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Physica E 23 (2004) 248–252

PHYSICA E

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Site selective growth of Ge quantum dots on AFM-patterned Si substrates

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Abstract

By combining the atomic force microscope (AFM) local anodic oxidation and etching, a periodic array of nanodimples of ∼40 nm in diameter and ∼3.5 nm in depth has been made on a Si surface. Ge atoms deposited onto this patterned substrate by the MBE method nucleate preferentially in the dimples and form an array of nano Ge dots of about 50 nm in diameter and 10 nm in height.

PACS: 81.16.Nd; 81.16.Pr; 81.16.Rf

Keywords: Si; Ge quantum dot; Atomic force microscopy; Nano lithography; Nano oxidation

1. Introduction

Growth in the Stranski–Krastanov (SK) mode has been employed in the past to fabricate self-organized Ge quantum dots on Si substrates. The dots grown in such manner are in the form of randomly positioned Ge islands consisting of a variety of sizes and structures (huts, pyramids, domes, etc.). The main goal of this study is to realize Ge quantum dots whose positions and sizes are controlled precisely. Such goal has been achieved to a certain degree in the past. Researchers have successfully produced periodic arrays of Ge quantum dots of approximately 100 nm in diameter on a variety of patterned Si substrates [1–4]. However, it is preferred to obtain an array of smaller diameter (<50 nm) quantum dots in order to highlight the quantum phenomena arising from the confinement of charges into small regions. A selective growth of very small (diameter <20 nm) Ge nano islands on a Si surface was reported by placing windows by a scanning tunneling microscope (STM) in an ultrathin SiO_2 overlayer [5]. In this case, the islands showed a variety of facets, partly because they were grown on a flat Si substrate [6]. Recently, Song et al. [7] reported the size- and position-controlled growth of smooth surfaced InGaAs quantum dots of the diameter ∼20 nm on the atomic force microscope (AFM) patterned GaAs substrates. An array of nanodimples of about 20 nm in diameter and 1.2 nm in depth was formed successfully by anodic oxidation

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doi:10.1016/j.physe.2003.12.130

using AFM tips followed by etching. InGaAs deposited on the surface nucleated preferentially in the dimples to produce a regular array of constant diameter InGaAs dots. Because InGaAs dots on a flat GaAs surface self-assemble by the SK mechanism, it is of great interest to apply the same AFM patterning recipe on Si substrates and investigate whether Ge quantum dots also nucleate preferentially in the dimples. Growth of dots in dimples rather than on a flat surface may be the key to fabricate nanodots with smooth surfaces. Such dots are expected to be useful for the investigation of isotope effects in nanostructures [8].

The procedure to form nano-oxide dots by AFM anodic oxidation and nanodimples by subsequent HF etching on a Si substrate was established more than 5 years ago [9,10]. To our knowledge, nano SiO_2 wires as narrow as 14 nm have been made in the past on Si by the AFM anodic oxidation method [11].

In this work, we show experimentally that Ge nanodots of ~ 50 nm in diameter indeed grow preferentially into nanodimples prepared on Si substrates by the AFM oxidation.

2. Experiments

Fig. 1 shows a schematic diagram of our process. Nano SiO_2 arrays were formed on a Si (1 0 0) surface by local anodic oxidation. An AFM system employed in this study was SPI3800 built by Seiko Instruments Inc. (SII). The AFM cantilever, Si_3N_4 with Au coating, was also made by SII (SN-AF01-A). The tip was electrically grounded and the positive bias was applied to the substrate to decompose H_2O in the air to $H^+ + OH^-$ to locally oxidize the Si surface with OH^-. Subsequent to the nano-oxide dot array formation, the nanodots were etched away with diluted hydrofluoric acid. The wafer with nanodimples was placed in the MBE chamber with a vacuum of about 10^{-10} Torr. The wafer was annealed at 850°C for 15 min to clean the surface prior to the MBE deposition of Ge. This low-temperature surface cleaning recipe is basically the same as the one developed by Ishizaka and Shiraki [12]. Finally, Ge atoms were deposited at the substrate temperature of 650°C with the growth rate of ~ 0.1 monolayer/s.

