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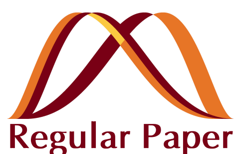
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Effect of Process Parameters of UV Enhanced Gas Phase Cleaning on the Removal of PMMA (Polymethylmethacrylate) from a Si Substrate

Sung Ku Kwon†
Department of Material Science and Engineering, Kunsan National University, Gunsan 54150, Korea

Do Hyun Kim
Department of Chemical & Biomolecular Engineering and Center for Ultramicrochemical Process Systems, KAIST, Daejon 34141, Korea

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Experimental study of UV-irradiated O_2/H_2 gas phase cleaning for PMMA (Polymethylmethacrylate) removal is carried out in a load-locked reactor equipped with a UV lamp and PBN heater. UV enhanced O_2/H_2 gas phase cleaning removes polymethylmethacrylate (PMMA) better at lower process pressure with higher content of H_2. O_2 gas compete for UV (184.9 nm) absorption with PMMA producing O_3, $O(^1D)$ and lower dissociation of PMMA. In our experimental conditions, etching reaction of PMMA at the substrate temperature between 75℃ and 125℃ had activation energy of about 5.86 kcal/mol indicating etching was controlled by surface reaction. Above the 180℃, PMMA removal was governed by a supply of reaction gas rather than by substrate temperature.

Keywords: UV-O_2/H_2, Gas phase cleaning, PMMA, Process parameter, Silicon substrate

1. INTRODUCTION

As the transistor scales down to nano-scaled device regime, raised source-drain technology by low-temperature selective silicon epitaxial film growth is a very important technology to reduce power consumption for mobile electronics. That causes the source and drain to be thicker than the channel film thickness in FDSOI CMOSFET (Fully Depleted Silicon on Insulator Complementary Metal On Silicon Field Effect Transistor). A thicker source and drain reduce resistance by about 30% allows the mobility of electrons to be faster so it can be possible for low voltage to be used to operate the transistor.

Surface cleaning has been known to influence the quality of silicon epitaxial film and success of low-temperature growth processes. Various methods have been investigated for *in situ* cleaning prior to silicon epitaxial growth. These cleaning methods include thermally assisted cleaning [1], photo assisted cleaning [2-7], plasma assisted cleaning [8-12] and HF vapor cleaning [13].

Problems with conventional thermal process executed by using H_2 gas at a high substrate temperature of more than 800℃ for removal of native oxide and organic contaminants are that it cannot desorb the residual carbon contaminant and SiC precipitates are formed which are the origin of strain in the epitaxial film. Under the critical condition such as high temperature treatments with H_2 gas, the induced strain relaxes via the formation of dislocations, which are fatal defects for devices [14].

Some examples of organic contaminants used during ULSI processing include the photo-resist [4,11], the RIE residue [15,16], and adsorbed trace hydrocarbon [17].

PMMA is a well-known organic material for microelectronics fabrication process as a candidate for one of a component of photoresist for deep UV lithography because of its weak absorbing properties to deep UV. Removal of organic contaminants

† Author to whom all correspondence should be addressed:
E-mail: skkwon @kunsan.ac.kr

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such as PMMA is essential for success of low temperature selective epitaxial film growth and via-hole processing.

In this work, experimental study on effects of process parameters in UV-irradiated O_2/H_2 gas phase cleaning for PMMA (Polymethylmethacrylate) removal was carried out in a load-locked reactor equipped with a UV lamp and PBN heater.

2. EXPERIMENT

For the sample preparation, thermal silicon oxide of 180nm thick film was grown on a 4-inch, p-type (100)-oriented wafer (RS = 22 ~ 38 Ω-cm) by wet oxidation at 950℃ in the furnace. Native (chemical) oxide was grown on the same kind of bare wafer after cleaning with acetone, ethanol and de-ionized water in a sonic bath for 10 min each and then dried with nitrogen blowing. The polymethylmethacrylate (PMMA, average molecular weight of 120,000) solution was prepared by dissolving 3~5 wt% of solid-state PMMA in tetrahydrofuran (THF) or acetonitrile solvent. The thin PMMA film of about 250 nm in thickness was coated by using a spin coater at 2,000 RPM for 30 sec and then baked to 100 ℃ for 15 min in the air. The samples were cut into pieces of 2×2 cm^2 to be mounted on the sample holder in the GPC (gas phase cleaning) chamber equipped with UV grid lamp and PBN (pyrolytic boron nitride) heater. A schematic diagram of UV enhanced gas phase cleaning(GPC) reactor is shown in Fig. 1.

