APPLICATION OF LIQUID CLUSTER ION BEAMS IN SURFACE PROCESSING

H. Ryuto*†, M. Takeuchi, and G. H. Takaoka
Photonics and Electronics Science and Engineering Center, Kyoto University
Nishikyo, Kyoto 615-8510, Japan

Abstract

To examine the possibility of applying the liquid cluster ion beam technique to the surface processing of semiconductors, an ethanol cluster ion beam was irradiated on photoresist masked silicon substrates. The ethanol cluster ion beam was produced by the adiabatic expansion method without a support of helium gas. The line patterns of the line widths of 1.0 μm and 0.5 μm were reproduced on the silicon substrates by the irradiation of an ethanol cluster ion beam.

INTRODUCTION

The ion beam technology has been utilized as an essential method for surface processing in the semiconductor industry as well as an ion implantation method. However, the radiation damage in the silicon wafers caused by the irradiation of ion beams during the processing became a serious drawback to the improvement in the performance of semiconductor devices. So, the semiconductor industry is in need of some processing methods of semiconductors that do not cause serious radiation damages. On the other hand, some micro-processing methods that can be applied to polymers are required for producing, for example, micro-reactors.

The liquid cluster ion beam technique is thought to be one of the promising techniques that fulfill these requirements. A cluster is an aggregate of atoms or molecules bound by intermolecular forces. Various cluster ion beams such as metal [1, 2], fullerene [3], silicon [4], gas [5], and liquid [6] cluster ion beams have attracted much interest. The number of molecules that comprise the cluster (cluster size) ranges from a few to thousands in accordance with the production methods and the materials that comprise the cluster. One of the production methods, the adiabatic expansion method [7], was employed here. The properties of the interaction between a cluster ion and solid surface are characterized by the high-density energy deposition and the low energy incident energy per molecule. For example, if an argon cluster at 10 keV whose cluster size is 2000 impacts on a solid surface, 2000 argon atoms hit almost simultaneously an area of a diameter of a few tens of nanometers, and the incident energy is as low as 5 eV/molecule which is sufficiently lower than the threshold energy of atom displacements. Moreover, a molecular dynamics simulation showed that the temperature of the bombarded area rises to a few tens of thousand degrees during approximately 0.2 ps [8]. The contribution of chemical interaction is expected in addition to the atomic collision processes when a cluster that consists of polyatomic molecules is bombarded on a solid surface. Therefore, the chemical interactions are expected to be enhanced by the high temperature when the clusters of polyatomic molecules are bombarded. In this study, the effects of the clusters of one of the polyatomic molecules, ethanol clusters, were investigated. The possibility of the simultaneous realization of the high sputtering yields and the low radiation damage using an ethanol cluster ion beam was reported [9]. The outstanding ability of oxidation of another kind of liquid cluster ion beam, a water cluster ion beam, was also reported [10]. As the first step to the actual application of the liquid cluster ion beam technology to the surface processing of silicon substrates, an ethanol cluster ion beam was irradiated on photoresist masked silicon substrates.

EXPERIMENTAL PROCEDURE

Ethanol clusters were produced by the adiabatic expansion method [7]. Figure 1 shows a schematic view of the liquid cluster ion beam apparatus. An ethanol in liquid phase was filled in a liquid container, and heated to 382 K using a heater attached onto the outer wall of the liquid container to increase vapor pressure. The typical vapor pressure used for the production of ethanol clusters was 0.3 MPa. The typical variation of the temperature is approximately ±1 K, which corresponds to ±10 kPa variation of ethanol vapor pressure. Ethanol clusters were produced by ejecting the vaporized ethanol through a Laval nozzle to a vacuum chamber [11]. No support helium gas was used to produce ethanol clusters [6]. The middle part of the flow of the ethanol vapor was selected using the skimmer to avoid the disintegration of clusters caused by shockwaves. A high vacuum downstream of the vacuum chamber was maintained by the differential pumping method to avoid the disintegration of ethanol clusters caused by the collisions with residual gases. The ethanol clusters were ionized by the electrons emitted from the loop of a tungsten filament. The acceleration voltage (V_e) and current (I_e) of the electrons for ionization were 200 V and 200

---

* ryuto@kuee.kyoto-u.ac.jp
† Formerly, H. Akiyoshi.

