Extended Abstracts of the 2011 International Conference on Solid State Devices and Materials, Nagoya, 2011, pp296-297

Growing high crystallinity Ge NCs on patterned Si substrate by post thermal annealing

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***Abstract* - The melting point of a Ge thin film can be controlled by a hole-array pattern on the host Si substrate due to the variations in the stress distribution and the surface morphology induced by the pattern. A simple annealing process is developed from this effect to produce Ge NCs with a single-domain-crystal size over 20 nm, confirmed by transmission electron microscopy, from an electron-gun evaporated Ge thin film on the patterned Si substrate. Photoluminescence observed around 1157 nm shows the possibility of improving the infrared emission capability by this proposed method. A non-destructive testing method based on near field scanning optical microscopy with a 1.55-μm wavelength infrared laser source, is introduced to examine the samples. At this wavelength, Si and SiO_2 are transparent, but Ge NCs are opaque. The scanning transmission image reveals the distribution of Ge buried in the samples directly. The size of Ge clusters is about 1 μm, much larger than the size of a single-crystal domain.**

1. Introduction

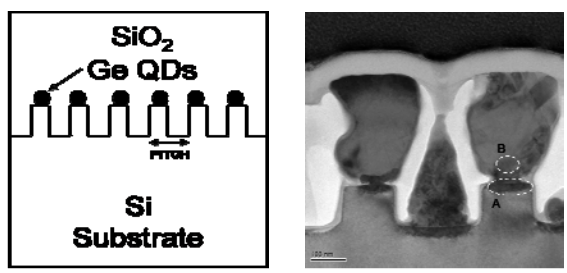
The growth of self-assembled Ge nanocrystals (NCs) on the Si substrate always attracts much attention because of the compatibility with the existing CMOS technology and its potential applications to optoelectronic devices [1]. However, the low cost and high quality fabrication of Ge NCs are very critical 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 NCs. 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 NCs size of 15 nm and the FWHM is near 5 cm^{-1} [3]. Recently, Sharp et al. have showed the NCs 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 NCs 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 500 nm, 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 300 nm 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 ^{0}C 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)

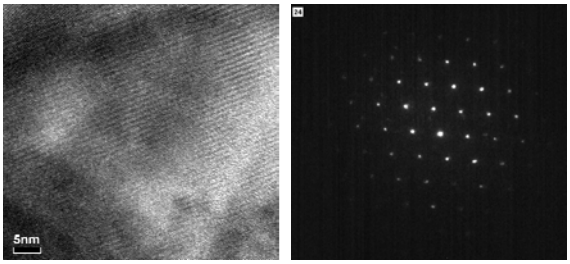
Fig. 1 (a) Schematic cross section of the sample. (b) TEM image of the sample with hole size of 240 nm and pitch of 500 nm.

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 NC on it. Ge NC grows on this seed, and then grows laterally to form the NC 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 NCs are almost fully relaxed. This property is also disclosed from the peak position of the Raman spectrum.

At high temperatures the Ge film inside the holes bears a compressive stress due to its larger thermal expansion coefficient relative to Si template, and therefore has a lower melting temperature than that outside the holes. Concurrently, the significant increase of the surface to bulk ratio of the Ge thin film inside the holes caused by the

hole-array template can also lower the melting point due to the increasing number of loosely bound surface atoms. This local melting effect can be attributed to the lowering of the melting point of Ge due to both the compressive stress and the morphology modified by the Si template. The melting points of Ge film inside every hole are lower than outside. This causes the flow of Oxgen and Si from the capping oxide and Si substrate. The Oxgen atoms further etch the Ge and Si interface outside the holes and reduce its contact area. This may decrease the stress due to the lattice mismatch of Si and Ge and then boost the crystallinity of Ge crystalline.

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 NCs. Figure 2(b) shows the selected diffraction pattern. The diameter of NC is over 20 nm.



(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).

3. PL spectrum

The sample exhibits clear infrared PL. Note that PL in the infrared region corresponding to the band to band transition is seldom addressed for Ge NCs formed by thermal agglomerating technologies in the literature. Figure 3 shows the PL spectrum of the sample at 11 K [1]. The excitation is provided by a 100-mW 532-nm He-Cd laser. The spectrum can be decomposed into two Gaussian curves: one centering at 1157 nm corresponds to $Si_{0.75}Ge_{0.25}$ and the other centering at 1347 nm corresponds to $Si_{0.22}Ge_{0.78}$.The broadening of the Gaussian curve at 1347 nm can be attributed to the composition variation of SiGe inside the holes. The emission at 1157 nm may be from the interface layer between SiGe NC and Si substrate.

