Molecular-beam epitaxy growth of site-controlled InAs/GaAs quantum dots defined by soft photocurable nanoimprint lithography

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Molecular-beam epitaxy grown InAs site-controlled quantum dots (SCQDs) have been demonstrated on GaAs substrates patterned with a dense array of 100 nm square nanopores in 200 nm pitch by soft photocurable nanoimprint lithography. The effects of different growth parameters, including GaAs buffer-layer thickness and arsenic overpressure, on SCQD formation are investigated. The buffer-layer thickness is found to be an influential factor affecting homogeneous quantum dot (QD) formation under a certain pore depth. After GaAs buffer-layer deposition with a suitable thickness, a single QD has been achieved in each patterned nanopore. Under an optimal arsenic overpressure, more uniformly distributed SCQDs have also been shown, confirmed by a narrower photoluminescence linewidth. Strong room-temperature photoluminescence indicates a high optical-quality QD layer on a defect-free interface. © 2010 American Vacuum Society. [DOI: 10.1116/1.3414824]

I. INTRODUCTION

Extensive research has been done on site-controlled quantum dots (SCQDs) through the years due to the advantages of improving QD size homogeneity and controlling QD nucleation position. So far, SCQDs have been reported through the growth on patterned substrates prepared by electron-beam lithography (EBL) and focused-ion beam (FIB) lithography. Photoluminescence (PL) spectra of SCQDs have only been reported either at low temperature ranges below 10 K (Ref. 1) or at room temperature from the top layers of vertically stacked QDs grown on a SCQD layer. Devices with improved optical performance have not been demonstrated. Surface damage caused by high-energy beams used in these patterning techniques is the main cause for the poor optical quality. Damage areas around QD nucleation sites act as nonradiative recombination centers and thus degrade optical quality of subsequently grown QDs. Furthermore, due to the serial nature of EBL and FIB lithography, the cost is excessive if large-area devices need to be fabricated. To overcome these problems, a new approach has been demonstrated by utilizing soft photocurable nanoimprint lithography (soft NIL) to create patterns of uniform nanoscale sites for QD growth. Details of soft NIL processing procedures have been described previously. In this study, we explore the characteristics of SCQD formation on soft NIL-patterned GaAs substrates by varying growth parameters, including buffer-layer thickness and arsenic overpressure, to gain insight into SCQD evolution. Surface morphologies, as well as photoluminescence spectra, are presented and discussed.

II. EXPERIMENT

The substrate used in this work was a (100) semi-insulating GaAs wafer. It was patterned by soft NIL before epitaxial growth of InAs QDs. The GaAs substrate was first coated with 50 nm silicon dioxide followed by an ultraviolet-curable photoresist (PR) of ~120 nm thickness. Next, the soft NIL technique was used to replicate the designed pattern in the silicon dioxide and PR layers (see Ref. 4 for details). Then the pattern was transferred to the GaAs substrate by wet etching, using a solution of ammonium, hydrogen peroxide, and de-ionized water mixture. Lastly, silicon dioxide with residual PR was stripped by hydrofluoric acid under ultrasonic agitation. In order to achieve high QD quality, a set of cleaning steps was carried out on all patterned samples before molecular-beam epitaxy (MBE) growth. After an oxygen plasma and degreasing treatment, hydrochloric acid and sulfuric acid etching were then applied in sequence to remove the surface oxides and passivate the surface, respectively. Afterward, samples were mounted on a molybdenum (Mo) puck with high-purity indium and loaded into a MBE system equipped with a valves arsenic-effusion cell.

In order to preserve the nanoscale patterns, the low-temperature atomic hydrogen-assisted desorption approach was chosen instead of conventional thermal desorption to desorb the GaAs native oxide. During the desorption process, thermally cracked atomic hydrogen was applied for 1 h with the samples held at 480 °C. GaAs and InAs layer thicknesses were controlled by the deposition time and reported in equivalent monolayer coverage. Arsenic overpressure was measured by a flux monitor at the growth position. After desorption, all samples were grown at 500 °C covered with GaAs buffer layers of various thicknesses. Then, 3 ML (monolayer) of InAs was deposited with a growth rate of 0.014 ML/s at the same temperature. After the deposition of the InAs QD layer, a 120 s growth interruption under a constant arsenic flux was inserted to enhance the formation of QDs. Finally, the sample was cooled to room temperature for surface morphology characterization and PL measurements.

A Digital Instruments 3100 atomic force microscope (AFM)
III. RESULTS AND DISCUSSION

The imprint pattern used in this study was a square array of 100 × 100 nm² nanopores on a 200 nm pitch, yielding an array density of 2.5 × 10⁹ cm⁻². Using imprint technology, higher array density is achievable and has been demonstrated using a 40 nm pitch.⁶ Figure 1 shows the AFM image of a nanopore array patterned on GaAs using wet etching. The image is 5 μm on a side. Patterns with low defect density and high fidelity were transferred from the silicon master into GaAs over a large area. Since the initial dimension of nanopores was proved to affect single-dot occupancy,⁷ an etching depth of only 15 nm was chosen to prevent widening of nanopores in the lateral direction caused by the isotropic wet etching step.

Figure 2 shows the AFM line scans, which were averaged over five different locations on the same samples, of nanopores prior to QD regrowth, after atomic hydrogen cleaning at 480 °C, and after 10, 30, and 50 ML GaAs buffer-layer depositions. Prior to and after atomic hydrogen-assisted cleaning, AFM line scans are similar, confirming the preservation of patterns after the desorption process. With the substrate temperature increased to 500 °C for the deposition of the GaAs buffer layers with various thicknesses, the edges of nanopores began to get blunt and the bottoms filled up, which is quite similar to the evolution of patterns on a microscale reported by Kan et al.⁸ The average pore depth decreased from an initial depth of 13.5 to 8.5 nm after 50 ML buffer-layer deposition, accompanying a sidewall-angle reduction measured relative to the nanopore bottom surface from 25.5° to 6.4°.