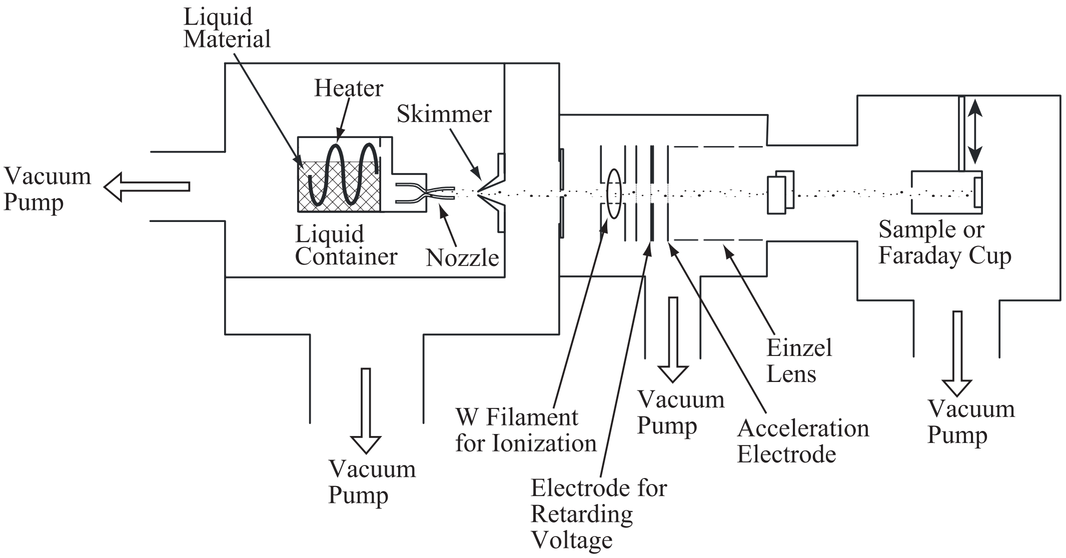


Figure 1: Schematic view of liquid cluster ion beam apparatus.

mA, respectively. The ethanol monomers and smaller clusters were eliminated by the retarding voltage method. The retarding voltage method is based on the phenomenon that the initial velocities of the clusters produced by the expanding nozzle flow are fairly uniform, typically within 10% [7, 12]. The ethanol clusters whose cluster sizes were approximately less than 94 were blocked by a retarding voltage of 27 V. The ethanol cluster ions were accelerated by the acceleration voltage typically from 3 to 9 kV. The transverse divergence of the beam was suppressed by an Einzel lens, then the ethanol cluster ion beam was transported to the target attached on a linear motion feedthrough. The intensity of the ethanol cluster ion beam was measured using a Faraday cup with an electron suppressor approximately at -300 V also attached on the linear motion feedthrough. The horizontal position of the beam was fine-tuned by an electrostatic deflector.

Figure 2 shows a cluster size distribution of the ethanol cluster ion beam measured by the time of flight method. Singly charged ethanol clusters were assumed. The cluster size distribution slightly depends on V_e and I_e [13]. The acceleration voltage and current of electrons for ionization were 200 V and 200 mA, respectively. The ethanol monomers and smaller clusters were eliminated by the retarding voltage of 27 V. The mode, median, and full width at half maximum (FWHM) of the cluster size distribution of ethanol clusters produced with these parameters were approximately 1600, 2200, and 2300, respectively. The typical beam current density of the ethanol cluster ion beam was approximately 290 nA/cm^2.

The surface of photoresist masked silicon substrates were irradiated with the ethanol cluster ion beam. The mask patterns were the line patterns whose line widths were 1.0 μm and 0.5 μm. The acceleration voltage of the ethanol cluster ion beam was 9 kV, and the dose was 2x10^{16} ions/cm^2. The surfaces of the silicon substrates were observed using a scanning electron microscope (SEM).

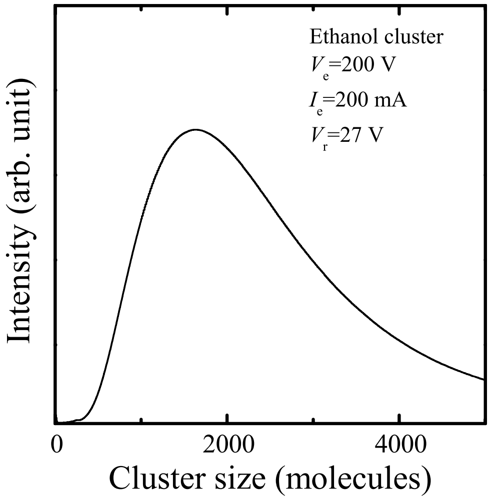
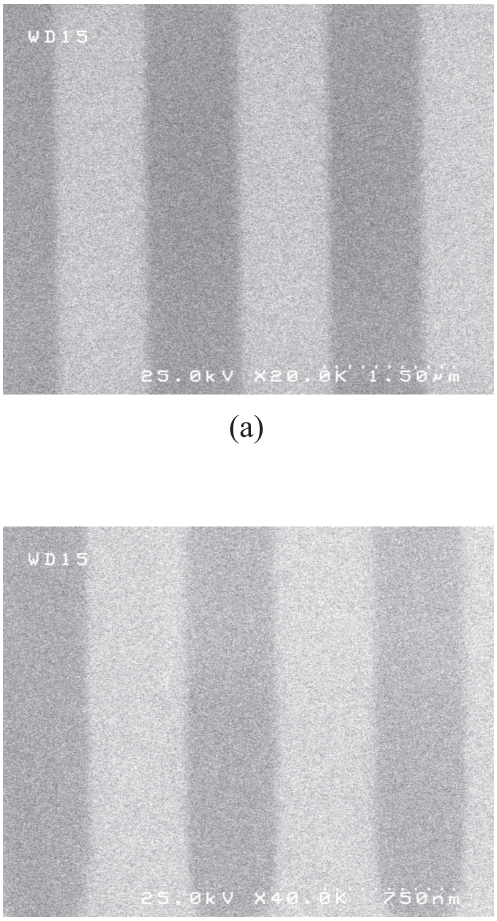


