Development of Environmental Harmony Resist Removal System using Cryogenic Particulate Spray

Jun Ishimoto and Hideo Horibe*

*Institute of Fluid Science, Tohoku University,
2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan*

**Applied Chemistry and Bioengineering, Osaka City University,
3-3-138 Sugimoto Sumiyoshi-ku, Osaka-shi, 558-8585
ishimoto@alba.ifs.tohoku.ac.jp*

Keywords: cryogenics, solid nitrogen, spray, atomization, multiphase flow

I. Introduction

Thermal-fluid mechanical high functionality of cryogenic fine solid particles of micron to nano size has been noted not only in the field of ultra-high heat flux cooling technology in application to high thermal emission devices [1], but also in the field of non-aqueous physical nano-device cleaning technologies [2]. In order to make effective use of the high performance of such cryogenic solid particles in the field of advanced nano technology, our laboratory has developed a new physical semiconductor cleaning method which employs cryogenic spray [3]. Especially in recent years, with the progress of high aspect ratio and fine cantilever in semiconductor nano structures, the ultimate cleaning method without use of water is strongly expected [4]. Because of the capillary force due to the surface tension of water that remains in the structure in the process of drying, the fine structure is deformed, finally causing collapse or adhesions [5]. Therefore, the application of cryogenic high-speed spray of micro-solid nitrogen (SN_2) to the resist-removal and ultra-cleaning system of semiconductor wafer is a focus of great interest. By utilizing high-speed micro-solid nitrogen spray, the complete chemical free, pure water free, dry type thermomechanical resist removal-cleaning system could be developed. The developed system utilizes the micro- SN_2 which consists of the fine solid nitrogen particle produced by the high-speed collision of subcooled liquid nitrogen and the cryogen through two-fluid nozzle. The photo resist can be removed and cleaned from wafer surface due to the interaction that the

hard particle impingement of inertial forces and the rapid thermal contraction effect (thermomechanical effect on the resist) which is based on ultra-high heat flux cooling effect of cryogenic solid particle's inherent characteristics accompany with phase change. In the conventional method for solid nitrogen particle generation proposed by the authors [2], the use of cryogenic gaseous helium were required as a refrigerant. However, since the helium is very expensive and it is specified in the strategic material and its rarity, there is a serious problem of cost for use in the cleaning process.

In order to overcome these problems, we have developed the new micro-nano SN_2 particle production method without use of helium refrigerant by using super adiabatic Laval nozzle (converging-diverging nozzle) as shown in Fig. 1. In this technique, micro-nano SN_2 particle is generated by adiabatic expansion of high-speed subcooled two-phase liquid nitrogen (LN_2) flow (in Fig. 2). When the flow was induced internal section of Laval nozzle, the subcooled LN_2 -gaseous nitrogen (GN_2) two-phase flow is atomized and LN_2 droplet is generated at the throat, and high-speed ultra-fine SN_2 particle is continuously generated due to the freezing of LN_2 droplet induced by rapid adiabatic expansion of transonic subcooled two-phase GN_2 - LN_2 flow passing through the Laval nozzle. Furthermore, in our previous research [1], the macroscopic thermal characteristics of solid nitrogen (SN_2) spray cooling performance has been partially made clear. However, microscopic heat transfer and hydrodynamic behavior of single cryogenic SN_2 particle impinging on heated substrate have not been sufficiently

Fig. 1 Resist removal measurement section by SN_2 particulate spray

Fig. 2 Principle of two-phase Laval nozzle for continuous SN_2 particle production

Fig. 3 Computational result of the SN_2 -phase volume fraction profile through the Laval nozzle

Fig. 4 Produced SN_2 particle by developed Laval nozzle in the present experiment

investigated. Therefore, we mainly focused on the microscopic thermal, hydrodynamic, kinematic behavior of single fine SN_2 particle with phase change.

