Available online at www.sciencedirect.com
SCIENCE DIRECT®
Physica E 28 (2005) 531–536
PHYSICA E
www.elsevier.com/locate/physe

Raman study of Si–Ge intermixing in Ge quantum rings and dots

V.I. Mashanov[a,*,1], H.-H. Cheng[a,b], C.-T. Chia[c], Y.-H. Chang[d]

[a]*Center for Condensed Matter Sciences, National Taiwan University, Taipei 106, Taiwan, ROC*
[b]*Graduate Institute of Electronic Engineering, National Taiwan University, Taipei 106, Taiwan, ROC*
[c]*Department of Physics, National Taiwan Normal University, Taipei 106, Taiwan, ROC*
[d]*Department of Physics, National Taiwan University, Taipei 106, Taiwan, ROC*

Received 24 May 2005; accepted 31 May 2005
Available online 25 July 2005

Abstract

The Ge/Si (1 0 0) nanostructures have been studied by atomic force microscopy (AFM) and Micro Raman optical spectroscopy. Two layers of Ge of total thickness 0.75 nm and Si cap with thickness 2.5 nm were deposited by the method of molecular beam epitaxy at the temperature range 640–700 °C. AFM shows both quantum dots and ring-shape Ge nanostructures. From the analysis of the intensity and energy shift of the Raman signal we have found that the average concentration of Ge decreases considerably from 44% to 27%, when the growth temperature increases, whereas the degree of strain relaxation remains roughly the same. This allows us to conclude that intermixing is a dominating mechanism for strain relaxation in processes of transformation of Ge quantum dots to quantum rings.

PACS: 68.65Hb; 81.07Ta; 81.16Dn

Keywords: Germanium; Quantum dots; Quantum rings; Raman scattering

1. Introduction

Ge quantum dots in a Si matrix promise good properties in infrared detection and light emission [1,2]. The overgrowth Ge dots with the Si cap layer is necessary for realization of optoelectronics devices. It is known, that the Si cap layer can change the shape and composition of the quantum dots. Ge dome clusters are transformed into hut clusters after the deposition of five monolayers of silicon, thereby decreasing in height and increasing in diameter [3]. Recently it was found that at high growth temperature after Si capping, Ge dots have been transformed into ring-shape structures with a

*Corresponding author.
E-mail address: mashanov@ms.ntu-ccms.ntu.edu.tw (V.I. Mashanov).
[1]On leave from the Institute of Semiconductor Physics, Siberian Branch of Russian Academy of Sciences, 630090, Novosibirsk, Russia.

1386-9477/$ - see front matter
doi:10.1016/j.physe.2005.05.060

hole in the middle, which was called quantum rings [4,5]. The formation mechanism of Si–Ge quantum rings has been discussed [4,5], in which the driving force is attributed to the strain energy relief after capping together with high Ge surface diffusion and surface segregation. But insufficiency of experimental data restricted us to develop a detail model of the transformation of Ge dots to quantum rings after Si capping. Earlier, ring-shape quantum dots have been known for InAs/GaAs and InAs/InP semiconductor heterostructures after capping InAs quantum dots by thin GaAs and InP layers, respectively [6,7]. To explain the formation of quantum rings in III–V system two kinds of growth models have been suggested. One is based on the minimization of surface free energy, [7,8] called the thermodynamic model. The other is based on the strong surface diffusion of In atoms [6,9,10] called the kinetic model. In this paper we report the Micro Raman data about intermixing of Ge and Si species in the process of formation of Ge–Si quantum rings at different growth temperatures.

