

Nitridation of Ge(100) Surfaces by Vacuum-ultra violet (VUV) Irradiation in NH₃ Ambience

H. Nakagawa, A. Ohta, M. Taira, H. Abe, H. Murakami, S. Higashi and S. Miyazaki

Graduate School of Advanced Sciences of Matter, Hiroshima University
Kagamiyama 1-4-1, Higashi-Hiroshima 739-8530, Japan
E-mail: semicon@hiroshima-u.ac.jp

Abstract

We have studied the nitridation of HF-last Ge(100) assisted by vacuum-ultra violet (VUV) irradiation in NH₃ ambience in the temperature range of 200~500°C by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared attenuated total reflection (FT-IR-ATR). Ge3d spectra taken just after wet-chemical cleaning steps show that there exists Ge oxide as thin as ~0.4nm in average thickness on Ge(100). In the cases without VUV irradiation, the thermal nitridation was not detected in the temperature range of 300-580°C although the thermal desorption of Ge oxide occurred around 500°C. Surface nitridation proceeded under the VUV irradiation in NH₃ ambience at 200~300°C, and Ge oxynitride as thin as ~0.76nm with an average nitrogen content of ~37at.% was formed at 300°C. At 500°C under VUV radiation, a Ge surface covered with ~0.43nm-thick nitride was obtained as a result of desorption of Ge-O bonds and surface termination with NH_x. Although surface roughness was increased from 0.22 to 0.82nm in root mean square (RMS) value by 500°C nitridation, the obtained surface was fairly stable against oxidation during exposure to clean room air. Also, p-polarized IR-ATR measurements using a Ge prism confirm the formation of the Ge-N network from the evolution of an absorption band peaked around 730cm⁻¹.

Key words: Ge(100) substrates, Vacuum-ultra violet (VUV), nitridation, XPS, FT-IR-ATR

1. INTRODUCTION

It will be a challenge to replace conventional materials in MOS structures with new ones such as metal gate, high-gate dielectric and advanced channel because of serious limitations in the continuous scaling of Si complementary metal-oxide-semiconductor (CMOS) devices. Germanium is a promising alternative for the channel material of advanced MOSFETs from the view points of its high carrier mobility for improved injection current density and small band gap for supply voltage scaling [1, 2]. Specifically, the combination of Ge channel and high-k dielectric stack is increasingly attractive because of its potential advantages of being able to realize a large driving current [3-5]. However, there are some concerns about the nature of oxide/Ge interfaces, including the poor thermal and chemical stability of Ge-O bonds. The thermal desorption of Ge oxide at a temperature as low as ~450°C causes the interface roughening during gate dielectric formation by chemical vapor deposition (CVD) [6, 7]. Also, in capacitance-voltage characteristics of Ge MOS capacitors, significant hysteresis and frequency dispersion associated with slow interface states are often observed [8]. To overcome such practical difficulties, the formation of ultrathin Ge nitrides and oxynitrides before high-k deposition is thought to be of great importance to improve the structural stability at the interface between gate dielectrics and Ge(100) substrates. In fact, the N₂-plasma nitridation of Ge(100) at 300°C leads to the formation of a flat interface between Ge₃N₄ and Ge(100) with a fairly low trap density [9] in contrast to the fact that thermal nitridation of Ge(100) in NH₃ ambience hardly occurs at temperatures lower than 600°C [10].

In this work, we examined how the surface nitridation of wet-chemically cleaned Ge(100) is

promoted by VUV radiation in a NH₃ ambience in the temperature range from 200 to 500°C.

2. EXPERIMENTAL

The substrates used in this study were p-type Ge(100) wafers with a resistivity of 0.019~0.026Ωcm. After degreasing by acetone and pure water rinse, Ge(100) substrates were immersed in 20%HCl solution to remove the native oxide. Subsequently, Ge(100) substrates were re-oxidized in 10%H₂O₂ solution at room temperature and dipped in a dilute HF-treatment. The surface roughness before and after the dilute HF-treatment are 0.22 and 0.23nm in root-mean-square (RMS) value, respectively. The HF-last Ge(100) surfaces were pre-heated at 100°C at a pressure of ~1.0x10⁻⁶ Pa for 5 min and nitrided in an ambient NH₃ at a pressure of 22Pa in the temperature range from 200 to 500°C under VUV irradiation peaked at 172nm from an excimer lamp for 5~60 min. A halogen lamp heating system was used for substrate heating. The chemical bonding features of the samples so prepared were characterized by x-ray photoelectron spectroscopy (XPS) using a monochromatized AlKα (1486.7eV) radiation and Fourier transform infrared attenuated total reflection (FT-IR-ATR). The surface roughness was also measured by an atomic force microscope (AFM) using a Rh-coated Si₃N₄ cantilever in clean room ambient.