3. Results and discussions

Fig. 2 shows the bias pulse sequences between the tip and substrate for the nano SiO_2 dot formation: (a) DC bias for 2 s, (b) a sequence of 0.1 s bias pulse and 0.03 s interval for the total of 2 s, and (c) a sequence of 0.05 s bias pulse and 0.02 s interval for the total of 2 s. Fig. 3(a)–(c) shows the height contour of the resulting dot corresponding to the pulse sequences in Fig. 2(a)–(c), respectively, for the bias $-V = 4$ V. As apparent in Fig. 3(a)–(c), the dot height with the DC bias saturates at ~ 0.5 nm (Fig. 2(a)) while that with the shortest pulse sequence (Fig. 2(c))

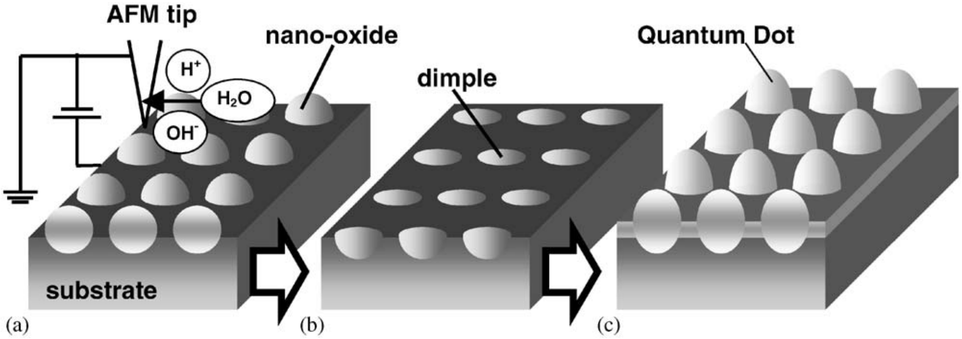

Fig. 1. Schematic of the experimental procedure; (a) nano-oxidation, (b) nanodimple formation by etching, and (c) Ge dot preferential growth by MBE.

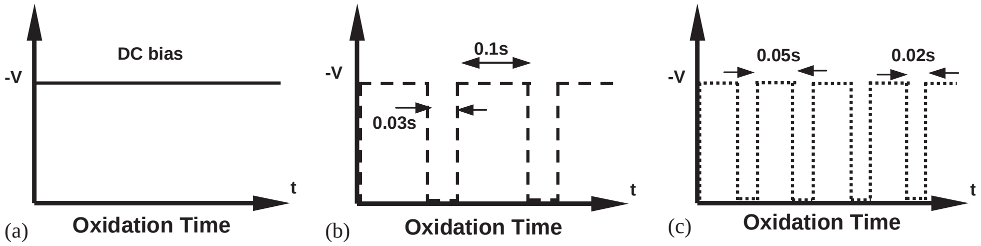

Fig. 2. Three bias pulse sequences; (a) DC bias for the total of 2 s, (b) 0.1 s pulses with 0.03 s intervals for the total of 2 s, and (c) 0.05 s pulses with 0.02 s intervals for the total of 2 s.

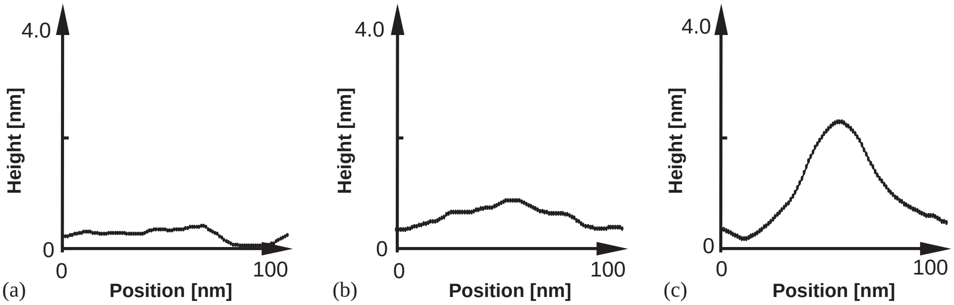

Fig. 3. Height contours of three dots formed with different pulse sequences. The dots of (a)–(c) were formed with the pulse sequences (a)–(c) in Fig. 2, respectively.