In the present study, the innovative characteristics of the cryogenic single-component micro-nano solid nitrogen (SN_2) particle production using Laval nozzle and its application to the physical resist removal-cleaning process are investigated by a new type of integrated ToF-SIMS, XPS measurement coupled supercomputing technique. To elucidate the detailed mechanism of micro-nano SN_2 particle generation, integrated CFD (Computational Fluid Dynamics) analysis was carried out to clarify the cryogenic particle heat transfer mechanism that is difficult to obtain by conventional measurement.

2. Computational modeling

To elucidate the ultra-high heat flux cooling heat transfer characteristics of a single micro-solid nitrogen (SN_2) particle, integrated CFD analysis was carried out to clarify the cryogenic solid particle heat transfer

mechanism that is difficult to obtain by conventional measurement. In the present numerical formulation, a micro- SN_2 particle is assumed to be formed by a quite high-viscous LN_2 droplet.

To investigate effective SN_2 particle generation, momentum behavior and heat transfer mechanism, a computational domain and 3D-mesh for Laval nozzle which is used in present experiment was created. The computational domain has the bounding box shape of 16.3 mm (Length) $\times$ 4.0 mm (Height) size mesh. As a compromise between computer memory and accuracy, we chose to use 3.2M structured grid for computational domain in the present calculations. The measurement data obtained by PIA-PTV were stored in a small database and the data was introduced into the initial numerical condition of the micro-nano SN_2 particulate flow. For standard initial numerical conditions are based on the measurement conditions in the present experiment.

3. Computational results

Fig. 3 shows the computational result of the SN_2 -phase volume fraction profile through the Laval nozzle. It is numerically found that the atomization of LN_2 droplet is induced by shear flow between LN_2 and gaseous nitrogen (GN_2) flow. Sequentially, liquid to solid phase change is enhanced and SN_2 particle is continuously created by LN_2 droplet freezing. This physical process is due to the latent heat release based on the adiabatic expansion of subcooled GN_2 - LN_2 transonic two-phase flow just downstream of Laval nozzle throat section. When LN_2 two-phase flow is continuously accelerated passing through the Laval nozzle, the pressure drops due to adiabatic expansion, then the pressure to become under saturated vapor pressure. Furthermore, the subcooled state is continued for some time, rapid SN_2 particle solidification is produced as a nucleation of LN_2 droplet. Solidification latent heat is released due to the freezing of LN_2 droplets. Since these phenomena give a similar effect with a decrease of the nozzle cross-sectional area, as a result, it appears as an effect that to reduce the velocity and to increase the pressure locally.

4. Experimental study for resist removal

In the original approach, the continuous production of micro- SN_2 particles is achieved by using a single component gas (GN_2)-liquid (LN_2) two-phase flow of subcooled nitrogen through a Laval nozzle (in Fig. 4). Furthermore, to enhance the solid phase nucleation and the solid particle atomization, an ultrasonic oscillator is attached to the tip side of nozzle, and to further enhance the SN_2 particle atomization process, a spiral device is used in the nozzle aperture. Micro- SN_2 particles are almost homogeneously formed as fine spray, and particles with a diameter of less than $5.0\ \mu\text{m}$ can be continuously produced. Ultrasonic atomization is operated under a frequency of 45 kHz and an amplitude of $30\ \mu\text{m}$. As a result, the new two-phase Laval nozzle developed in the present study is capable of continuously producing micro- SN_2 particles with average atomizing velocity of approximate $v_p=120\ \text{m/s}$ under conditions of a nozzle inlet GN_2 pressure of $p_{n(\text{GN}_2)} = 0.4\ \text{MPa}$, atmospheric pressure in the nozzle aperture outlet section, and a pre-cooling condition of ambient temperature of surrounding SN_2 particulate flow.

For the wafer samples employed in the present experiment, stripping performance in the case of positive KrF photoresist-coated (OFPR 200cp) poly-crystalline

silicon substrate was examined. An HMDS (Hexamethyldisilazane) layer was applied to the surface of the poly-Si to assist in adhesion of photoresist to the poly-Si, and then a photoresist layer was formed over the HMDS layer with the use of a spin coater. The photoresist was patterned using super-high pressure UV lamp at 360 nm.

