Chemical Modification of Solid Surfaces at Nano-level by Water Cluster Ion Irradiation

Gikan H. Takaoka,† Gaku Ichihashi, Hiromichi Ryuto, and Mitsuki Takeuchi
Photonics and Electronics Science and Engineering Center, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan
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We have investigated impact-process of water cluster ions on solid surfaces. Various kinds of substrates such as Si(100), SiO$_2$ and PMMA substrates were irradiated by adjusting the acceleration voltage and the ion dose. The sputtered depth of these substrates increased with increase of the acceleration voltage, and it was 37 nm for Si, 49 nm for SiO$_2$, and 2.9 µm for PMMA substrates, respectively at an acceleration voltage of 9 kV and an ion dose of 1.0×10$^{16}$ ions/cm$^2$. The sputtering yield calculated was 19 atoms per ion for Si and 13 molecules per ion for SiO$_2$, which was approximately ten times larger than that for Ar monomer ion irradiation. The XPS measurement showed that the Si substrate surfaces sputtered at an ion dose of 1.0×10$^{16}$ ions/cm$^2$ had an oxide layer such as SiO$_2$. The oxide layer thickness increased with increase of the acceleration voltage, and it was approximately 10 nm at an acceleration voltage of 6 kV. On the other hand, at lower ion doses such as 1.0×10$^{14}$ ions/cm$^2$, the ratio of the sputtered depth of Si surface to SiO$_2$ surface became approximately 10. This indicated that the chemical erosion such as silicon hydride occurred, resulting in enhancement of chemical sputtering of Si substrates. Furthermore, for the case of PMMA substrates, the chemical erosion of the substrate surfaces occurred probably through the exchange between CH$_3$ and H radicals, and the chemical sputtering by the ejection of methacrylic acid molecule was enhanced. The surface roughness of PMMA substrates irradiated was less than 2 nm, and the smooth surface at the nano-level was obtained. In addition, micro-patterning was demonstrated with the water cluster ion beams on the PMMA substrates. [DOI: 10.1380/ejssnt.2011.163]

Keywords: Polyatomic molecule; Water; Cluster; Ion bombardment; Ion-solid interactions; Sputtering; Surface chemical reaction; X-ray photoelectron spectroscopy

I. INTRODUCTION

Water is well-known liquid material which exists on earth and in human body, and it has an important role in maintaining clean environment and safe life. It is also important solvent which is used in cleaning process for various kinds of devices fabricated in semiconductor industries. On the other hand, ion beam process is one of the basic technologies in nanostructure fabrications [1, 2]. It represents several features in material processing, one of which is that it can transfer charge, energy and mass employed for material surface treatment. Another feature is that various kinds of species such as atomic, molecular and cluster ions are available [3, 4]. In particular, polyatomic ions such as water and alcohol ions contain several kinds of radicals such as hydroxyl and alkyl radicals, and these radicals have an important role in surface modification and chemical erosion of the surface [5, 6]. Furthermore, in polyatomic cluster ions, their irradiation effects such as high density irradiation and low energy irradiation effects can be applied effectively to the surface treatment. Another feature is that local heating of impact region by the cluster ion irradiation can enhance chemical reaction on the surface even at room temperature [7, 8].

We have developed several kinds of polyatomic cluster ion sources, and have investigated the interactions of cluster ions with solid surface atoms [9, 10]. When polyatomic clusters such as water clusters are ionized and accelerated toward a substrate, impact of the cluster ions on the surface represents high-chemical reactivity of radicals such as hydroxyl radical and excited hydrogen atom. Furthermore, accelerating energy of water cluster ions enhances the chemical reactivity due to the high density irradiation effect, which is not obtained by monomer ion beam process. In this article, water cluster ion irradiation on various kinds of substrates such as Si(100), SiO$_2$ and poly-methyl-methacrylate (PMMA) is performed by changing the acceleration voltage and the ion dose, and the sputtered depth and the surface morphology are investigated. Furthermore, the X-ray photoelectron spectroscopy (XPS) measurement for the irradiated surfaces is performed, and the chemical modification of irradiated surfaces is discussed. On the basis of these results, micro-patterning is demonstrated with the water cluster ion beams on the PMMA substrates.

