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Growing evaporated Ge dots with high crystallinity on patterned Si substrate by post thermal annealing

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***Abstract*- To obtain the evaporated Ge dots with high crystallinity on Si substrate, a method of using nano-structure and post thermal annealing is demonstrated. The Si substrate is patterned with nano-hole array. After evaporating the Ge thin film layer, SiO_2 is capped on it and then thermally annealed. With well-designed hole-array pitch, the distribution of oxygen and quality of Ge QDs can be optimized. The processed Ge QDs size is over 20 nm which is estimated with the phonon confinement model of Raman scattering and confirmed by TEM image.**

1. Introduction

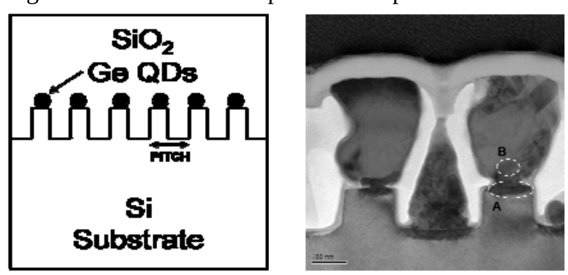
The growth of self-assembled Ge quantum dots (QDs) on the Si substrate always attracts much attention because of the compatibility with the existing CMOS technology and its potential applications to optoelectronic devices [1]. However, the low cost and high quality fabrication of Ge QDs are very critical to realistic device application. To date, there are several growth technologies such as ion implantation [2], rf-cosputtering [3], chemical vapor deposition [4] et al, have been used for the fabrication of Ge QDs. In 1990, Fujii et al. have demonstrated the size dependence of the full width at half maximum (FWHM) of the Ge-Ge vibration peak in Raman spectrum and they achieved the QDs size of 15 nm and the FWHM is near 5 cm^{-1} [3]. Recently, Sharp et al. have showed the QDs size of 5.1 nm and FWHM is 3.9 cm^{-1} [4].

Instead of the above description growth techniques, E-gun evaporator and post-thermal annealing are applied here [5]. High temperature annealing would induce the thin film layer transform from amorphous phase into crystal phase and form the QDs because of the high cohesion of the Ge. TEM image and phonon confinement model of Raman scattering is used to characterize the Ge crystalline, and the result shows that the size of the Ge crystalline is over 20nm [6].

2. Experiments and results

Through the process by the Electron Beam Lithography system (Japanese Elionix ELS-7000), and Reactive Ion Etching, the two-dimensional array of the circle holes with the diameter of 240 nm and the pitches of 400 nm to 1000 nm, all with the depth about 120 nm, are fabricated and uniformly distributed on the surface of the Si substrate. Figure 1(a) depicts the cross section sketch of the sample.

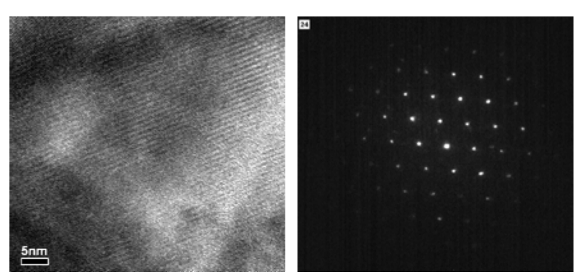
Before Ge deposition, the residual of the resist was cleaned by plasma O_2 treatment for 3 minutes followed by an HF dipping process to remove the native oxide on the surface of Si substrate. On the surface of the Si substrate, Ge thin film layer of 300nm thick is deposited by E-Gun evaporator. Ge atoms fill the nanohole array and coalesce with neighboring holes. An epitaxial lateral overgrowth (ELO) layer is formed. A following 100 nm capping SiO_2 layer is deposited by Plasma Enhance Chemical Vapor Deposition (PECVD) system. The three-layer (Si patterned substrate/Ge thin film layer/SiO_2 capping layer) structure is then annealed by furnace annealing treatment in a dry N_2 ambient at 900^0C for 10 minutes. After thermal annealing, the sample is studied by the cross-sectional transmission electron microscopy (TEM). Figure 1(b) shows the TEM image of the fabricated sample with the pitch of 500 nm.



(a) (b)

Fig. 1 (a) Schematic cross section of the sample. (b) TEM image of the sample with hole size of 240 nm and pitch of 500 nm.

The nano-hole array modifies the surface strain and the chemical potential of the substrate [7]. This would affect the oxygen profile after thermal annealing. From the Fig. 1(b), the region A servers as the seed to grow Ge QD on it. Ge QD grows on this seed, and then grows laterally to form the QD like region B. Region A is suggested to suffer all of the strain from the lattice mismatch of Ge and Si. Thus, the stress is blocked by the region A and Ge QDs are almost fully relaxed. This property is also disclosed from the peak position of the Raman spectrum.



(a) (b)

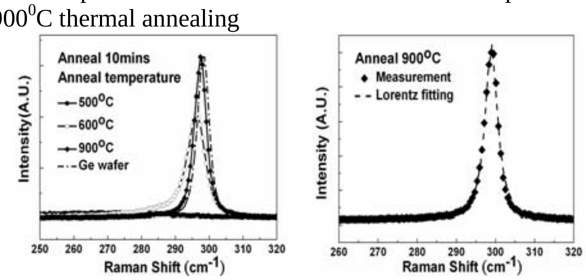
Fig. 2 (a) Magnified view of the region B in the Fig. 1(b). (b) Selected diffraction pattern of the region B in the Fig. 1(b).