2. Experimental

The growth of quantum dots and rings were performed in molecular beam epitaxy (MBE) system (Riber SIVA 32) with two electron beam evaporators for Ge and Si. N-type Si (1 0 0) wafer with a resistivity of 1–10 Ω cm is used as substrate. Prior to the growth, the wafer is flushed with low Si flux to remove the thin SiO_2 protective layer. The procedure is repeated several times until the sharp 2×1 pattern is observed by the reflection high-energy electron diffraction (RHEED) to ensure the clean surface. For all the samples, thin Si buffer layer of 30 nm is deposited at 700 °C. Low growth flux is employed for the structure with a rate of 0.01 and 0.06 nm/s for Ge and Si, respectively. The structure consists of (a) a layer of 0.7 nm Ge, (b) a thin layer of 0.05 nm of Ge, and (c) a Si cap layer of 2.5 nm. In between layer (a) and (b), both Si and Ge shutter is closed for 5 min to ensure the uniformity of the Ge layer [4]. Four samples are grown at various temperatures of 640, 660, 680 and 700 °C. The structure and technological parameters of samples are shown in Fig. 1.

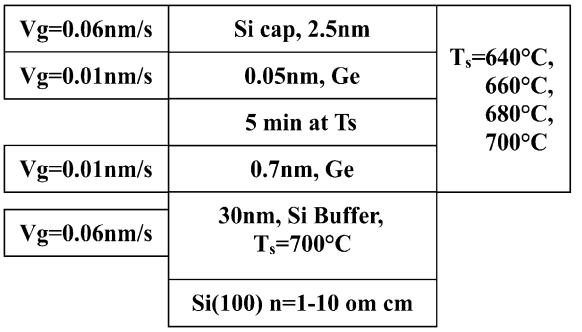

Fig. 1. Schematic diagram of sample structures. T_S is a growth temperature of substrate, V_g is the growth rate.

Raman scattering measurements were performed at room temperature using the 514.5 nm line of an Ar+ with a power of 100 mW. The scattered light was analyzed in a backscattering geometry using a Dilor XY-800 triple monochromator equipped with liquid nitrogen cooling charge-coupled device (CCD) detector. The obtained Raman spectra exhibited approximately a 0.2 cm^{-1} resolution. The focusing spot is about 1 μm. Atomic force microscopy (AFM) images were obtained in the semicontact mode after growth at air.

3. Results and discussion

In the images of AFM pictures from samples grown at different temperatures, both quantum dots and rings were observed. The typical AFM image is shown in Fig. 2. For the dots, in the four samples, the diameters ranged from 200 to 340 nm with a height of 3–11 nm. For the rings the diameter were larger than the dots ranging from 250 to 580 nm but with height ranging from 1 to 16 nm. The density of rings and dots were $\sim 1.5 \times 10^8$ cm^{-2} and $3–9 \times 10^8$ cm^{-2}, respectively.

According to AFM data, after Si capping, Ge dots increase their outer diameter and decrease their height. These data are in accordance with measurements by ultra-high vacuum scanning tunneling microscopy of parameters of Ge dots after Si capping [3] and AFM data of Ref. [4]. For