II. EXPERIMENTAL PROCEDURE

The details of experimental apparatus were described elsewhere [11]. Water was introduced into the cluster source, and it was heated up to 150°C by a wire heater attached around the source. When water vapors without helium gas were ejected through a nozzle into a vacuum region, water clusters were produced at vapor pressures larger than 0.1 MPa. The cluster size measured by the time-of-flight (TOF) method was distributed between a few hundreds and a few tens of thousands, and the peak size was approximately 4000 molecules per cluster. The peak size as well as the intensity of water clusters increased with increase of the vapor pressure. The water clusters produced passed through a collimator and entered an ionizer. In the ionizer, neutral clusters were ionized by an electron bombardment method. The electron voltage for ionization ($V_e$) was adjusted between 0 V...
and 300 V, and the electron current for ionization ($I_e$) was adjusted between 0 mA and 250 mA. The peak size decreased slightly with increase of the electron current for ionization, although it did not change with respect to the electron energy for ionization. The cluster ions were size-separated by a retarding potential method. The minimum size of cluster ions was controlled by adjusting the retarding voltage, and it was adjusted between 300 molecules per cluster and 1,000 molecules per cluster. The size-separated cluster ions were accelerated toward a substrate, which was set on a substrate holder. The acceleration voltage ($V_a$) was adjusted between 0 kV and 10 kV. The substrates used were Si(100), SiO$_2$ and PMMA. The substrate temperature was at room temperature. The substrate surfaces irradiated with water cluster ions were measured by using an atomic force microscope (AFM), and the composition and the chemical bond state were measured by the X-ray photoelectron spectroscopy (XPS). Furthermore, mask patterns demonstrated on the PMMA substrates with water cluster ion beams were observed by the laser microscope.

### III. RESULTS AND DISCUSSION

In order to investigate the dissociation of water cluster ions, we measured a mass spectrum for the vacuum chamber by using the quadrupole mass-spectrometry (Q-Mass). Figure 1 shows the mass spectra (a) after impact of water cluster ions on Si(100) surface and (b) at water vapor atmosphere.

**FIG. 1: Mass spectra (a) after impact of water cluster ions and (b) at the atmosphere of water vapors.**

The acceleration voltage was 6 kV, and the cluster size used was larger than 300 molecules per cluster. As shown in the figure, the sputtered depth increases with increase of the acceleration voltage, and it is 37 nm for Si, 49 nm for SiO$_2$, and 2.9 μm for PMMA substrates, respectively at an acceleration voltage of 9 kV. The sputtering yield calculated is 19 atoms per ion for Si and 13 molecules per ion for SiO$_2$, which was approximately ten times larger than that for Ar (mass number: 40) or Ne (mass number: 20) monomer ion irradiation [12, 13]. For the Si surfaces, OH radicals or oxygen atoms produced have important roles in the oxidation due to implantation and/or diffusion processes, and the oxidation depends on both the kinetic energy and the reactivity of the bombarding species. Since the silicon oxide layer has a higher surface binding energy than the Si surface [14], chemical sputtering of the oxide layer decrease. Instead, the kinetic energy of another cluster ion bombarded is used for the physical sputtering of the oxide layer. As a result, the sputtered depth of Si surfaces is similar to that of SiO$_2$ surfaces.

Furthermore, for the PMMA substrates, the chemical erosion of the substrate surfaces occurs through the exchange of CH$_3$ radical in COOCH$_3$ with H atom of the water cluster or the exchange of OCH$_3$ radical with OH radical. As a result, the PMMA surface changes to polymer methacrylic acid surface, which represents the low melting point less than room temperature and is dissolved by water. The impact of water cluster ions following-up enhances the ejection of methacrylic acid molecule at the monomer state from the surface. Thus, the high rate sputtering of PMMA surfaces is achieved by both the chemical erosion of the surface and the momentum transfer of the incident energy, which is different from the sputtering of PMMA surfaces reported elsewhere [15–17].

**FIG. 2: Dependence of sputtered depth for Si(100), SiO$_2$ and PMMA on the acceleration voltage.**

Figure 2 shows the dependence of sputtered depth for Si(100) and SiO$_2$ surfaces on the ion dose. The acceleration voltage was 6 kV, and the cluster size used was larger than 300 molecules per cluster. As shown in the figure, the sputtered depth increases with increase of the ion dose. However, the sputtered depth for the Si surface does not increase linearly with increase of the dose, and it increases gradually toward a given depth at an ion dose of $1.0 \times 10^{16}$ ions/cm$^2$. At a lower ion dose of $1.0 \times 10^{14}$ ions/cm$^2$, the ratio of the sputtered depth of Si surface to SiO$_2$ surface becomes approximately 10, which indicates the sputtered depth for Si surfaces is similar to that of SiO$_2$ surfaces.
cates that the chemical erosion such as silicon hydride occurs, resulting in enhancement of chemical sputtering of Si surface. When water cluster ions are irradiated on the Si surface, some of water molecules are dissociated into OH radical and hydrogen atom which is described in Eq. (1). Therefore, both oxide and hydride reactions on the Si surface occur at the initial stage of irradiation, and silicon oxide formation as well as chemical sputtering of Si surface is performed. However, the oxide reaction rather than the hydride reaction increases with increase of the ion dose, and the Si surface is oxidized, which results in decrease of the chemical sputtering by hydride reaction. As a result, the sputtered depth of Si(100) surface at the ion dose of $1.0 \times 10^{16}$ ions/cm$^2$ is similar to that of SiO$_2$.