UV excited O_2/H_2 gas phase cleaning was carried out for removal of organic contaminants such as PMMA - the main component of the photoresist- according to process parameters such as pressure, O_2/H_2 composition in feed gas and substrate temperature. The power of the UV lamp was fixed at 40 ~ 50 mW/cm^2 and 2.9 ~ 3.6 mW/cm^2 at a distance of 2.54 cm for wavelengths of 254 nm and 185 nm, respectively. The PMMA film's thickness was measured by using an α-step profiler before and after the cleaning experiments to figure out etch rates for the various cleaning conditions.

Figure 2 shows the experimental procedure. Total flow rate, the distance between the wafer and the UV lamp and cleaning time were all fixed at the conditions of 20 sccm, 3.5 cm, and 30 minutes, respectively. During the gas cleaning, the substrate was heated from room temperature to about 200℃ by UV irradiation.

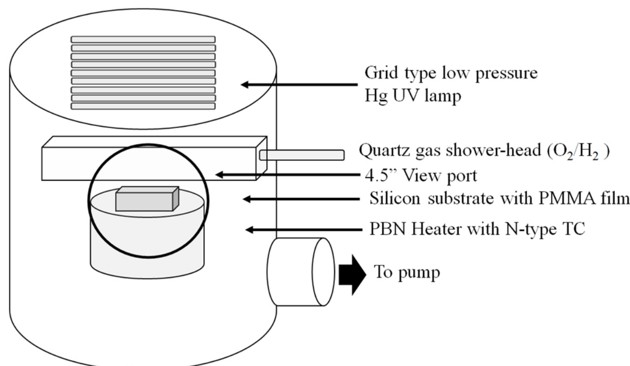

Fig. 1. Schematic diagram of UV-GPC reactor.

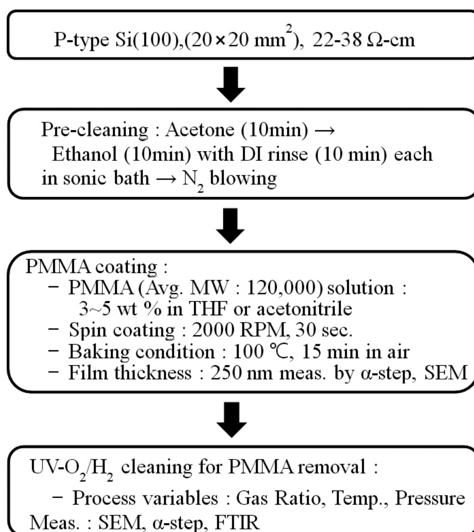

Fig. 2. Schematic diagram of the experimental procedure.

3. RESULTS AND DISCUSSION

The combination of UV excited O_2/H_2 and UV exposure was used for enhancing the removal rate of polymethylmethacrylate (PMMA) coated on a silicon wafer. We examined the effects of processing variables such as O_2 flow rate, process pressure, composition of H_2/O_2 and substrate temperature on removal characteristics of PMMA.

Figure 3 shows the etch rate of PMMA as a function of O_2 flow rate at the pressure of 0.5 Torr. Removal rate of PMMA decreases with increasing flow rate of O_2. Etching mechanism of PMMA by UV/O_2 was known as occurred by combined effects of photodissociation of PMMA and photo-oxidation with O (^1D), •OH and PMMA. A reaction mechanism was shown in figure 4 with photochemical-reaction between O_2 and UV light. O_2 exposed by UV (184.9 nm) was dissociated 2O (^3P) which were still unreactive with PMMA, and then react with 2O_2 to produce 2O_3. After that, O_3 exposed by UV (254 nm) was dissociated O_2^* and O (^1D), and then followed by a reaction with H_2O to produce hydroxyl radical. Finally, reactive O (^1D) and hydroxyl radical react with PMMA to produce volatile products such as CO_x, H_2O and etc. [18]. Therefore, excitation of O_2 exposed by UV light for reaction with PMMA took several steps with considerable time. With the increase of O_2 flow rate, residence time of O_2 in chamber was shorten, insufficient time made the removal rate of PMMA decrease. In the point of view with the photo-dissociation of PMMA, photo-degradation of PMMA mainly proceeded with UV irradiation at the wavelength of 184.9 nm as shown in Fig. 5(a). But, increase of O_2 flow rate compete UV (184.9 nm) absorption with PMMA. Therefore, both shorten residence time of O_2 and