3. RESULTS AND DISCUSSION

The Ge3d, O1s and N1s spectra taken before and after NH₃ annealing at 300 and 580°C for 10 min without VUV irradiation are shown in Fig. 1. The binding energy was calibrated with metallic signals of Ge(100) substrates peaked at 29.9eV. For the

as-cleaned Ge(100) surface, the chemically-shifted Ge3d signals around 33.0eV show the existence of a Ge oxide layer. From the intensity ratio of the chemically-shifted Ge3d signals to the substrate Ge3d signals, a Ge oxide layer thickness just after wet-chemically steps was estimated to be ~0.31nm. No N1s signals even after NH₃-anneal indicate that surface nitridation did not proceed in the temperature range of 300~580°C without VUV irradiation as reported previously [10]. In the case of NH₃-annealing at 300°C for 10 min, an increase in each of the chemically shifted Ge3d and O1s signals show the growth of the Ge oxide, being attributable to residual moisture in the NH₃ ambience. The oxide thickness was evaluated to be 0.72nm. In contrast, NH₃-annealing at 580°C for 10 min causes a significant decrease in each of the chemically shifted Ge3d and O1s signals, which suggests progress in the thermal desorption of Ge-O bonds.

By VUV irradiation in NH₃ ambience at 300°C for

10 min, the chemically-shifted Ge3d signals are slightly increased in the lower binding energy side and decreased in the higher binding energy side as shown in Fig. 2. Correspondingly, N1s signals at approximately 398eV were detected and O1s signals were markedly decreased. This result indicates that surface nitridation is enhanced by VUV irradiation. The thickness of the resultant GeON layer was estimated to be ~0.56nm and the N content was 32.5at%. Notice that, for 1.4nm-thick Ge oxide grown by UV-O₃ oxidation at 100°C, no surface nitridation under VUV irradiation in NH₃ ambience at 300°C occurs. It is likely that the nitridation of HF-last Ge(100) under VUV irradiation is rate-limited by the substitution of O atoms in sub-oxides with N atoms. With an increase in VUV irradiation time over 60 min, the surface nitridation of HF-last Ge(100) at 300°C tends to be saturated to ~0.76nm in oxynitride thickness with a nitrogen content of ~37at% as represented in Fig. 3. When the VUV-assisted NH₃-nitridation temperature is

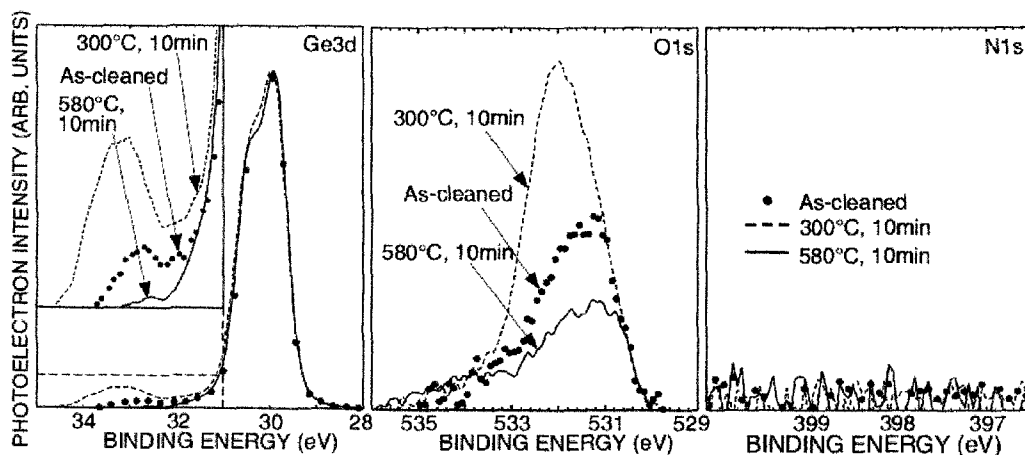


Fig. 1. Ge3d, O1s and N1s spectra taken for the Ge(100) surfaces before and after NH₃ annealing at 300 and 580°C for 10 min. The binding energy was calibrated with the Ge3d^{5/2} peaked at 29.9eV and the photoelectron intensity was normalized by the peak intensity of Ge3d signals from the Ge(100) substrate. Ge LMM Auger signals that peaked at ~534eV are superimposed on the high binding energy tail of O1s core line signals.

