Smaller Ge Quantum Dots Obtained by ArF Excimer Laser Annealing*

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Abstract: Ge self-assembled quantum dots (SAQDs) are grown with a self-assembled UHV/CVD epitaxy system. Then, the as-grown Ge quantum dots are annealed by ArF excimer laser. In the ultra-shot laser pulse duration, ~20ns, bulk diffusion is forbidden, and only surface diffusion occurs, resulting in a laser induced quantum dot (LIQD). The diameter of the LIQD is 20~25nm which is much smaller than the as-grown dot and the LIQD has a higher density of about $6\times10^{10}cm^{-2}$. The surface morphology evolution is investigated by AFM.

Key words: Ge quantum dot; ArF excimer laser annealing; LIQD; AFM
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1 Introduction

Ge and SiGe self-assembled quantum dots (SAQDs) have been widely studied in the last two decades. The mismatch of 4.2% between Ge and Si causes a SiGe island and was proven to have no defects in 1990[1]. Ge and SiGe QDs have been the focus of research because nano-scale quantum dots can confine carriers in 3 dimensions. For example, quantum dots with small sizes can be used to fabricate single electron transistors (SET) by means of the Coulomb blockade effect. Large quantum dots can be used to fabricate 1.55μm infrared photodetectors. SiGe material can also have optical nonlinearity for the enhancement of the interface asymmetry of the type-II band structure[2]. But, the application of Ge and SiGe SAQDs is hindered because of the large size and low density of the islands. When growing Ge and SiGe SAQDs, the Stranski-Krastanow (S-K) mode is widely accepted and understood. In the S-K mode, the island is driven by the lattice mismatched strain. The size of the SAQD is usually large. The average diameter grown by the UHV/CVD system is about 80nm or even larger[3,4], which results in no obvious quantum confinement effect. The composition measured by XRD shows that all the SAQDs are SiGe islands due to the Ge and Si interdiffusion between the dots and the substrate. Recently, other methods for decreasing the diameter and enhancing the density have been proposed[5].

In this paper, we report that much smaller and higher density Ge excimer-laser-induced quantum dots (LIQD) have been obtained by the ArF excimer laser annealing of Ge films. The diameter of the Ge LIQD is 20~25nm and the density is $6\times10^{10}cm^{-2}$. In the laser annealing process, the thermal effect induced by the ArF excimer laser is simulated by ANSYS. The simulation results show that the short-distance surface diffusion leads to much smaller and higher density Ge LIQDs.

2 Experiments and setup

The Ge film was grown by an ultra high vacuum chemical vapor deposition (UHV-CVD) epitaxy system on the (001)-oriented silicon substrate. The substrate is a 100mm diameter (001) p-type Si wafer with a resistivity of 8~12Ω·cm. The wafer is processed with the RCA cleaning process: it is boiled in $H_2SO_4 : H_2O=4:1$ for 1 minute, rinsed in de-ionized water tens of times, boiled in $H_2O : H_2O_2 : NH_3\cdot H_2O = 5:2:1$ for several seconds, rinsed in HF for 30s, boiled in $H_2O : H_2O_2 : HCl=7:2:1$ for several seconds, boiled in $H_2O : HCl=8:1$ for a few seconds, rinsed in $HF : H_2O=1:10$ for several minutes, and finally rinsed in de-ionized water 30 times. After the RCA process, the thin native oxide on the Si wafer surface is removed. When the wafer is dried, it is put into the process chamber and degassed at higher than 300℃ for several hours. Finally, the wafer is transferred into the growth chamber with a basic pressure of about 2×10^{-8}Pa.

The Si substrate is heated to 950℃ to deoxidize.

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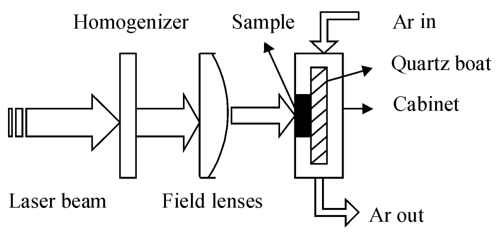

Fig. 1 Schematic diagram of the excimer laser annealing set-up

A Si buffer layer with a thickness of about 200nm is grown at 700℃ first. Then, a SiGe buffer layer is grown at 550℃ with the source gases disilane and germane (Si_2H_6 and GeH_4). The flux of the disilane and germane is 6sccm and 1sccm, respectively. The double crystal X-ray diffraction (D-XRD) shows that the Ge composition is ~23% and the thickness is about 20nm. Finally, at 500℃, the Ge layer is deposited with the flux of the germane 1sccm.