Figure 3 illustrates the variation in surface morphologies after QD regrowth as a function of GaAs buffer-layer thicknesses. The thicknesses of deposited GaAs buffer layers are 10, 30, and 50 ML, corresponding to Figs. 3(a)–3(c), respectively. For all samples, 3 ML of InAs was grown right after buffer-layer deposition and the arsenic overpressure during QD regrowth was kept at 5 × 10⁻⁷ torr. First of all, no QDs are observed on the surface between nanopores, suggesting that the growth conditions for SCQD regrowth are appropriate. Second, as shown in Fig. 3(a), some small dots are found inside each nanopore if only 10 ML GaAs is deposited prior to QD regrowth. This result indicates that a thin buffer layer is not enough to smooth out the surface, leading to multiple nucleation sites at the nanopore bottoms, and therefore multiple InAs QDs form accordingly. However, if the buffer-layer thickness is increased to 50 ML, overgrown nonuniform QDs as well as unoccupied nanopores are observed, as seen in Fig. 3(c). When the average depths of nanopores reduce with increasing buffer-layer thickness, the chemical potential difference between the top and bottom of a nanopore gradually lessens. Eventually, In adatoms will no longer be confined within a nanopore due to insufficient lateral constraint during QD regrowth.⁹ Consequently, In adatoms will migrate to nucleation sites with the least surface energy, rather than be uniformly distributed in each nanopore. Under this circumstance, the uniformity of QDs will be mainly determined by growth parameters, instead of defined patterns. In contrast, when the buffer-layer thickness is suitable, small QDs will then coalesce into a single QD due to a preferential migration toward the bottom of the nanopore driven by the...
surface curvature. As seen in Fig. 3(b), after deposition of 30 ML GaAs, uniform SCQDs are demonstrated. Based on this result, a buffer-layer thickness of 30 ML was chosen for the rest of this study.

Next, the effect of arsenic overpressures on SCQDs and self-assembled QD (SAQD) formation is shown in Fig. 4. Unpatterned epiready GaAs wafers were used as reference samples for SAQD growth and were mounted on the same Mo sample holder alongside the SCQD samples. Both samples were grown under the same growth condition simultaneously. In Figs. 4(a) and 4(d), the arsenic overpressure is $1 \times 10^{-6}$ torr and the dot density on SAQD sample is 43 $\mu m^{-2}$. Although a single dot forms in each patterned site, dot size distribution is broad. On the other hand, when the arsenic overpressure is decreased to $5 \times 10^{-7}$ torr, as shown in Figs. 4(b) and 4(e), a lower dot density of 24 $\mu m^{-2}$ on the SAQD sample is observed. This phenomenon is due to a longer diffusion length of In adatoms on the surface with decreasing arsenic overpressure. Moreover, the increase in diffusion length is also beneficial for more uniform SCQDs, as displayed in Fig. 4(b). However, if the arsenic overpressure is further reduced to $2 \times 10^{-7}$ torr, as shown in Figs. 4(c) and 4(f), there is no dot formation on the SAQD sample, while some small dots, which can barely be seen, are formed on the SCQD sample.

PL spectra of uncapped SCQD samples grown at different arsenic overpressures are shown in Fig. 5. No light emission from the SCQD sample grown at $2 \times 10^{-7}$ torr is observed, while room temperature PL spectra are detected from those grown at $5 \times 10^{-7}$ and $1 \times 10^{-6}$ torr. The PL linewidth of the SCQD sample grown at $5 \times 10^{-7}$ torr is 8% narrower than that grown at $1 \times 10^{-6}$ torr and is attributed to the more-uniform QD formation under lower arsenic overpressure, as observed in Fig. 4(b). The PL peak positions for SCQDs grown at arsenic overpressure $1 \times 10^{-6}$ and $5 \times 10^{-7}$ torr are 0.954 and 1.008 eV, respectively. The shift of the PL peak position results from the difference in QD heights grown at various arsenic overpressures. Although the growth temperature and the deposited InAs amount are identical for both samples, higher V/III ratio caused more abundant arsenic atoms to bond with incoming In atoms in the vertical direction and was thus more favorable for taller InAs QD formation, causing a smaller ground-state transition energy.

This is also confirmed from the AFM image in Fig. 4(a), in which several big and irregular dots can be clearly seen under the high V/III ratio growth condition. On the other hand, the integrated PL intensity of the SCQDs grown at $1 \times 10^{-6}$ torr is about two times higher than that of the SCQDs grown at $5 \times 10^{-7}$ torr, which requires further investigation. Lastly and most importantly, the PL linewidth from the SCQD sample is narrower than that from the SAQD sample grown simultaneously on an unpatterned GaAs substrate with comparable integrated PL intensities.

### IV. CONCLUSION

In summary, MBE-grown InAs site-controlled QDs have been demonstrated on (100) GaAs substrates patterned by soft photocurable nanoimprint lithography. By selecting proper GaAs buffer-layer thickness and arsenic overpressure, uniform QD arrays were achieved with a single QD at each designed nucleation site. Room-temperature PL spectra of SCQDs suggest defect-free and high quality QD growth. In addition, a narrower PL linewidth under optimal arsenic overpressure is also an indication of improved QD homogeneity. Combined with the advantages of low cost and high throughput of the NIL technique, SCQDs grown on soft NIL-patterned substrate are very promising to achieve highly uniform QDs with precise positioning and good optical quality for future device applications.

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