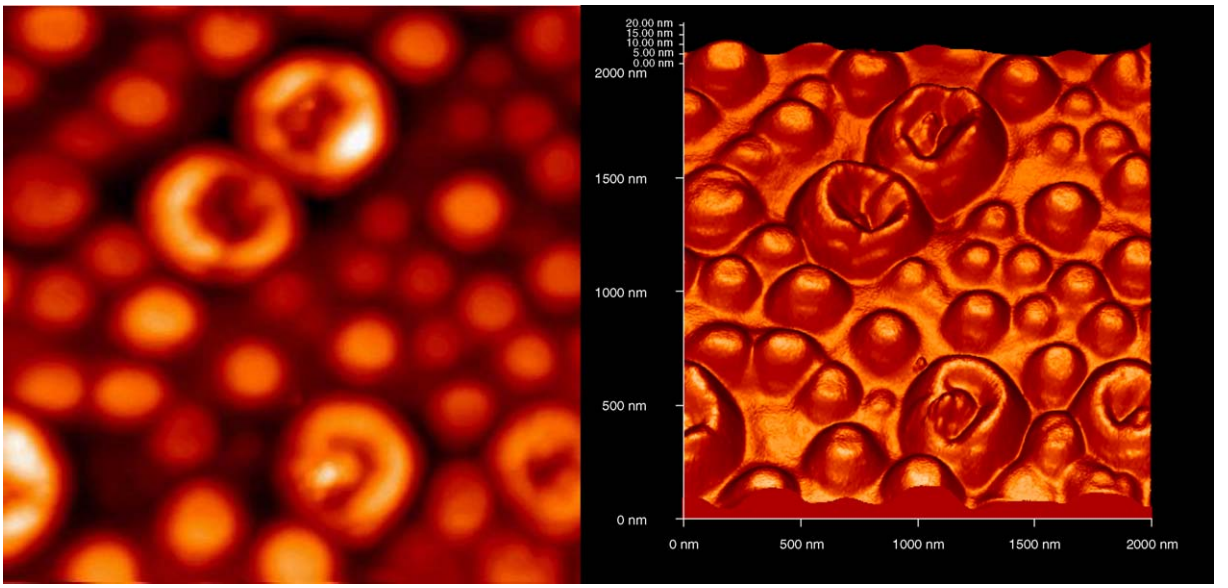

Fig. 2. The typical 2D and 3D AFM images, showing both quantum rings and dots. Growth temperature is equal to 680 °C. Dimensions of AFM scan are equal to 2 mkm × 2 mkm. The outer diameter of rings and dots are 550–580 and 230–340 nm with heights 7–16 and 3–10 nm, respectively.

instance, the average diameter of Ge quantum dots after two-step deposition with the same thickness of Ge (0.75 nm) at growth temperature 680 °C, but without a Si cap layer, is ~150 nm and the height of the dots varied from 35 to 45 nm. After Si capping of these dots at a temperature of 680 °C we obtained both rings and dots (Fig. 2) with bigger diameters. The outer diameters of the rings and dots were 550–580 and 230–340 nm with heights of 7–16 and 3–10 nm, respectively.

The laser beam diameter used in our Raman spectrometer was large enough to cover both quantum dots and rings. Raman spectra from the samples and from the Si blank wafer are shown in Fig. 3(a). The so-called two-phonon peak coming from the silicon substrate can be seen at the Raman spectra from the wafer at nearly 300 cm^{-1} [11]. Raman data were performed after averaging of signals at room temperature. Due to the very thin Ge–Si epilayer (~3 nm), the intensity variation of the two-phonon peak near 300 cm^{-1} caused by the laser local heating for Si wafer and for Ge–Si nanostructures on Si substrates are approximately the same. Therefore, the two-phonon signals of Ge–Si nanostructure samples can be subtracted form the Si-wafer signal without losing any substantial information of the Ge–Ge phonons of the Ge–Si epilayer.

The spectra, after the background subtraction of the Si wafer, are shown in Fig. 3(b). Two clear features were observed at wave numbers around 300 and 413 cm^{-1}, corresponding to the Ge–Ge, and Si–Ge phonon modes. (The strong Si–Si phonon mode at 520 cm^{-1} is not shown in the figure). From the plot, it shows two characteristics. Firstly, the intensity of both Ge–Ge and Si–Ge modes decrease as the growth temperature increases. Secondly, the peak position of the Ge–Ge line remains at the same position within ± 1 cm^{-1}. Probably the peak position of the Ge–Ge mode has been determined with a smaller accuracy than the position of Si–Ge mode because of the appreciable background two-phonon peak from the silicon substrate. The peak position of the Si–Ge mode is shown to have a small shift of ~2.5 cm^{-1} toward higher wave numbers when the temperature of substrate was decreased. It is well known that strain introduces the shift of Raman peaks in the same direction. The dependence of the intensity of the Ge–Ge mode and Si–Ge mode as a