The wavelength of the ArF excimer laser is 193nm. The FWHM of the laser pulse is about 20ns and the laser device is operated in 40Hz. The laser ex-situ anneals the samples in argon ambient. A top-flat beam profile of 10mm × 10mm is obtained by a homogenizer to ensure the uniform annealing of the samples. The annealing energy density is 180 ± 10mJ/cm^2. The samples have different annealing times and their surface morphology is observed by a SPA-300HV atomic-force-microscopy (AFM).

Figure 1 shows the schematic diagram of the excimer laser annealing (ELA) setup. The original ArF excimer laser beam, which is Gaussian distribution and whose dimensions are 24mm × 6mm, exits the laser device, then transverses a homogenizer which homogenizes the laser beam. Next, the homogeneous beam goes through the field lenses, resulting in a 10mm × 10mm beam. The sample is put on a quartz boat in the annealing cabinet. In order to prevent the sample from being oxygenized, an inert gas such as Ar is introduced into the cabinet. The flux of the inert gas is about 3L/min.

3 Results and discussion

Figure 2 shows the AFM image of the as-grown Ge SAQDs on the Si substrate. The image shows that the Ge SAQDs are bi-model distributed, which is consistent with other experiments. The average diameter of the QD is about 50nm and the density of the Ge SAQD is very low.

Figure 3 shows the AFM image of the Ge LIQDs annealed for 2.5h in argon ambient. The AFM picture shows that the average diameter of the LIQDs is smaller than 25nm. The density of the LIQDs is about $6 \times 10^{10} cm^{-2}$.

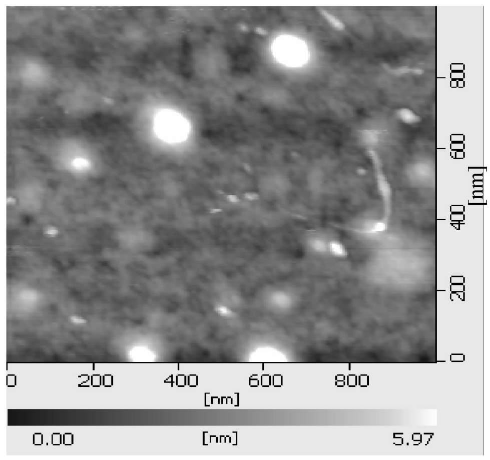

Fig. 2 AFM image of the as-grown Ge SAQDs

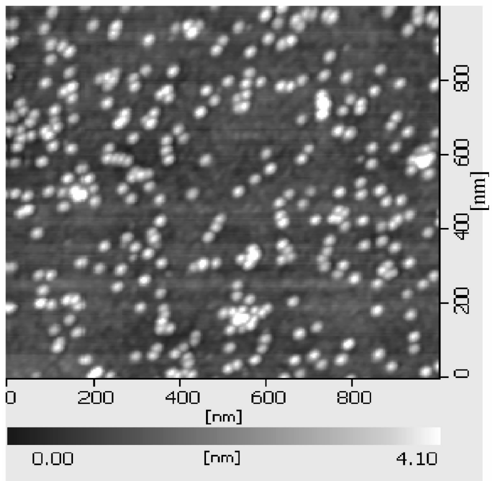

Fig. 3 AFM image of the Ge LIQDs annealed for 2.5h

Figure 4 is the Rutherford back scattering (RBS) spectra of the Ge sample after ELA. From this picture, we observe that no other atoms, such as O, N and Ar, are implanted into the sample. The result shows that the sample is protected well when annealed in argon ambient.