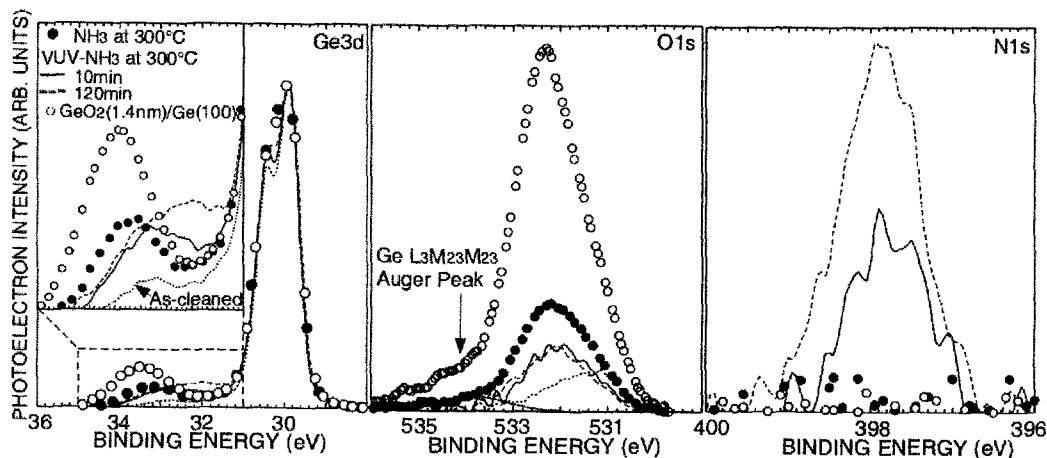


Fig. 2. Ge3d, O1s and N1s spectra taken before and after VUV irradiation in NH₃ ambience at 300°C for 10~120 min. The spectra after NH₃ annealing at 300°C (dot circles) without VUV irradiation and the spectra after NH₃-annealing at 300°C under VUV irradiation of 1.4nm-thick Ge oxide grown by UV-O₃ oxidation at 100°C (open circles) are also shown as references.

increased to 500°C, the chemically shifted Ge3d signals and O1s signals at approximately 531.5eV were markedly decreased and the N1s signals were slightly increased (Fig. 4). There was no significant difference in surface nitridation between the cases for 10 min and 60 min in VUV irradiation time, and the surface nitridation on Ge(100) was limited in a monolayer level, ~0.23nm in nominal thickness, which implies a balanced condition among thermal desorption of Ge oxide, surface oxidation by residual moisture and surface nitridation. To gain insight into the uniformity of the surface nitridation, the change in the surface morphology with VUV-assisted NH₃ nitridation was examined as represented in Fig. 5. AFM images clearly show that 500°C nitridation causes a significant increase in the surface microroughness up to 0.82nm in RMS value, presumably as a result of surface nitridation competition with surface oxidation and thermal desorption. The formation of a Ge oxynitride network by VUV-assisted NH₃-nitridation was also measured by using a p-polarized infrared attenuated total reflection (IR-ATR) method as shown in Fig. 6. Infrared absorption bands due to a Ge-O-Ge network around 850 and 940cm⁻¹ appear as seen in the IR-ATR spectra of Ge oxide with a thickness of 1.6nm formed by UV-O₃ oxidation at 300°C. VUV-assisted NH₃ nitridation of HF-last Ge(100) at 200

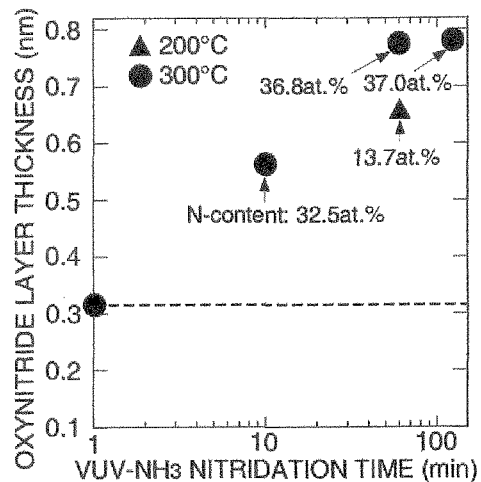


Fig. 3. The oxynitride layer thickness obtained at different VUV-irradiation times at 300°C. The nitrogen content in each case is also shown and the data point obtained at 200°C is plotted as well. The dashed line denotes nominal oxide thickness estimated for the HF-last Ge(100) surface.

