

Raman Spectroscopy of Ge Nanoparticles Formed in Thin SiO₂ Films by Negative Ion Implantation

Nobutoshi Arai*, Hiroshi Tsuji, Takashi Minotani, Hiroyuki Nakatsuka, Kenji Kojima, Kouichirou Adachi*, Hiroshi Kotaki*, Toyotsugu Ishibashi, Yasuhito Gotoh and Junzo Ishikawa

Department of Electronic Science and Engineering, Kyoto University, Nishikyo-ku, Kyoto 606-8501, Japan
Fax: 81-75-383-2284, e-mail: arainko@racing.mbox.media.kyoto-u.ac.jp

*Advanced Technology Research Laboratories, SHARP Corporation, Tenri 632-8567, Japan
Fax: 81-743-65-2393, e-mail: arai@ulab.tnr.sharp.co.jp

Germanium nanoparticle in SiO₂ is expected to be used as a charge trap, light emission source, etc. Ge nanoparticles can be formed in silicon dioxide films by negative ion implantation and heat treatment. However, under the heat treatment, these nanoparticles may be oxidized by residual oxygen in the heat treatment atmosphere, or combination with oxygen in a silicon oxide film. The XPS analysis showed the oxidation of some implanted Ge atoms. Raman spectra were investigated to confirm the existence of Ge-Ge bonds in the nanoparticles. Ge negative ions were implanted into a thermally grown 100 nm-thick SiO₂ film on Si substrate. After implantation, the samples were annealed at various temperatures. After annealing at temperature more than 600°C, each Raman spectra showed a peak around 270 - 300 cm⁻¹. These peaks corresponded to the Ge-Ge bonding depending on the size of Ge nanoparticles. The sample after annealing at 800°C showed strong peak at 300 cm⁻¹. The largest Ge nanoparticles are expected to form in the layer. However, there is no peak in the sample after annealing at 900°C.

Key words: Nanoparticles, Ion implantation, Oxide film, Germanium Negative ion, Raman spectroscopy

1. INTRODUCTION

A substance in nanoparticles has many different properties from its bulk state. Nanoparticles embedded in dielectric materials are attractive materials for the development of single electron devices and light emission devices. Formations of nanoparticles in thermally grown silicon dioxide films, which is a high quality SiO₂ films, with implantation and heat treatment technique have been already reported [1-5]. However, under the heat treatment at hundreds of degrees, these nanoparticles may be oxidized by residual oxygen in the heat treatment atmosphere, or combination with oxygen in a silicon oxide film. We made samples of Germanium nanoparticles in SiO₂ with implantation and heat treatment technique [6]. The XPS analysis of the samples showed the oxidation of some implanted Ge atoms [7]. Then it was afraid that there are not metallic (without oxidation) Ge nanoparticles but GeO₂ nanoparticles. Therefore Raman spectra were investigated to confirm the existence of Ge-Ge bonds in the nanoparticles. Thermally grown SiO₂ was implanted by Ge ion implantation and annealed at various temperatures to form nanoparticles. The Raman spectra for some samples showed peaks corresponding to the Ge-Ge bonding depending on the size of Ge nanoparticles.

2. EXPERIMENTAL

Germanium negative-ion implantation was performed by a negative ion implanter (Nissin Electric Corp., Japan) [8] equipped with an RF (radio frequency) plasma-sputtering type heavy negative ion source [9, 10].

Ge⁻ extracted from the source at 10 keV were mass separated by a sector magnet and then accelerated up to desired implantation energy. After eliminating fast neutrals from the beam by electrostatic potential, the ⁷⁴Ge⁻ beam was introduced into a collector cup with a limiting aperture of diameter 8 mm in an implantation chamber of the negative ion implanter. In the collector cup, Ge⁻ were implanted at room temperature into a thermally grown silicon dioxide layer with a thickness of 100 nm on silicon substrate (15 mm x 15 mm). We used a multi-energy implantation technique to make a flat profile of Ge atomic density in some region. In the multi-energy implantation, the Ge⁻ were implanted three times into the same SiO₂ layer by changing the energy of