Figure 2: Cluster size distribution of ethanol cluster ion beam. The V_e, I_e, and V_r were 200 V, 200 mA, and 27 V, respectively.

RESULTS AND DISCUSSION

Figure 3 shows SEM images of the line patterns on silicon substrates produced by irradiating an ethanol cluster ion beam on photoresist masked silicon surfaces. The width of the line patterns were (a) 1.0 μm and (b) 0.5 μm, respectively. The photoresist was removed by acetone treatment after the irradiation. The etch depth in the Si(100) substrate without a photoresist mask sputtered by the ethanol cluster ion beam produced with approximately the same parameters as the beam parameters used in the present experiment was reported to be approximately 0.5 μm [14]. The mask patterns of both line widths of 1.0



(a)

(b)

Figure 3: SEM images of photoresist masked silicon surface after processing by ethanol cluster ion beam technique. The width of the line patterns are (a) 1.0 μm and (b) 0.5 μm.

μm and 0.5 μm were clearly reproduced by the irradiation of the ethanol cluster ion beam. So, the liquid cluster ion beam technique may be a promising processing technique that can be applied in the semiconductor industry.

CONCLUSION

The surfaces of the photoresist masked silicon substrates were irradiated with an ethanol cluster ion beam to examine the possibility of applying the liquid cluster ion beam technique to the surface processing of semiconductors. The line patterns whose line widths are 1.0 μm and 0.5 μm were used for the mask patterns. The line patterns were clearly etched by the irradiation of the ethanol cluster ion beam.

ACKNOWLEDGEMENT

A part of this work was conducted in Kyoto-Advanced Nanotechnology Network, supported by “Nanotechnology Network” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

REFERENCES

[1] I. Yamada and G. H. Takaoka, Jpn. J. Appl. Phys. 32 (1993) 2121.

[2] A. Herrmann, S. Leutwyler, E. Schumacher, and L. Wöste, Helv. Chim. Acta 61 (1978) 453.

[3] H. Shen, C. Brink, P. Hvelplund, S. Shiryaev, P. X. Shi, and J. A. Davies, Nucl. Instrum. Meth. B 129 (1997) 203.

[4] Y. Iwata, M. Kishida, M. Muto, S. Yu, T. Sawada, A. Fukuda, T. Takiya, A. Komura, and K. Nakajima, Chem. Phys. Lett. 358 (2002) 36.

[5] I. Yamada, Nucl. Instrum. Meth. B 148 (1999) 1.

[6] G. H. Takaoka, H. Noguchi, T. Yamamoto, T. Seki, Jpn. J. Appl. Phys. 42 (2003) L1032.

[7] O. F. Hagena and W. Obert, J. Chem. Phys. 56 (1972) 1793.

[8] Z. Insepov and I. Yamada, Surface Review and Letters 3 (1996) 1023.

[9] H. Ryuto, K. Sugiyama, R. Ozaki, and G. H. Takaoka, Applied Physics Express 2 (2009) 016504.

[10] H. Ryuto, K. Tada, and G. H. Takaoka, Vacuum 84 (2010) 501.

[11] O. F. Hagena, Molecular beams and low density gas dynamics, ed. by P. P. Wegener (Dekker, New York, 1974), pp. 93-181.

[12] O. F. Hagena and K. Varma, Rev. Sci. Instrum. 39 (1968) 47.

[13] H. Ryuto, R. Ozaki, Y. Kubo, M. Takeuchi, and G. H. Takaoka, Rev. Sci. Instrum. 81 (2010) 02B902.

[14] G. H. Takaoka, T. Okada, M. Kawashita, Vacuum 83 (2009) 459.