-situ annealed samples. As shown in Fig. 1(a), the as-grown sample has a very uniform dot size distribution and high dot area density. The averaged base diameter is 32 nm by AFM [6], but it is often enlarged by the finite tip-radius convolution effects. Cross-sectional TEM observations show no structural defect in these dots, and the averaged dot diameter and height are about 24 and 5 nm, respectively. After annealing for 2 min Fig. 1(b), some very large dots with base sizes of around 100 nm are formed and dot size distribution becomes multimodal. At the same time dot density is much reduced. With increasing annealing time, both the large dots and the small dots grow bigger and the dot density decreases further, as shown by Fig. 1(c) and (d). Fig. 1(e) shows the dot density as a function of in-situ annealing time. The solid line is an exponential decay fit with a time constant of 1.3 ± 0.2 min.

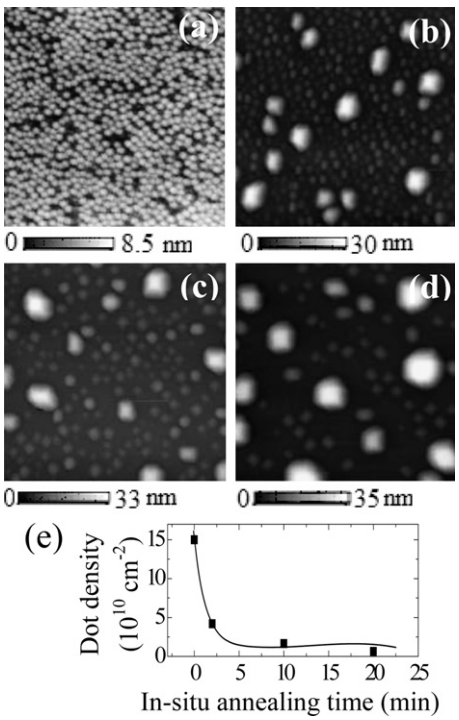

Fig. 1. AFM images (1×1 μm^2) of the as-grown sample (a) and samples in-situ annealed for 2 min (b), 10 min (c), and 20 min (d) after finishing Ge deposition, respectively. (e) Dot area density vs. in-situ annealing time at growth temperature of 550 °C. The solid line is an exponential decay fit with a time constant of 1.3 ± 0.2 min.

A natural question following this result is: what are the phenomena controlling this change of morphology during in-situ annealing? There are two processes most likely involved during in-situ annealing: the coalescence of small dots via surface migration of Ge atoms between dots, and substrate Si atom incorporation into dots due to atomic intermixing. In order to make clear which process plays a major role in the evolution of dot morphology, samples were investigated by selective wet chemical etching experiments and Raman scattering measurements.

Chemical etching experiments were performed at room temperature for 20 min using 30% H_2O_2, which can selectively remove GeSi material with Ge composition higher than $65 \pm 5\%$ and stop at this Ge composition [12]. The reliability of etching experiment was checked by etching the samples for different periods of time (from 2 to 25 min), and no significant differences were found in the morphologies of the etched samples with an etching time longer than 15 min. The etching result shows that dots are almost completely etched away for the as-grown sample, leaving a quite flat surface, indicating that Ge composition in as-grown dots is higher than $65 \pm 5\%$. However, some residual matter is left on the surface of the sample annealed for 2 min, and much more residual matter is left on the surfaces of the samples annealed for 10 and 20 min. Fig. 2(a) and (b) show AFM images of 2- and 20-min annealed samples after etching, respectively. This etching result indicates a lower Ge composition at certain regions of dots after annealing, which is obviously due to the intermixing of Si atoms into Ge dots during annealing. The Si atoms are mixed into the Ge dots via surface-mediated effect as stated before [13]: first the Si atoms from subsurface

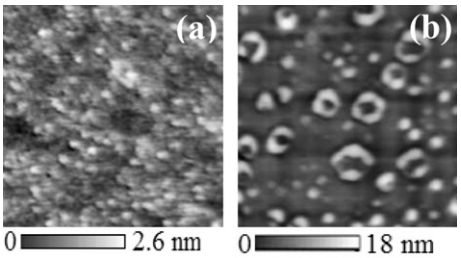

Fig. 2. AFM images (1×1 μm^2) of the 2-min (a) and 20-min (b) in-situ annealed samples after etching.