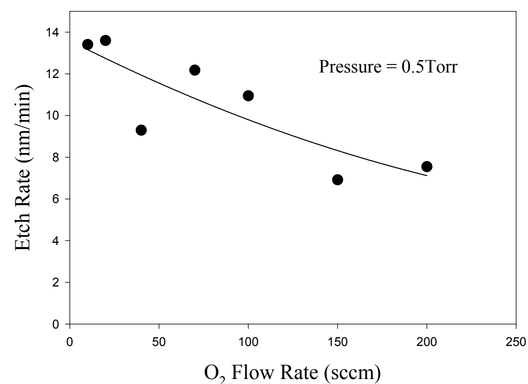

Fig. 3. The etch rate of PMMA as a function of O_2 flow rate. (Pressure = 0.5 Torr, Substrate temperature = 100℃, Distance between sample and UV lamp = 9 cm)

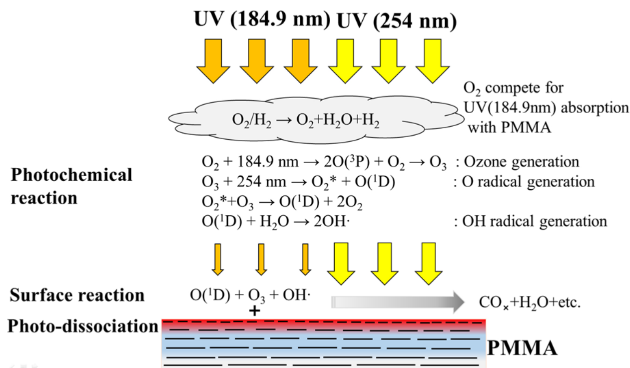

Fig. 4. Reaction mechanism of PMMA by UV/O_2.

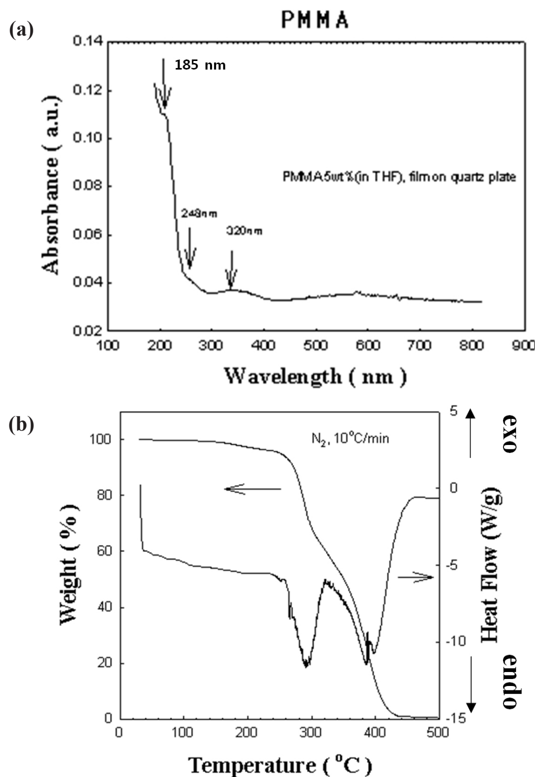

Fig. 5. (a) UV photo-absorption spectra of PMMA film and (b) TGA/DSC spectra of PMMA as a function of temperature at a heating rate of 10℃/min in N2 ambient film. PMMA was coated on quartz plate by spin coater at the condition of 1,800 RPM for 120 sec. and then dried at the condition of 100℃, 30 min in the air.

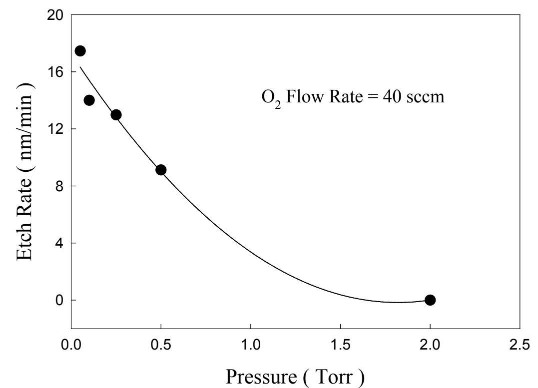

Fig. 6. The etch rate of PMMA as a function of pressure. (Total flow rate = 40 sccm, substrate temperature = 100℃, distance between sample and UV lamp = 9 cm).