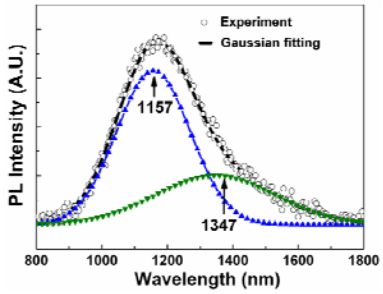


Fig. 3 PL spectrum of the sample at 11 K. The spectrum can be fitted with two Gaussian distribution curves: one of peak at 1157 nm and the other at 1347 nm.

4. SNOM images

A non-destructive testing method based on near field scanning optical microscopy with a 1.55-μm wavelength infrared laser source, is introduced to examine the samples. At this wavelength, Si and SiO_2 are transparent, but Ge NCs are opaque. Figure 4 (a) and (b) the surface morphology and transparent images of the samples with different hole-array pitches. The bright regions are corresponding to Ge, Si, O intermixed material and dark regions are Ge NCs. Thus, the transmission images reveal the distribution of Ge NCs in the samples without destroying them. Furthermore, from the transmission images, the size of Ge crystalline is almost 1 μm but the size of a single-crystal domain is much smaller. This indicates that there is some distortion in TEM images because of it only gives two-dimensional and cross-sectional images. Hence, the size of the crystalline in the TEM image may be determined by which part of the crystalline is milled and observed. In the other hand, the transmission images show the top view images of the Ge crystalline and may reveal the real Ge crystalline size

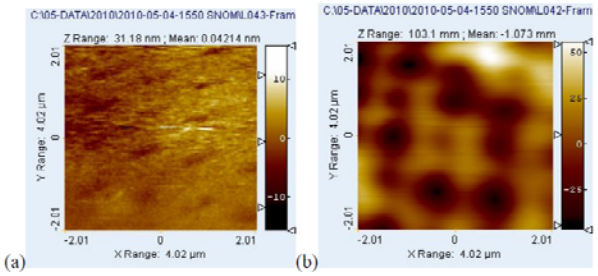


Fig. 4 The surface morphology and tranmission images of the samples with P = 1000 nm.

5. Conclusion

In conclusion, the spatial variation of the melting point of a Ge thin film can be controlled by adjusting the hole-array pattern on the host Si substrate. A simple method of fabricating high-quality Ge NCs with a single-domain-crystal size over 20 nm is developed therefrom. Besides, SiGe with infrared light emission capability can be formed in the holes simultaneously. This fabrication method provides a new route to form large-sized Ge NCs with high crystallinity.

A non-destructive testing method based on near field scanning optical microscopy with a 1.55-um wavelength infrared laser source, is introduced to examine the samples. At this wavelength, Si and SiO_2 are transparent, but Ge NCs are opaque. The scanning transmission image reveals the distribution of Ge buried in the samples directly. Besides, from the transmission images, the size of Ge crystalline is almost 1 μm but the crystalline size of that in TEM image is much smaller.

References

[1] Y. H. Peng, C. -H. Hsu, C. H. Kuan, C. W. Liu, P. S. Chen, M.-J. Tsai, and Y. W. Suen, Appl. Phys. Lett. **85**, 6107 (2004).
[2] I. D. Sharp, D. O. Yi, Q. Xu, C. Y. Liao, J. W. Beeman, Z. L. Weber, K. M. Yu, D. N. Zakharov, J. W. Ager III, D. C. Chrzen and E. E. Haller, Appl. Phys. Lett. **86** 063107-1 (2005).
[3] M. Fujii, S. Hayashi and K. Yamamoto, Appl. Phys. Lett. **57**, 2692 (1990).
[4] Y. R. Chen, C. H. Kuan, Y. W. Suen, Y. H. Peng, P. S. Chen, C. H. Chao, E. Z. Liang, C. F. Lin, and H. C. Lo, Appl. Phys. Lett. **93**, 083101 (2008).
[5] K. H. Chiang, S. W. Lu, Y. H. Peng, C. H. Kuan, and C. S. Tsai, J. Appl. Phys. **104**, 014506 (2008).
[6] X. L. Wu, T. Gao, X. M. Bao, F. Yan, S. S. Jiang, and D. Feng, J. Appl. Phys. **82**, 2704 (1997).
[7] S. Luryi, and E. Suhir, Appl. Phys. Lett. **49**, 140 (1986).