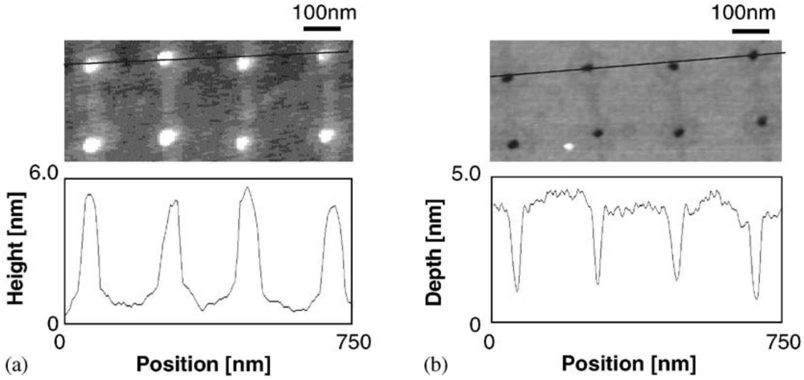

Fig. 4. AFM images and corresponding height contours of (a) SiO_2 nanodot arrays and (b) nanodimple arrays.

leads to the height of ~2.5 nm. Interestingly, the dependence of the height contour on the pulse sequence is very similar to that observed for the AFM oxidation of GaAs [13]. Because the depth of SiO_2 dots into the substrate increases with the height above the substrate, it is important to form SiO_2 as high as possible to realize an array of deep dimples. Therefore, the short pulsing of the bias is employed in this study.

Fig. 4 shows the AFM images and corresponding height contours of arrays of (a) nano SiO_2 dots and (b) dimples after the SiO_2 dots are etched

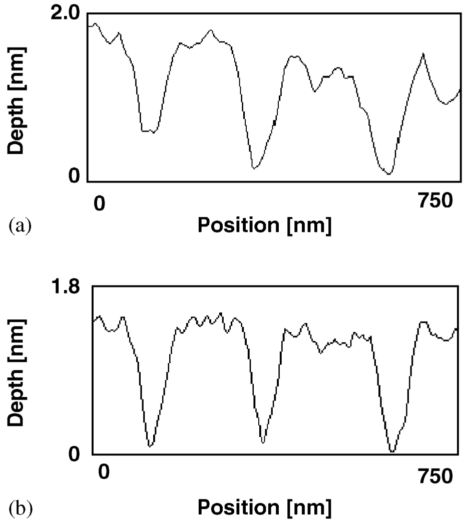

Fig. 5. AFM height contours of nanodimples (a) before and (b) after the 850°C, 15 min surface cleaning in a MBE chamber.

away. The height contour along the line indicated in the AFM picture in Fig. 4(a) shows successful formation of the periodic arrays of SiO_2 dots of the diameter ~45 nm and height ~5 nm. Each dot was formed with the bias of $-V = 4$ V with 0.04 s bias pulses for the total of 2 s. The height contour along the line in Fig. 4(b) shows successful formation of periodic arrays of nanodimples of the diameter ~40 nm and depth ~4 nm.

Fig. 5 shows the height contour of the nanodimples (a) before and (b) after the 850°C, 15 min surface cleaning in our ultra-high vacuum MBE chamber. Fortunately, the height contour hardly changes after the thermal cleaning process. The shape of the nanodimples are preserved perfectly. Therefore, it is of great interest to see how the deposited Ge atoms onto such a patterned surface behave.