It is noted that smooth surface with a roughness less than 2 nm is obtained even for PMMA surfaces at a sputtered depth of 2.9 \mu m.

The Si(100) surfaces irradiated with water cluster ions were investigated by XPS measurement. Figure 5 shows the depth profiles of XPS peak intensities for (a) Si 2$p$ spectra and (b) O 1$s$ spectra. The acceleration voltage was 6 kV, and the ion dose was $1.0 \times 10^{16}$ ions/cm$^2$. As shown in the figure, Si 2$p$ peak on the surface is split into two peaks, one of which is shifted to the higher value of binding energy corresponding to the peak for SiO$_2$. Another peak corresponds to the peak for Si. This indicates that the silicon oxide layer such as SiO$_x$ ($x < 2$) is formed near the surface. Also, Si 2$p$ peak for SiO$_2$ as well as the O 1$s$ peak decreases with increase of the depth, and it disappears at a depth of 10.5 nm. These indicate that the silicon oxide layer is formed by the water cluster ion irradiation, and the oxide layer thickness is approximately 10 nm at an acceleration voltage of 6 kV.

Figure 6 shows C 1$s$ peaks for the PMMA surfaces (a) unirradiated and irradiated at acceleration voltages of (b) 6 kV and (c) 9 kV. The ion dose was $1.0 \times 10^{16}$ ions/cm$^2$, and the cluster size used was larger than 300 molecules per cluster. As shown in Fig. 6(a), the PMMA unirradiated substrate exhibits peaks assigned to –CH at 285.0 eV, –C\(<\) around 285.7 eV, –O-(C=O) around 286.8 eV and \(-(C=O)-O\) around 289.0 eV, respectively [18]. Compared with unirradiated surface, the PMMA surface irradiated
FIG. 6: XPS C 1s spectra for PMMA surfaces (a) unirradiated and irradiated at acceleration voltages of (b) 6 kV and (c) 9 kV, respectively by water cluster ions. The ion dose was 1.0×10^16 ions/cm^2.

at an acceleration voltage of 6 kV exhibits the decrease of the peak assigned to –O–(C=O) around 286.8 eV. This indicates that R-COOCH_3 is changed to R-COOH, in which R is the alkyl radical. Namely, OCH_3 radical or CH_3 radical in COOCH_3 is removed, and it might be exchanged by another radical such as OH radical or H atom. Furthermore, the C 1s peak for the PMMA surface irradiated at an acceleration voltage of 9 kV decreases, and the peaks assigned to –C< around 285.7 eV and –(C=O)-O around 289.0 eV becomes smaller than the peak around 286.8 eV. This indicates that the bond scissions occur, which results in the ejection of PMMA monomers as well as COOCH_3 radicals from the surface irradiated with the water cluster ion beams. Thus, the sputtering of PMMA surfaces by the water cluster ion irradiation represents unique features, which are different from the ablation and scission of PMMA surfaces during monomer ion and photon deposition induced surface modification [19–21].

Figure 7 shows the micro-patterning of PMMA substrate demonstrated with water cluster ion beams. The acceleration voltage was 9 kV, and the ion dose was 3.0×10^16 ions/cm^2. A mask-pattern representing the letters “KYOTO” is prepared on the PMMA substrate, and the sputtered depth of the substrate is approximately 10 µm. Also, the width of a letter prepared is larger than the original one, that is 50 µm, and the increase of the width is ascribed to the lateral sputtering effect of the PMMA surface under the mask by the water cluster ion irradiation. If the sharp-edged pattern is performed, the contact of the mask on the substrate should be improved.