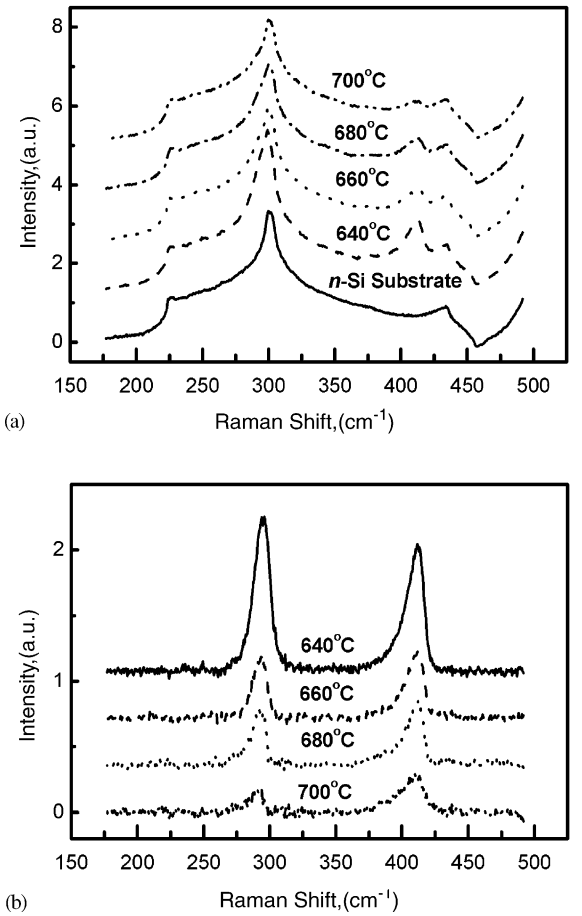

Fig. 3. (a) Raman spectra from samples and from the blank Si substrate, (b) Raman spectra from samples after the background subtraction of the Si wafer.

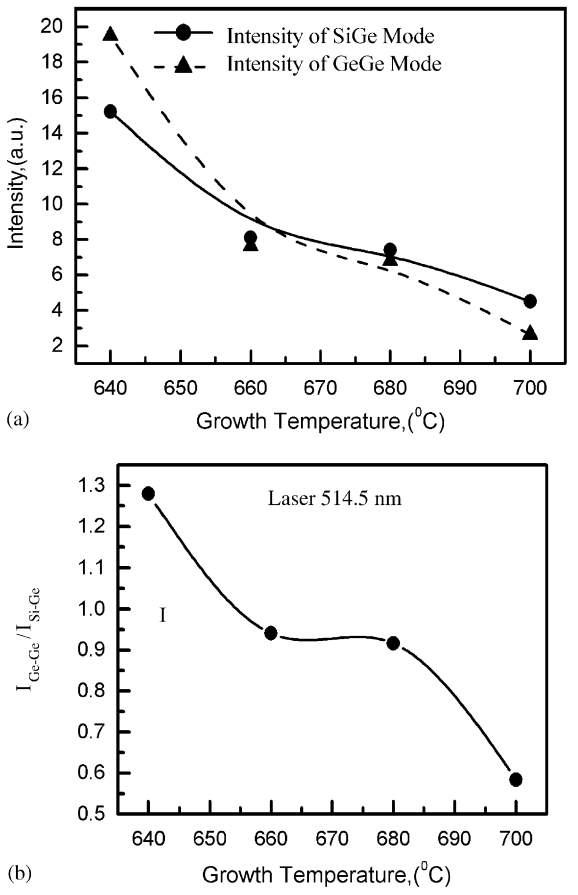

Fig. 4. (a) Dependence of intensity of Ge–Ge mode and Si–Ge mode from the growth temperature and (b) dependence of the intensity ratio of Ge–Ge mode and Si–Ge mode from the growth temperature.

function of the growth temperature are shown in Fig. 4(a).