5. Measurements for resist removal performance

ToF-SIMS investigation of resist components residue in resist removal portion has been conducted (in Fig. 5). For resist removal portion, resist derived ($\bullet$) (m/z 121; positive, m/z 107; negative) fragments are detected. In addition, with respect to the peak of oxidized Si matrix ($\blacksquare$) delivered (m/z 137; negative), since the strength in resist removal portion is weakened compared to around region, it is considered that the resist residue exists at the resist removal portion (in the Figure; $\square$, $\square$).

At the portion of the grid-like pattern where the resist does not remain by the visual confirmation, the outermost surface XPS analysis was conducted to the portion (in Fig. 6). As a result, elements of C, Si, O were detected. Subsequently, the waveform separation for Si was conducted, the ratio of Si in the SiOC compound has been determined. In addition, waveform analysis with respect to Si2p was conducted. Si is considered to exist in a metallic state and oxide form (SiOC, SiO_2 , etc.), it is found that many SiOC compound tend to exist. C is mainly exists C-C or C-H combined form. SiOC compound also considered to exist because of Si2p spectrum data. Furthermore, according to ToF-SIMS analysis, SiOC is assumed to be SiO_1C_3 form, three times amount of C in Si of the SiOC form is estimated to be present as SiO_1C_3 .

It is considered that total amount of C is composed by 1) C of surface organic contamination, 2) C of resist, 3) C of SiO_1C_3 . Therefore, the C amount of 1) + 2) was calculated by subtracting the amount of 3) from quantitative values of C. For surface measurement, the detection of the 1) surface organic contamination C is unavoidable (It relies on storage environment, typically more than 10 atomic %) that C content in 1) is considered to trace amount. Namely, the C amount of 1) + 2) was almost regarded as C amount of 2). As a result, The C quantity (atomic %) of resist which subtracted from C quantity of SiOC form is introduced as 7.0 atomic%.

Here, as C is assumed to be hydrocarbon, C film thickness of resist removal section has been obtained by

Fig. 5 ToF-SIMS investigation of resist components residue in resist removal portion

Fig. 6 XPS quantitative analysis of resist components residue in resist removal portion

using several XPS parameters. The obtained C film thickness of resist removal section is 0.2 nm.

Therefore, the photo resist can be successfully removed by using cryogenic solid particulate spray method.

6. Conclusion

- [1] It is numerically found that the atomization of LN_2 droplet is induced by shear flow between LN_2 and gaseous nitrogen (GN_2) flow. Sequentially, liquid to solid phase change is enhanced and solid nitrogen (SN_2) particle is continuously created by LN_2 droplet freezing.
- [2] By using ToF-SIMS and XPS analysis for resist removal experiment, the obtained C film thickness of resist removal section is 0.2 nm. Therefore, the photo resist can be successfully removed by using cryogenic solid particulate spray method.

Acknowledgments

This research was supported by a Support Program for Interdisciplinary Research from Frontier Research Institute for Interdisciplinary Sciences (FRIS), Tohoku

University. This work was partly supported by the JSPS Core-to-Core Program, A. Advanced Research Networks, “International research core on smart layered materials and structures for energy saving,” and also supported by the Collaborative Research Project of the IFS, Tohoku University. The numerical simulations were performed using the SGI Altix UV1000 and UV2000 scalar parallel computers at the Institute of Fluid Science, Tohoku University.

References

1. J. Ishimoto, U. Oh, D. Tan, *Cryogenics*, **52** (2012) 505.
2. J. Ishimoto, U. Oh, T. Koike, N. Ochiai, *ECS J. Solid State Science and Technol.*, **3** (2014) N3046.
3. H. Choi, H. Kim, D. Yoon, J.W. Lee, B.K. Kang, M.S. Kim, J.G. Park, S.B. Kwon, T. Kim, *Microelectronic Eng.*, **102** (2013) 87.
4. T.H. Kim, A. Busnaina, J.G. Park, D. Kim, *ECS J. Solid State Science Technol.*, **1** (2012) 70.
5. T. Hattori, *ECS J. Solid State Science Technol.*, **3** (2014) N3054.