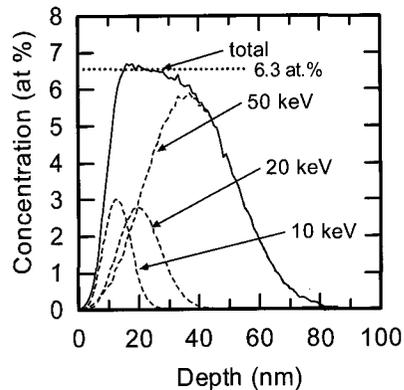


Fig. 1. Depth profile of Ge atoms implanted into SiO₂ medium calculated by using TRIM-DYN program under conditions of multi-energy implanted at 50 keV with 1.4×10^{16} , 20 keV with 3.2×10^{15} and 10 keV with 2.2×10^{15} .

50, 20 and 10 keV in this order. Each dose amount for these energies is 1.4×10^{16} , 3.2×10^{15} , and 3.2×10^{15} ions/cm², respectively, or 2.3×10^{16} , 5.3×10^{15} , and 3.6×10^{15} ions/cm², respectively, with a current density of $0.8 \mu\text{A}/\text{cm}^2$, $0.4 \mu\text{A}/\text{cm}^2$, and $0.4 \mu\text{A}/\text{cm}^2$, respectively. Calculative Ge atomic densities in maximum were 6.3 at.% and 12 at.%, respectively. For example, the calculated depth profile of Ge in the multi-energy implantation (50 keV, 1.4×10^{16} ions/cm²; 20 keV, 3.2×10^{15} ions/cm²; 10 keV, 2.2×10^{15} ions/cm²) is shown in Fig. 1. The calculation was executed by using a PC version program of DYNAMIC MONTE-CARLO PROGRAM TRIM-DYN (dynamic ion transport in matter incl. recoil cascades, (c)Biersack, Berlin 1983 & 89) [11] with including dose effect. As seen from the total concentration curve, Ge implanted layer with a concentration of about 6 at.% is expected to be formed from 10 nm to 50 nm in depth are shown in the figure. The gas pressure during the implantation was kept less than 1×10^{-4} Pa (background pressure was 3×10^{-5} Pa). We expected to obtain Ge implanted layer with a thickness of about 40 nm by this multi-energy implantation. After implantation, the samples were annealed by an electrical oven at various temperatures of 600, 700, 800 and 900°C in a quartz tube under vacuum condition by a rotary pump (400 l/min).

The depth distribution of implanted Ge atoms and fractions of metallic and oxidized Ge atoms were measured by X-ray induced photoelectron spectroscopy (XPS, AXIS-165S, Shimadu/Kratos, Japan) with Ar ion etching. We measured survey spectra in a range of 1300 – 0 eV in binding energy and narrow spectra in a range of 1235 – 1205 eV with a monochromatic Al K α of 1486.6 eV in photon energy after every etching for 300 s by Ar⁺ irradiation at 4 keV. After etching for a total time of 4000 s, the Ge signal was disappeared. Therefore, the etching speed is about 0.017 nm/s (5.1 nm for 300 s). We obtained Ge atomic fractions in SiO₂ from the comparison of peak area for detected photoelectrons of Ge 2p_{3/2}, O 1s and Si 2p in the survey with taking into account of each sensitivity of the apparatus. As for fractions of metallic and oxidized Ge atoms, a chemical shift due to oxidation of Ge atoms is about 1.4 and 2.8 eV higher in binding energy for GeO and GeO₂, respectively. In the experiment, only chemical shift by GeO was distinguished. Therefore, we divided the detected Ge 2p_{3/2} peak into two Gaussian distributions

from metallic (Ge-Ge) and mono-oxide (Ge-O) ones by the peak fitting. Then, the ratio of metallic Ge atoms was calculated.

Raman spectra of the annealed samples were measured for confirming the formation of Ge-Ge bonds in the sample. Ar ion laser of 458 nm in wavelength was used as a probe source and the Raman shift from 152 to 503 cm⁻¹ was measured at room temperature. Ge-Ge bond shows Raman shift in a range of 250 – 300 cm⁻¹. Since penetration length of the source laser light is about 250 nm, a small satellite signal due to Si-Si bond also appeared in a range of 220 – 304 cm⁻¹ for the 100-nm-SiO₂ layer on Si substrate. Therefore, we subtracted the disturbing Si signal from the detected ones as to loose the step increase at Raman shift of 220 cm⁻¹.