To analyze the change of average Ge content for quantum dots and quantum rings, we take the intensity ratio of Ge–Ge mode and Si–Ge mode (I_{Ge-Ge}/I_{Si-Ge}). The result is depicted in Fig. 4(b). It shows that the ratio decreases with increasing growth temperature. From the Raman data of monocrystal Ge_xSi_{1-x} films, Alonco and Winer [12] found that when the concentration of x increases from 0.28 to 0.77, the ratio of I_{Ge-Ge}/I_{Si-Ge} decreases. According to Mooney et al. [13] the dependence of the intensity ratio of Ge–Ge mode and Si–Ge mode can be written as

$$\frac{I_{Ge-Ge}}{I_{Si-Ge}} = B\frac{x}{2(1-x)}, \quad (1)$$

where x is the Ge content and B is a material-dependent parameter, which for Ge–Si system is 3.2.

These ratios of integrated intensities are independent of the degree of strain and proportional to the number of the nearest-neighbor bonds [14]. Therefore, the change of the relative intensity of the two lines reflects a change of the Ge concentration. The energy shift depends strongly

on both the composition and strain in the structure. From the ratio intensity of Ge–Ge and Ge–Si mode, we can estimate that at a temperature of 640 °C, the average concentration for Ge is $x\sim0.44$, and at a temperature of 700 °C, $x\sim0.27$. The local concentration of Ge in quantum dots and quantum rings has been determined by energy dispersion spectrometer in transmission electron microscopy in Ref. [5]. For hut clusters after 1.9 nm Si capping, a Ge concentration of $x\sim0.42$ was observed. At the center of the quantum ring $x\sim0.30$, and at the two opposite edges of quantum ring, $x\sim0.14$ and $x\sim0.17$ were observed [5]. The average concentration x for quantum dots and ring is equal to 0.26. This average concentration is close with our estimation of $x\sim0.27$ at 700 °C. At higher temperatures we have a bigger intermixing of Ge and Si components.

As is well known the Raman shift of Si–Ge mode is proportional to the concentration and strain in the Ge–Si alloy [15,16],

$$\omega_{\mathrm{Si-Ge}} = 400.5 + 14.2x - 575\varepsilon, \quad (2)$$

where $\omega_{\mathrm{Si-Ge}}$ is the phonon mode in Raman spectra, x the concentration of Ge in Ge–Si layer, and ε the average residual in plane strain in Ge–Si layer. From the position of the Si–Ge vibration mode and the quantity of x for samples we can estimate the residual strain in quantum dots and rings at different growth temperatures. The average residual plane strains are equal to −1.08% and −1.06% at 640 and 700 °C, respectively. The initial strains in Ge pseudomorphic film on Si (1 0 0) substrate are −4.0%. A relative level of relaxation of strain in structures with quantum dots and rings is approximately equal to 73%. There is a small difference in the level of relaxation of strain in samples, which was grown at different temperatures because the Raman shift was little. A similar level of residual in the plane strain (−1.2%) has been measured within of the Ge quantum dots in X-ray diffraction measurements [17]. These Ge dots have been grown at similar growth conditions by MBE on the Si (1 0 0) substrate [17].It is well known that in the epitaxial growth Ge/Si (1 0 0) heterostructure, the strain energy resulting from lattice mismatch is reduced by the formation of Ge islands or dots. It has been shown that strain relaxation at high temperatures can proceed, alternatively, via diffusion of Si atoms from the substrate into the Ge dots, since intermixing reduces the effective lattice mismatch [18,19]. SiGe intermixing in Ge/Si (1 0 0) self-assembled dots have been studied by AFM and X-ray photoemission spectroscopy at a deposition temperature in the 500–850 °C range [19]. The silicon content of the islands varies from 0% at 550 °C up to 72% at 850 °C. This data reflects a larger degree of intermixing at higher growth temperature and the Ge concentration of the dots is 68% grown at 640 °C and 50% at 700 °C from Ref. [19]. Naturally, the Ge concentrations in the quantum dots are higher in comparison with our estimation, because in our case we have additional quantity of Si atoms from the cap layer and probably the different mixing mechanisms in forming ring-shape structures from Ge dots by enhanced surface diffusion and lateral processes of Ge segregation. It is well known that the activation energy of the surface diffusion is smaller than the activation energy of the volume diffusion. At the stage of deposition of Ge film, strain relaxation is going on by the formation of Ge dots and intermixing by volume diffusion of Si into Ge layer, then at the stage of Si capping the process of surface mass transportation of Ge and Si atoms may start from the top to the bottom side of Ge dots.