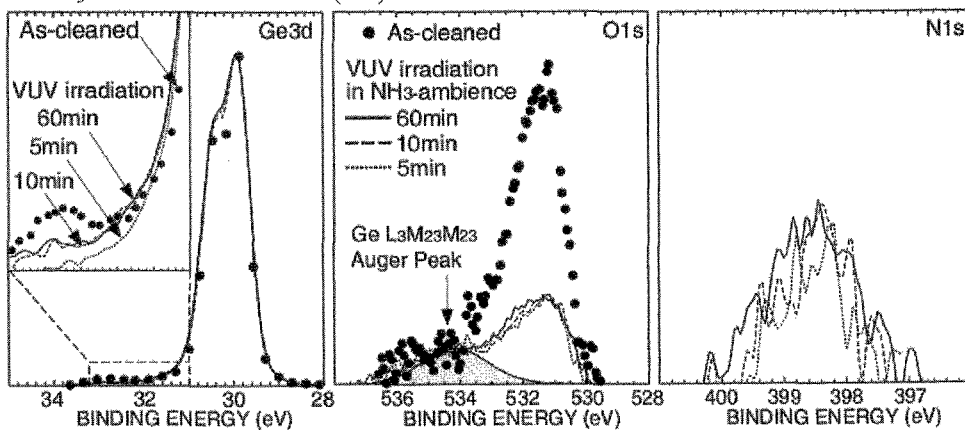


Fig. 4. Ge3d, O1s and N1s spectra taken after VUV-assisted NH₃ nitridation at 500°C for 5~60 min. The Ge3d and O1s spectra after wet-chemical steps are also shown as references. Ge LMM Auger signals peaked at ~534eV are superimposed on the high binding energy tail of O1s core line signals.

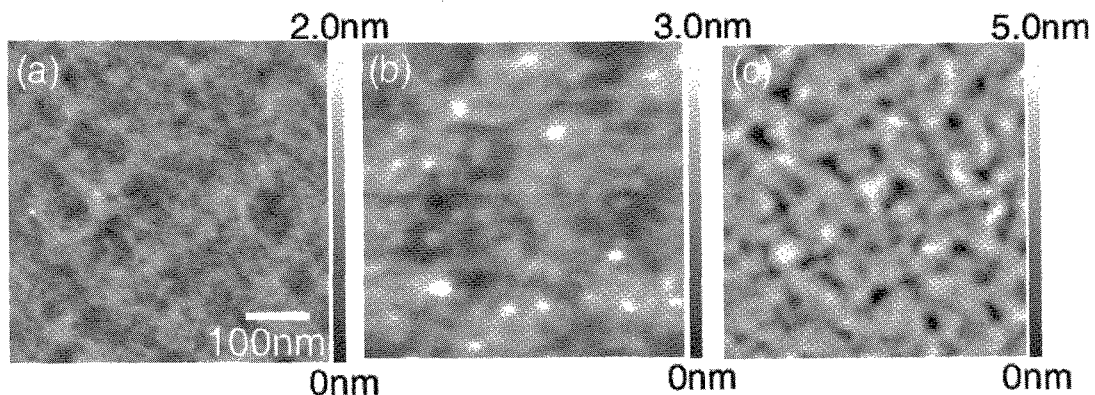


Fig. 5. AFM topographic images taken (a) just after wet-chemical steps and after VUV-assisted NH₃-nitridation of Ge(100) surfaces at (b) 300°C and (c) 500°C for 10 min.