Figure 2(a) is the magnified view of the region B in Fig. 1(b). The significant lattice fringes are pronounced the well-crystallized Ge QDs. Figure 2(b) shows the selected diffraction pattern. The diameter of QD is over 20 nm.

To characterize strain relaxation and modest QD quality, micro-Raman spectrometer is employed. Light from the 532 nm laser is focused through the 50x objective. Raman spectroscopy reveals the information about the crystallinity, the degree of alloying, and stress effect of the material. Raman spectrum peak would be broadened by the presence of amorphous phases, whose spectrum exhibit spectrum at lower wave numbers than bulk single crystal material. As the annealing temperatures are below 600^0C, the Ge thin film layers are in amorphous phase and have the broad Raman spectrum whose peak positions are at 270 cm^{-1}, as shown in Fig. 3(a) However, after 900^0C thermal annealing, there is neither significant asymmetry of the line shape nor line width broadening[6].

To characterize the phenomenon, the spectrum is fitted with the Lorentz distribution. In spectroscopy, as the spectrum can be fitted well with Lorentian distribution, all of the phonons interact in the same way. Fig. 3(b) shows the result of that annealed at 900^0C for 10 minutes. The Raman spectrum of annealed 900^0C sample can fit well with one Lorentian distribution.

The FWHM of the Raman spectrum can be the index of the crystallinity because it increases as the material is damaged or disordered [8]. To compare with the Raman spectra of Ge wafer and the sample after 900^0C thermal annealing, the FWHM and peak position is very close. This implies that the quality of the processed Ge crystalline QDs is very close to single crystal Ge. The intensity of Ge wafer Raman spectrum is normalized to that of the sample with 900^0C thermal annealing



(a) (b)

Fig. 3 (a) Raman spectrum of the Ge wafer and the samples with different annealing temperatures for 10 minutes. (b) Lorentz distribution fitting result of the sample with annealing temperature of 900^0C

The FWHM of the samples with different pitches are shown in Fig. 4. The sample with nano-hole pitch of 500 nm has the narrowest FWHM of 3.775 cm^{-1} which is only slightly wider than that of single crystal Ge and peak position is at 298 cm^{-1}. According to the phonon confinement model of Raman scattering, the size of the measured Ge QDs is over 20nm and this is coincided to the TEM image. The FWHM of the single crystal Ge is 3 cm^{-1} [3]. The FWHM of the Ge wafer which is measured by this system is 3.5 cm^{-1} and peak position is 299 cm^{-1}. The similar peak position of Raman spectrum of Ge QDs and Ge wafer indicates that the processed Ge crystalline QDs are almost fully relaxed [3]. As the pitch decreases, the FWHM is decreased, indicating that smaller hole-array pitch may result in larger crystalline. The FWHM of the Ge crystalline on the nano-structures are significantly narrow compared to the unpatterned substrate, which means that the crystallinity of the Ge QDs on patterned substrate is better than that on the unpatterned one.

During the high temperature thermal process, the oxygen would travel deep into the Ge film and arrive at the bottom corner of the hole finally. Ge is believed to scavenge oxygen from SiO_2 and to form GeO and SiO and GeO sublimates at 625^0C [9]. The oxygen would occupy the vacancy of the Ge and Si. The occupied oxygen would compress the Ge QDs and help the formation of the Ge crystalline. However, as the pitch decreases below the critical pitch, the FWHM increases. The oxygen may get into the Ge QDs and damage the crystallinity. The sample with pitch of 500 nm has the narrowest Raman peak. Therefore, there is an optimum value of the pitch for the growth of Ge QDs.

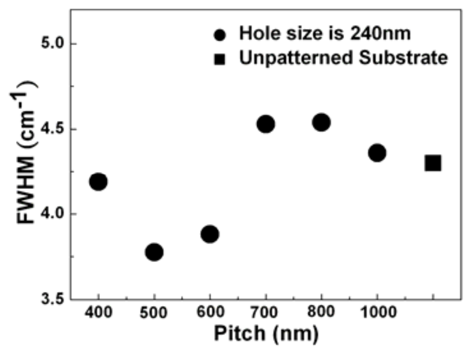


Fig. 4 FWHM of the samples with the different pitches and hole sizes.

3. Conclusion

In conclusion, high quality and large Ge QDs on patterned Si substrate are experimentally achieved with well-designed hole-array pitch. The circle-hole array on the Si substrate has been fabricated by the Electron Beam Lithography to modify the Ge/Si interface strain. The processed Ge QDs size is over 20 nm which is estimated with the phonon confinement model of Raman scattering and confirmed by TEM image. Because the trade-off of the oxygen diffuse and Ge crystallinity, the crystallinity of Ge QDs can be optimized within well-designed hole-array pitch. The processed Ge crystalline can be very close to single crystal and the strain be almost fully relaxed.

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