Fig. 6 shows the AFM image of an array of nano Ge dots and their height contour along the line in the image. In this case 6.2 monolayers of Ge were deposited. Interestingly, the Ge dots form preferentially in the dimples. For this particular growth, the substrate temperature was maintained for 30 s after the end of deposition. This short annealing process seemed to be important for Ge atoms to migrate into each dimple because our several growth attempts without this short annealing did not lead to formation of the dots at the dimples. For example, the second dot from the right in Fig. 6 is incomplete possibly because the annealing of 30 s may have been too short for a sufficient number of Ge atoms to reach the dimple. The height contour in the figure also indicates the formation of several structures between the dots formed at dimples, possibly smaller dots. Therefore, it is important in the future to understand and optimize the relation between the dimple size, position, Ge deposition rate, substrate temperature, and post-deposition annealing condition.

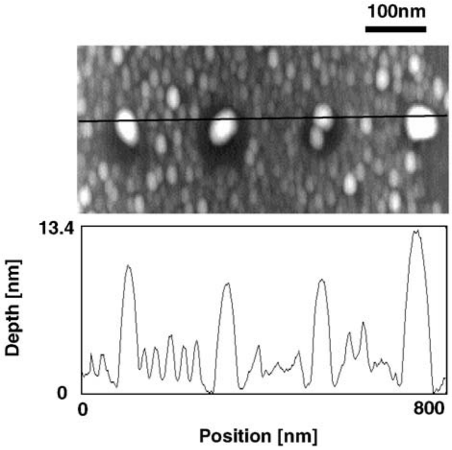

Fig. 6. An AFM image and corresponding height contour of the Ge nanodot array.

4. Summary

Ge quantum dots have been grown preferentially in nanodimples formed by the anodic oxidation of the Si surface by the AFM tip. Considering the fact that the method was originally developed for the size and position control of the InGaAs dots on GaAs [7] and now proven useful for the case of Ge dots on Si, it will be of great interest to apply the same method for a wide variety of the SK-mode quantum dot systems.

Acknowledgements

We would like to thank H.Z. Song, T. Ohshima, and Y. Okada for their advices on AFM nanooxidation and the technical staff of the Central Service Facilities for Research at Keio University for the assistance with AFM. The work is supported in part by the Fujitsu Laboratories and in part by a Grant-in-Aid for Scientific Research in Priority Areas "Semiconductor Nanospintronics (♯14076215)."

References

[1] T.I. Kamins, R.S. Williams, Appl. Phys. Lett. 71 (1997) 1201.
[2] E.S. Kim, N. Usami, Y. Shiraki, Appl. Phys. Lett. 72 (1998) 1617.
[3] O.G. Schmidt, N.Y. Jin-Phillipp, C. Lange, U. Denker, K. Eberl, R. Schreiner, H. Gräbeldinger, H. Schweizer, Appl. Phys. Lett. 77 (2000) 4139.
[4] Z. Zhong, A. Halilovic, T. Fromherz, F. Schäffler, G. Bauer, Appl. Phys. Lett. 82 (2003) 4779.
[5] M. Ichikawa, IEEE J. Quantum Electron. 38 (2002) 988.
[6] M. Shibata, Y. Nitta, K. Fujita, M. Ichikawa, Phys. Rev. B 61 (2000) 7499.
[7] H.Z. Song, T. Ohshima, Y. Okada, K. Akahane, T. Miyazawa, M. Kawabe, N. Yokoyama, in: A.R. Long, J.H. Davies, (Eds.), Proceedings of the 26th International Conference on Physics of Semiconductors, Institute of Physics Conference Series No. 171, 2003, p. 32.
[8] A.V. Kolobov, K. Morita, K.M. Itoh, E.E. Haller, Appl. Phys. Lett. 81 (2002) 3855.
[9] Ph. Avouris, T. Hertel, R. Martel, Appl. Phys. Lett. 71 (1997) 285.
[10] Ph. Avouris, R. Martel, T. Hertel, R. Sandstrom, Appl. Phys. A 66 (1998) S659.
[11] M. Tello, F. Garcia, R. Garcia, J. Appl. Phys. 92 (2002) 4075.
[12] A. Ishizaka, Y. Shiraki, J. Electrochem. Soc. 133 (1986) 666.
[13] Y. Okada, Y. Iuchi, M. Kawabe, J. Appl. Phys. 87 (2000) 8754.