Comparing Fig. 2 with Fig. 3, the surface morphology of the sample changes greatly. This change must be caused by the laser pulses. We simulated the

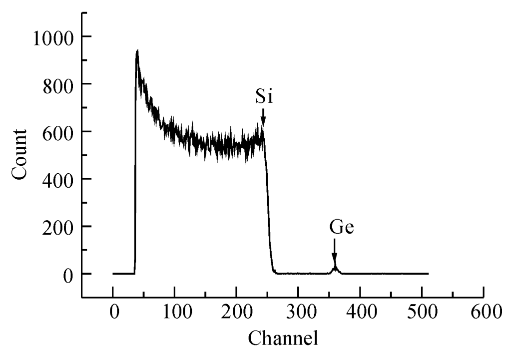

Fig. 4 RBS spectrum of the Ge sample after ELA for 2.5h

thermal effect on the surfaces induced by the excimer laser pulse by ANSYS[6]. The FWHM of the ArF excimer laser pulse is about 20ns. The simulation shows that the temperature induced by a single laser pulse will drop to room temperature in about 50 nanoseconds. However, the laser pulse interval is about 25ms (the laser device is operated in 40Hz). So, in the whole annealing process, no thermal energy accumulates. According to diffusion theory, the atom's diffusion length is about $\sqrt{4D_b t}$[7]. The bulk diffusion coefficient (D_b) of Si in Ge is $10^{-17}\mathrm{cm^2/s}$[8], and the diffusion length when $t = 50$ns is about 10^{-12}cm, which is too small for bulk diffusion and bulk Ge atoms to occur. However, the surface diffusion coefficient of the Ge is much larger than $10^{-12}\mathrm{cm^2/s}$[9]. The diffusion length when $t = 50$ns is about 10^{-9}cm, so the surface diffusion of Ge atoms and Si atoms can take place.

Based on the above calculations, we determined that bulk diffusion is forbidden. However, surface diffusion happens, but over a short-distance. The surface diffusion is controlled position-to-position with pulse-to-pulse energy uniformity during the ELA process. Thus, in the ELA process, the Ge atom in the Ge island will move out of the island slightly. When the laser pulses are abundant, the as-grown Ge island becomes smaller and can even disappear. On the contrary, new islands (called LIQDs, resulting from the diffusing atoms from the as-grown Ge islands) come into being. Finally, we have LIQDs with much smaller diameter and higher density.

Compared with the ELA, during the conventional thermal annealing, the atom's diffusion length is long enough and the movement of the diffusion atoms is continuous. Therefore, the thermal annealing cannot control the diffusion position to position. Using the ELA method, QDs with a quantum coefficient effect can be obtained, thus high quantum efficiency luminescence emitters and photodetectors can be fabricated in the future.

4 Conclusion

In conclusion, a Ge LIQD with the diameter of the LIQD 20～25nm, which is much smaller than the as-grown dot, and the density of $6\times10^{10}\mathrm{cm^{-2}}$ is achieved by 193nm ArF excimer laser annealing. By simulating the heat effect of the laser pulse, we show that the formation of the LIQD is induced only by the surface diffusion. When annealing, only surface diffusion occurs but the diffusion length is short. The surface diffusion is controlled position-to-position with pulse-to-pulse energy uniformity during the ELA process. The surface atom diffusion is controlled strictly from one position to another by the excimer laser pulse, so it is difficult for surface atoms to diffuse to another Ge island. The high density and the small size of the LIQD are determined by kinetic constraints, resulting in much smaller and higher density LIQDs.

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利用ArF准分子激光退火获得小锗量子点的研究*

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摘要：使用ArF准分子激光脉冲对UHV/CVD条件下生长的Ge量子点进行退火处理，获得了底宽为20～25nm的光致量子点(LIQD)，远小于退火前的量子点大小.LIQD的密度约为$6\times10^{10}cm^{-2}$.分析表明，在ArF准分子激光脉冲作用下，退火样品只有表面扩散，并没有体扩散.激光脉冲对表面Ge原子的扩散控制导致了Ge量子点形貌发生了巨大的改变.该方法为获得高密度小尺寸的Ge量子点提供了新的途径.采用原子力显微镜对光致量子点的表面形貌进行了研究.

关键词：Ge量子点；ArF准分子激光退火；光致量子点；原子力显微镜

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