3. RESULTS AND DISCUSSION

Figure 2(a) shows the narrow spectra of Ge 2p_{3/2}, where the depth value was calculated from the etching time. Two peaks in the Ge 2p_{3/2} photoelectrons were observed in the etched sample. The peaks at 1217.5 eV and 1220 eV are corresponded to Ge 2p_{3/2} peaks from metallic Ge-Ge and Ge oxide of Ge-O, respectively.

By fitting with two Gaussian-type distributions of Ge 2p_{3/2} peaks, we can calculate the ratio of metallic Ge. Figure 2(b) shows the percentage of metallic Ge as a function of depth. After annealing at 900°C, Ge atoms in the surface region was oxidized. This was considered to be due to penetration of oxygen from the residual gas to the sample surface during the annealing. On the contrary, the both of the as-implanted and 600°C-annealed samples showed oxidation of Ge atoms in the deep-depth region more than those in the surface region. In these samples, it is not expected oxygen invasion from the residual gas in annealing. This oxidation at deep depth is considered due to the local excess of oxygen atoms resulted by implantation [7].

The XPS analysis showed the oxidation of implanted Ge atoms at a deep depth. Raman spectra were investigated to confirm that the Ge nanoparticles have Ge-Ge bonds in them. Figure 3 shows Raman spectra obtained for the 6.3 at.% Ge-implanted samples after annealing at 600°C, 900°C for 1 h and as-implanted, and for unimplanted sample and Si-substrate without SiO₂ layer. Si-Si bonding results the satellite peak near Raman shift of 304.1 cm⁻¹. As-implanted and annealed

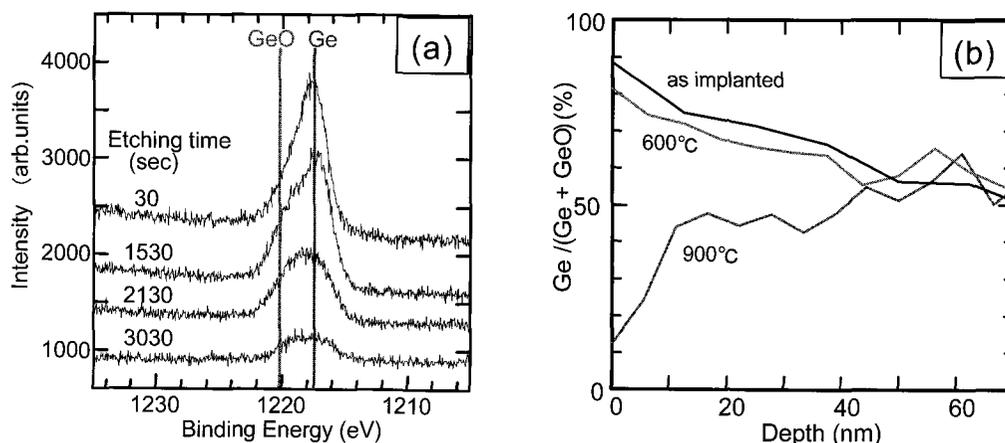


Fig. 2. (a) Ge 2p_{3/2} peak and (b) Ge/(Ge+GeO)-depth profiles obtained from XPS for Ge-implanted 100-nm-SiO₂/Si samples with 6.3 at.% implanted Ge peak concentration after annealing at various temperatures.

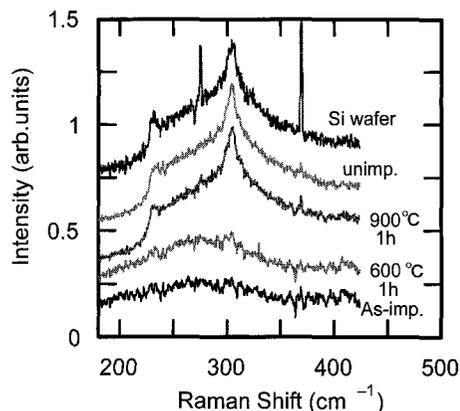


Fig. 3. Raman shifts obtained from Laser Raman spectroscopy for Ge-implanted 100-nm-SiO₂/Si samples with 6.3 at.% implanted Ge peak concentration after annealing at various temperature.

at 600°C sample had different Raman spectra from unimplanted sample. The Raman spectra showed broad peaks around 250 - 300 cm⁻¹. These peaks seem reflect the existence of the Ge-Ge bonding and are consistent with the results of Kolobov *et al.* [12].

