

Influence of Chemical Structure in Base Polymer Material for Photoresist Process on Thin Film Removal Characteristics using Microwave Excited Bubble Plasma in Water

レジスト用ベースポリマーの化学構造が
マイクロ波励起水中気泡プラズマによる薄膜除去特性に及ぼす影響

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Microwave excited bubble plasma in water (MWBP) has been applied to a high-speed removal process of a positive-tone novolak resist film with low environmental impact since it is possible to generate large amounts of reactive species without using chemicals. In this paper, we evaluated the removal characteristics of polymer thin film with different chemical structures in order to apply various photoresist removal process using MWBP. As a result, the suppression of removal rate is suggested due to the benzene ring in the polymer film.

1. Introduction

In a semiconductor device manufacturing process, several processes have been carried out such as cleaning, photoresist coating, patterning by lithography, etching, photoresist removal and so on. In general a photoresist film is removed by either wet technology using a chemical solution such as mixture of sulfuric acid (H₂SO₄), hydrogen peroxide (H₂O₂) and deionized water (SPM) or dry process technology such as oxygen plasma ashing. In the case of the wet process, SPM solution becomes most active for photoresist removal process just after the mixture of H₂SO₄ and H₂O₂. Therefore much SPM solution is required. A large amount of SPM is not only environmentally-unfriendly due to its harmfulness but also is expensive. On the other hand, oxygen plasma ashing process causes damage to the electronic devices on a wafer derived from a charge from the plasma irradiation and an oxidation due to the increase of substrate temperature in order to increase the photoresist removal rate. In industrial process, it is desired to develop both an environmentally-friendly and a rapid photoresist removal method under low substrate temperature to reduce heat damage.

Recently, non-equilibrium reactive plasma

processing in and in contact with liquid has investigated intensively due to its potential of applications. We have been developing a novel photoresist removal method to reduce environmental load without using any chemicals under low substrate temperature condition. The reactive species for the photoresist removal can be supplied from water in a chamber by microwave excited plasma production in a water vapor bubble. The microwave excited bubble plasma (MWBP) treatment enables us to keep the substrate temperature low since the substrate is located in the ultrapure water environment. A high-speed photoresist removal rate of more than 1 μm/min was realized in a positive tone novolak resist film[1].

To date, polymeric materials are used in a photoresist as decrease the electronic device scale and diversify its applications. Novolak resin has been used for g/i-ray lithography process. In order to apply fine patterning process, a polymethyl methacrylate (PMMA) and a polyvinyl phenol (PVP) are used for ArF and KrF excimer laser lithography process, respectively.

In this paper, we evaluated the polymer film removal characteristics using MWBP. The Novolak resin, PMMA, and poly-α-methyl

styrene(PMS) thin films on silicon (Si) wafer are examined to clarify a correlation between the chemical structures of polymer and the polymer removal characteristics.

2. Experimental Apparatus

Experimental apparatus is shown in Fig. 1. An acrylic vessel ($13 \times 13 \times 8.5 \text{ cm}^3$) was attached at the bottom of a stainless steel (SUS) plate with a quartz waveguide to realize reduced pressure condition in the vessel. A slot antenna was installed at the end of the quartz-filled waveguide. The slot antenna made from SUS was 56 mm in length and 0.5 mm in thickness. The vessel was equipped with a scroll pump to reduce the pressure in the vessel at a pressure of $\sim 6 \text{ kPa}$ after ultrapure water at room temperature was supplied to immerse the slot antenna. A 2.45 GHz microwave was excited at a repetition frequency of 10 kHz and duty ratio of 20% with a peak power of $P < 2 \text{ kW}$ (unless otherwise stated). The pulsed microwave was injected into the ultrapure water through a slot antenna from a quartz-filled rectangular waveguide. MWBP was easily generated in the vicinity of the slot antenna without using a bubble control plate[2]. The distance between the slot antenna and the polymer film surface was fixed at $d=4.6 \text{ mm}$ using a polytetrafluoroethylene spacer. The thickness of the polymer thin film after MWBP treatment was measured using a step profiler (ET-200 was made Kosaka Laboratory). A polymer thin film was coated using a spin coater (ACT-300A ; Active). Si wafers coated with polymer films were cut about 2 cm^2 . The centers of the Si substrate were placed in front of the slot antenna center. The coated polymer film thicknesses were $0.9\text{--}1.2 \mu\text{m}$.