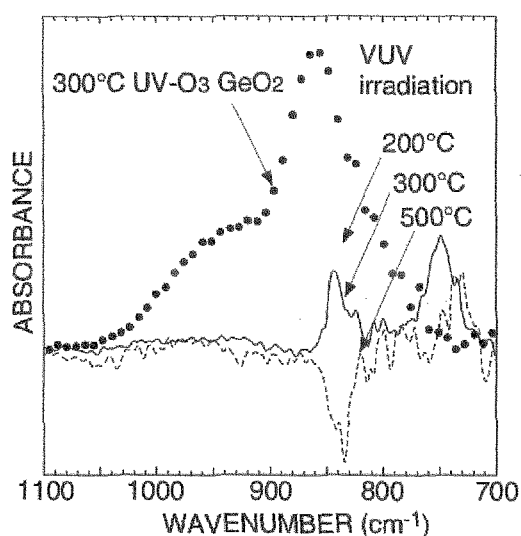


Fig. 6. P-polarized FT-IR-ATR spectra taken after VUV-assisted NH₃-nitridation at 200–500°C. The spectrum for 1.6nm-thick Ge oxide grown by UV-O₃ oxidation at 300°C (dotted circles) is also shown as a reference.

or 300°C causes an increase in the absorption band at approximately 740cm⁻¹ due to the Ge-N network [11] accompanied by an increase in the absorption band due to the Ge-O bonds. At a nitridation temperature of 500°C, a decrease in the IR absorption due to Ge-O bond, which indicates the thermal desorption of native Ge oxide on HF-last Ge(100), and a corresponding slight increase of Ge-N bonds were observable, consistent with the results obtained by XPS analysis.

4. SUMMARY

In direct thermal NH₃ nitridation at 300–580°C, surface nitridation was not detected and the thermal desorption of Ge oxide around 500°C was confirmed. In VUV irradiation in NH₃ ambience at 200–500°C, the surface nitridation of chemically cleaned Ge(100) is promoted with VUV irradiation at 200–300°C, and Ge oxynitride as thin as ~0.76nm with an average nitrogen content of ~37at.% was obtained. In VUV-NH₃

nitridation at 500°C, a surface nitridation as thin as ~0.23nm in thickness was obtained and the surface roughness was markedly increased (~0.82nm) as a result of the desorption of Ge oxides. The formation of the Ge-N network is also confirmed from the evolution of an absorption band peaked around 730cm⁻¹.

ACKNOWLEDGEMENTS

This work was partly supported by the NEDO/MIRAI project and the 21st Century COE program “Nanoelectronics for Terra-Bit Information Processing” from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

REFERENCES

- [1] L. Huang, J.O. Chu, S.A. Goma, C.P. D’Emic, S.J. Koester, D.F. Canaperi, P.M. Mooney, S.A. Cordes, J.L. Speidel, R.M. Anderson and H.S.P. Wong, *IEEE Trans. Electron Devices* **49**, (2002) 1556.
- [2] C.O. Chui, H. Kim, D. Chi, B.B. Triplett, P.C. McIntyre and K.C. Saraswat, *Tech. Dig. Int. Electron Devices Meet.* 2002, 437.
- [3] H. Shang, H. Okorn-Schmidt, K.K. Chan, M. Copel, J.A. Ott, P.M. Kozlowski, S.E. Steen, H.S.P. Wong, E.C. Jones and W.E. Haensch, *Tech. Dig. Int. Electron Devices Meet.* 2002, 441.
- [4] W.P. Bai, N.Lu, J. Liu, A. Ramirez, D.L. Kwong, D. Wrister, A. Ritenour, L. Lee and D. Antoniadis, *Tech. Dig. VLSI Symp.* **2003**, 121.
- [5] K. Kita, K. Kyuno and A. Toriumi, *Appl. Phys. Lett.* **85** (2004) 52.
- [6] K. Prabhakaran, T. Ogino, *Surf. Sci.* **325**, (1995) 263.
- [7] S. Van Elshocht, B. Brijs, M. Caymax, T. Conard, T. Chiarella, S. De Gendt, B. De Jaeger, S. Kubicek, M. Meuris, B. Onsia, O. Richard, I. Teerlinck, J. Van Steenberghe, C. Zhao and M. Heyns, *Appl. Phys. Lett.* **85** (2004) 3824.
- [8] H. Kim, P.C. McIntyre, C.O. Choi, K.C. Saraswat, M.-H. Cho, *Appl. Phys. Lett.* **85** (2004) 2902.
- [9] T. Maeda, T. Yasuda, M. Nishizawa, N. Miyata, Y. Morita, S. Takagi, *Appl. Phys. Lett.* **85** (2004) 3181.
- [10] D. Aubel, M. Diani, L. Kubler, J.L. Bischoff, D. Bolmont, *J. Non-Cryst. Solids* **187** (1995) 319.
- [11] J. Xu, S. Miyazaki and M. Hirose, *Jpn. J. Appl. Phys.* **35** (1996) 2043.

(Received December 22, 2005; Accepted January 31, 2006)