However, the sample after annealing at 900°C had almost same spectra with unimplanted sample. This result seems reflect oxidation of Ge or few Ge-Ge bonding. It was well corresponded to the XPS result of Ge oxidation shown in Fig. 2(b).

Figure 4(a) shows Raman spectra obtained for the 12 at.% Ge-implanted samples after annealing at 600°C for 4 h, 700°C for 1h, 700°C for 4 h and 800°C for 1 h and for Si-substrate without SiO₂ layer. Si-Si bonding results the satellite peak near Raman shift of 304.1 cm⁻¹. The each curve of Raman spectra in Fig. 4(b) were eliminated the Si-Si effect from the spectra in Fig. 4(a). After annealing at 600°C or more, each Raman spectra showed a peak around 250 - 300 cm⁻¹. These peaks suggested the existence of Ge-Ge bonding. Then, after annealing at 800°C and or less, the peak around 300 cm⁻¹ is larger as the annealing temperature is higher. The peak positions for 600°C for 4 h, 700°C for 1h, 700°C for 4 h and 800°C for 1 h were about 275 cm⁻¹, 290 cm⁻¹, 292 cm⁻¹ and 297 cm⁻¹, respectively.

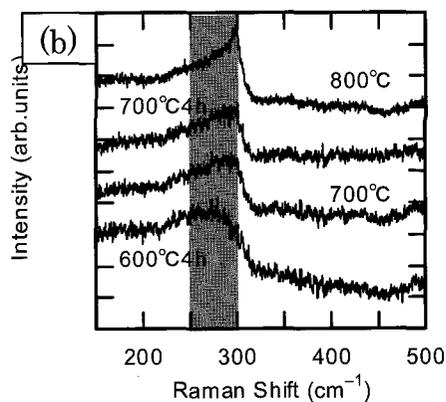
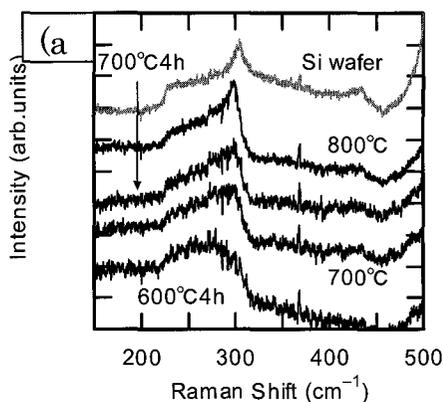


Fig. 4. (a) Raman shifts and (b) Raman shifts without influence of Si-substrate obtained from Laser Raman spectroscopy for Ge-implanted 100-nm-SiO₂/Si samples with 12 at.% implanted Ge peak concentration after annealing at various temperature.

Figure 5 shows results of Raman shifts and width of

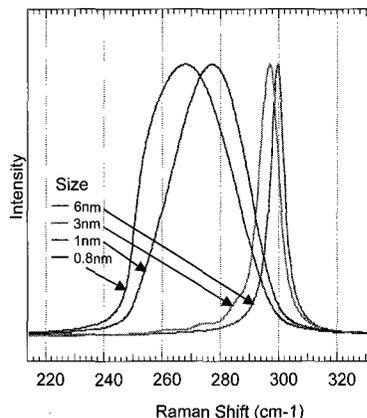


Fig. 5. Calculated Raman shifts under conditions of various size of Ge nanoparticle.

half maximum at various size of Ge nanoparticle as a parameter calculated with a model of Wellner *et al.* [13]. The peak shifts to smaller wave number and widens its width of half maximum as the size of nanoparticle becomes small. In comparison with Fig. 4(b), Ge nanoparticles seem to grow as annealing temperature rises. The sample after annealing at 800°C for 1h showed a strong peak at 297 cm⁻¹ with a longer tail at smaller wave number. Therefore, the maximum size of Ge nanoparticles is expected to be about 3 nm and many smaller nanoparticles are expected to form in the layer.