4. Conclusion

From the analysis of the intensity and energy shift of the Raman signal we have found that the average concentration of Ge decreases considerably, on increasing the growth temperature, whereas the degree of strain relaxation remains roughly the same. Therefore, we conclude that intermixing is a dominating mechanism for strain relaxation in the processes of transformation of Ge quantum dots to quantum rings.

Acknowledgements

The author would like to acknowledge Dr. L. Pai from the Center for Condensed Matter

Sciences, National Taiwan University for help with AFM measurements. This work was supported by the National Science Council (Taiwan, ROC) under Contract NSC93-2811-M-002-088.

References

[1] J. Phillips, J. Appl. Phys. 91 (2002) 4590.
[2] A. Beyer, E. Müller, H. Stutz, D. Grützmacher, Appl. Phys. Lett. 77 (2000) 3218.
[3] O. Kirftel, E. Müller, D. Grützmacher, K. Kern, Physica E 16 (2003) 602.
[4] J. Cui, Q. He, X.M. Jiang, Y.L. Fan, X.J. Yang, F. Xue, Z.M. Jiang, Appl. Phys. Lett. 83 (2003) 2907.
[5] S.W. Lee, L.J. Chen, P.S. Chen, M.-J. Tsai, C.W. Liu, T.Y. Chien, C.T. Chia, Appl. Phys. Lett. 83 (2003) 5283.
[6] J.M. Garcia, G. Medeiros-Ribeiro, K. Schmidt, T. Ngo, J.L. Feng, A. Lorke, J. Kotthaus, P.M. Petroff, Appl. Phys. Lett. 71 (1997) 2014.
[7] T. Raz, D. Ritter, G. Bahir, Appl. Phys. Lett. 82 (2003) 1706.
[8] R. Blossey, A. Lorke, Phys. Rev. E 65 (2002) 021603.
[9] A. Lorke, R.J. Luyken, J.M. Garcia, P.M. Petroff, Jpn. J. Appl. Phys. Part 1 40 (2001) 1857.
[10] R. Songmuang, S. Kiravittaya, O.G. Schmidt, J. Cryst. Growth 249 (2003) 416.
[11] A.V. Kolobov, J. Appl. Phys. 87 (2000) 2926.
[12] M.I. Alonso, K. Winer, Phys. Rev. B 39 (1989) 10056.
[13] P.M. Mooney, F.H. Dacol, J.C. Tsang, J.O. Chu, Appl. Phys. Lett. 62 (1993) 2069.
[14] S. Rath, M.L. Hsieh, P. Etchegoin, R.A. Stradling, Sem. Sci. Technol. 18 (2003) 566.
[15] J. Groenen, R. Carles, S. Christianen, M. Albrecht, W. Dorsch, H.P. Strunk, H. Wawra, G. Wagner, Appl. Phys. Lett. 71 (1997) 3856.
[16] J.C. Tsang, P.M. Mooney, F. Dacol, J.O. Chu, J. Appl. Phys. 75 (1994) 8098.
[17] Z.M. Jiang, X.M. Jiang, W.R. Jiang, Q.J. Jia, W.L. Zheng, D.C. Qian, Appl. Phys. Lett. 76 (2000) 3397.
[18] X.Z. Liao, J. Zou, D.J.H. Cockayne, J. Qin, Z.M. Jiang, X. Wang, R. Leon, Phys. Rev. B 60 (1999) 15605.
[19] G. Capellini, M. De Seta, F. Evangelisti, Appl. Phys. Lett. 78 (2001) 303.