3. Results and Discussions

Figure 2 shows a remained polymer film thickness after MWBP treatment as a function of irradiation time. The polymer film thickness was decreased monotonically with increasing MWBP irradiation time regardless of the polymer type. The polymer removal rate was evaluated using the least-squares method on the plots in Fig. 2. The removal rates of PMMA, Novolak resin, and PMS are 1.6 , 1.0 , $0.63 \mu\text{m}/\text{min}$, respectively. PMMA removal rate is fastest among these three polymers. The chemical structures of polymer film are shown in Fig. 3 to reveal the relation between the chemical structure and the removal rate. PMMA does not include benzene ring in the polymer structure. However, other polymers (Novolak and PMS) include the benzene ring. The polymer including the benzene ring has the resistance for the etching

due to its resonance stabilization effect. The decomposition reaction of the polymer owing to radicals produced by MWBP would be suppressed. To obtain more detailed polymer removal characteristics using MWBP, other vinyl polymers such as main chain scission type and main chain cross linking type [3-5] will be presented.

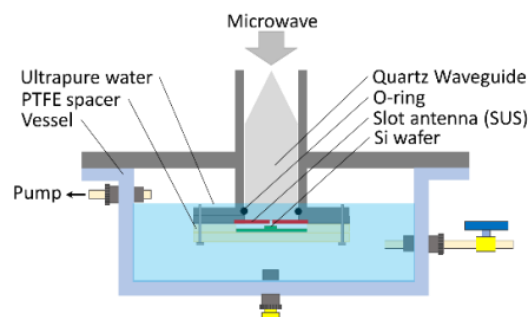


Fig. 1. Experimental apparatus of MWBP.

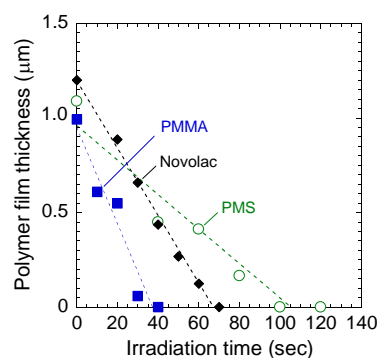


Fig. 2. Polymer film thickness as a function of MWBP irradiation time.

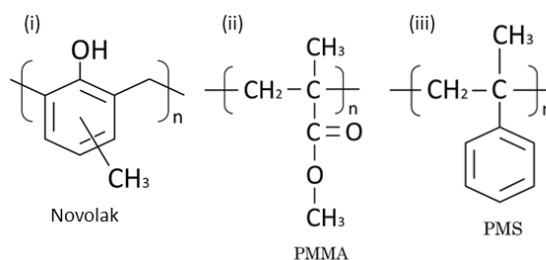


Fig. 3. Chemical structure of each polymer. (i) Novolak, (ii) PMMA, (iii) PMS

References

- [1] T. Ishijima, K. Nosaka, Y. Tanaka, Y. Uesugi, Y. Goto, and H. Horibe: *Appl. Phys. Lett.* **103** (2013) 142101.
- [2] T. Ishijima, H. Sugiura, R. Saito, H. Toyoda, and H. Sugai: *Plasma Source Sci. Technol.* **19** (2010) 015010.
- [3] A. Miller, E. J. Lawton, and J. S. Balwit: *J. Polym. Sci.* **14** (1954) 503-504.
- [4] A.A. Miller, E. J. Lawton: *J. Electrochem. Soc.* **120** (1973) 1722.
- [5] H. Horibe, M. Yamamoto, E. Kusano, T. Ichikawa, and S. Tagawa: *J. Photopolym. Sci. Technol.* **21** (2008) 293.