4. CONCLUSION

We have investigated the existence of Ge-Ge bonding in the samples with Laser Raman spectroscopy. The samples of thermally grown 100 nm thick SiO₂ on Si substrate were implanted with triple-energy Ge⁻ and annealed at various temperatures. The implanted Ge atoms were also evaluated by XPS. For the sample annealed at 900°C, Ge-Ge bonding could not be detected by the Laser Raman spectroscopy. This suggests oxidation of Ge atoms or few Ge-Ge bonding. For 800°C or less, the spectra suggest the existence of Ge-Ge bonding. The evaluations of Ge particle size from the Raman shifts and width of half maximum of the peaks indicated larger Ge nanoparticles as higher annealing temperature within 600 - 800°C. For 800°C, Raman spectra indicated

Ge nanoparticles of about 3 nm or less. These results

suggest size of Ge nanoparticles formed with ion implantation in the thermally grown SiO₂ can be controlled with annealing temperature and oxidation.

ACKNOWLEDGEMENT

The authors are grateful to Prof. H. Harima of Kyoto Institute of Technology for the support of the Laser Raman spectroscopy measurement and analysis.

REFERENCES

- [1] A. Nakajima, T. Futatsugi, N. Horiguchi, H. Nakao, and N. Yokoyama: *Tech. Dig. IEDM*, (1997) 159.
- [2] Y. Takeda, C.G. Lee, N. Kishimoto: *Nucl. Instr. and Meth., B* 191 (2002) 422.
- [3] K. H Heining, T. Mueller, B. Schmidt, M. Strobel, W. Moeller, *Appl. Phys. A* 77 (2003) 17-25..
- [4] H. Tsuji, N. Arai, T. Matsumoto, K. Ueno, K. Adachi, H. Kotaki, Y. Gotoh, J. Ishikawa, *Surf. Coat. Tech.* 196 (2005) 39.
- [5] J. Ishikawa, H. Tsuji, N. Arai, T. Matsumoto, K. Ueno, K. Adachi, H. Kotaki, Y. Gotoh, *Nucl. Instr. Meth. B* 237 (2005) 422.
- [6] N. Arai, H. Tsuji, N. Gotoh, T. Minotani, H. Nakatsuka, K. Kojima, T. Yanagitani, T. Okumine, H. Ohnishi, T. Satoh, M. Harada, K. Adachi, H. Kotaki, Y. Gotoh and J. Ishikawa: *J. Vac. Soc. Jpn.*, 49 (2006) 180.
- [7] H. Nakatsuka, H. Tsuji, N. Arai, T. Minotani, K. Kojima, N. Gotoh, T. Okumine, K. Adachi, H. Kotaki, Y. Gotoh and J. Ishikawa: *Spring Meeting of Jpn. Soc. Appl. Phys.* (2006) 24a-F-6.
- [8] J. Ishikawa, H. Tsuji, Y. Toyota, Y. Gotoh, K. Matsuda, M. Tanho, and S. Sakai, *Nucl. Instr. Methods, B*96 (1995) 7-12.
- [9] J. Ishikawa, *Rev. Sci. Instrum.* 67 [3] (1996) 1410-1416.
- [10] H. Tsuji, J. Ishikawa, T. Tomita, and Y. Gotoh, *Rev. Sci. Instrum.* 67 [3] (1996) 1012-1014.
- [11] J.P. Biersack, *Nucl. Instr. Methods, B*27 (1987) 21-36.
- [12] A. V. Kolobov, Y. Maeda, and K. Tanaka: *J. Appl. Phys.*, 88 (2000) 3285.
- [13] A. Wellner, V. Paillard, C. Bonafos, H. Coffin, A. Claverie, B. Schmidt, K.H. Heinig, *J. Appl. Phys.* 94 (2003) 5639-5642.

(Received December 10, 2006; Accepted May 15, 2007)