IV. CONCLUSION

We investigated interactions of water cluster ions with solid surfaces such as Si(100), SiO_2 and PMMA surfaces. The sputtered depth of these surfaces increased with increase of the acceleration voltage, and it was 37 nm for Si, 49 nm for SiO_2, and 2.9 µm for PMMA substrates, respectively at an acceleration voltage of 9 kV and an ion dose of 1.0×10^16 ions/cm^2. The sputtering yield calculated was 19 atoms per ion for Si and 13 molecules per ion for SiO_2, which was approximately ten times larger than that for Ar monomer ion irradiation. The XPS measurement showed that Si surfaces sputtered at an ion dose of 1.0×10^16 ions/cm^2 had an oxide layer such as SiO_x. This was due to the oxidation of Si surfaces by hydroxyl radicals. The oxide layer thickness increased with increase of the acceleration voltage, and it was approximately 10 nm at an acceleration voltage of 6 kV. Furthermore, it was noted that the hydride reaction of Si surface occurred at a lower dose of 1.0×10^{14} ions/cm^2, and it resulted in enhancement of chemical sputtering of Si surface. The hydrogen atom in water molecule, which was dissociated during impact of the water cluster ions on the Si surface, had an important role in the chemical sputtering.

With regard to the high-rate sputtering of PMMA surfaces, the XPS analysis indicated that the chemical ero-
sion of the substrate surfaces occurred through the exchange between CH$_3$ and H radicals, and the chemical sputtering by the ejection of methacrylic acid molecule was enhanced. The AFM analysis showed that the surface roughness of Si, SiO$_2$, and PMMA substrates irradiated was less than 2 nm, and the smooth surface at the nano-level was obtained. On the basis of these results, the micro-patterning of PMMA substrate surfaces was demonstrated with water cluster ion beams, and the mask patterns such as KYOTO were performed on the substrate.

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[1] Mater. Res. Soc. Proc. Vol.1020 (2007), Chap. Session: Ion Beam Nanofab: Tools, Techniques, and Applications, p. 3.
[2] Proc. 17th Int. Conf. on Ion Implant. Technol. IIT2008, (AIP Conf. Proc., Vol.1066, 2008), Chap. Session: Implant Technology, p.257.
[3] Proc. 17th Int. Conf. on Ion Implant. Technol. IIT2008, (AIP Conf. Proc., Vol.1066, 2008), Chap. Session: Molecular and Cluster Ion Beams, p.387.
[4] J. Ishikawa, Rev. Sci. Instrum. 79, 02C506 (2008).
[5] G. H. Takaoka, Chemical Reactions on Surfaces, Eds. J. I. Duncan and A. B. Klein (Nova Science Publishers, Inc, New York, 2008), p. 89.
[6] G. H. Takaoka, K. Nakayama, T. Takeda, and M. Kawashita, Proc. 16th Int. Conf. on Ion Implant. Technol. IIT2006, (AIP CP 866, 2006), p.190.
[7] Z. Insepov and I. Yamada, Surf. Rev. Lett. 3, 1023 (1996).
[8] Z. Insepov and I. Yamada, Nucl. Instrum. Methods Phys. Res. B 121, 44 (1997).
[9] G. H. Takaoka, K. Nakayama, H. Noguchi, and M. Kawashita, Surf. Interface Anal. 38, 1534 (2006).
[10] G. H. Takaoka and M. Kawashita, Synth. Reactiv. in Inorganic Metal-Organic and Nano-Metal Chem. 38, 111 (2008).
[11] H. Ryuto, K. Tada, and G. H. Takaoka, Vacuum 84, 501 (2010).
[12] N. Laegreid and G. K. Wehner, J. Appl. Phys. 32, 365 (1961).
[13] P. C. Zalm, J. Appl. Phys. 54, 2660 (1983).
[14] N. Matsunami, Y. Yamamura, Y. Ichikawa, N. Itoh, Y. Kazumata, S. Miyagawa, K. Morita, R. Shimizu, and H. Tawara, Atomic Data and Nuclear Data Tables Vol. 31 (Academic Press Inc., 1984), p. 1.
[15] I. L. Bolotin, S. H. Tetzler, and L. Hanley, Appl. Surf. Sci. 252, 6533 (2006).
[16] I. L. Boltin, S. H. Tetzler, and L. Hanley, J. Phys. Chem. C. 111, 9953 (2007).
[17] L. Houssiau, B. Douhard, and N. Mine, Appl. Surf. Sci. 255, 970 (2008).
[18] G. Beamson and D. Briggs (Eds.), High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database (John Wiley & Sons, Ltd., Chichester, New York, Brisbane, Toronto, Singapore, 1992), p. 119.
[19] H. Ryssel, K. Haberger, and H. Kranz, J. Vac. Sci. Technol. A 19, 1358 (1981).
[20] A. Licciardello, M. E. Fragal, G. Foti, G. Compagnini, and O. Puglisi, Nucl. Instrum. Methods Phys. Res. B 116, 168 (1996).
[21] P. F. Conforti, M. Prasad, and B. J. Garrison, Appl. Surf. Sci. 253, 6386 (2007)