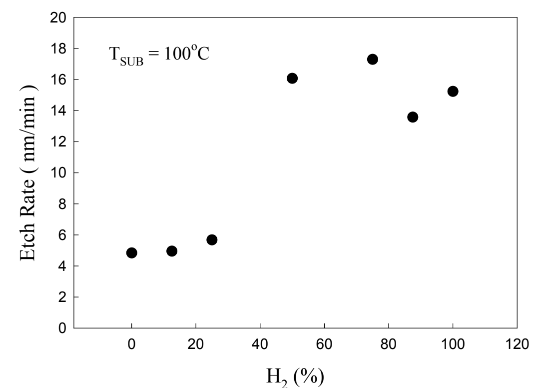

Fig. 7. The etch rate of PMMA in H_2/O_2 gas mixture as a function of H_2 proportion in feed gas. (Total flow rate = 40 sccm, pressure = 0.5 Torr, substrate temperature = 100℃, distance between sample and UV lamp = 9 cm).

insufficient photo-dissociation of PMMA with the increase of the O_2 flow rate decreases the removal rate of PMMA.

Figure 6 shows the PMMA etch rate as a function of pressure at the O_2 flow rate of 40 sccm. Etch rate of PMMA decreases with increasing pressure. At high pressure, quenching rate of excited molecules is high due to the increased collision between excited molecules and cold molecules and thus the final concentration of excited species will be low at the surface region. With the pressure of O_2 gas, both quenching effect of reactive species and deterioration of photo-dissociation of PMMA by screening effect decreases the etch rate of PMMA. In the case of PMMA, it may be speculated that decomposition of film by UV is the dominant mechanism in PMMA removal.

Figure 7 shows the etch rate of PMMA in the H_2/O_2 etching gas mixture as a function of H_2 content in feed gas with UV irradiation at the substrate temperature of 100℃ and total flow rate of 40 sccm. The etch rate of PMMA increases with the increase of H_2 proportion in H_2/O_2 gas mixture. When the content of H_2 is more than O_2, etch rate shows almost constant value. This again confirms the validity of our speculation that decomposition of PMMA by UV rather than gas-PMMA reaction governs the PMMA etch reaction. Furthermore, reaction between hydrogen and oxygen makes water and hydroxyl radical, which then reacts with PMMA more actively than the O radical. Higher etch rate with higher contents of H_2 may be explained by the lower absorption of UV by hydrogen molecules and higher UV energy available for decomposition of PMMA. In Fig. 8, etch rate of PMMA is much more temperature-sensitive at low temperature than at high temperatures. First of all, photochemical and photo-dissociation of PMMA have to differentiate from thermal dissociation. Therefore thermal dissociation of PMMA was examined by using thermal gravimetric analysis (TGA) differential scanning calorimetry (DSC) spectra. Figure 5(b) showed the thermo-gravimetric analysis(TGA) and differential scanning calorimeter (DSC) spectra of PMMA from room temperature to 600℃ in N2 atmosphere at a heating rate of 10℃/min.

The first thermal dissociation of PMMA was started at 260℃ and ended at around 310℃ by breaking of ester functional group. The second thermal dissociation of PMMA was started at 370℃ and ended at around 420℃ due to the bonds of the back-

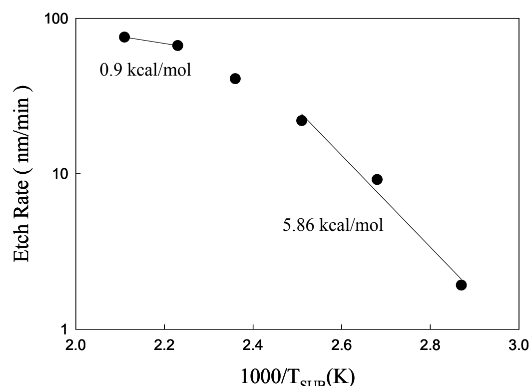

Fig. 8. The etch rate of PMMA as a function of substrate temperature. (Pressure = 0.5 Torr, O_2 flow rate =40 sccm, distance between sample and UV lamp = 9 cm).

bone chain breaking. Therefore, the substrate temperature was restricted to 200℃ at which thermal dissociation of PMMA was not substantially occurred. Etch rate of PMMA increased with increasing substrate temperature between 75℃ and 125℃ and had activation energy of about 5.86 kcal/mol indicating etching was controlled by surface reaction. Above the 180℃, PMMA removal reaction was governed by a supply of reaction gas rather than by substrate temperature.

Organic removal condition for UV excited O_2 cleaning was fixed at 5 min, 0.5 Torr, and 100℃, respectively for proper native oxide growth. At this condition, perfect removal of organic contaminants was confirmed by successive native oxide removal and successful growth of epitaxial film on that surface. But, results of both oxide removal and epitaxial film growth were not shown in this paper.

4. CONCLUSIONS

UV excited O_2 /H_2 gas phase cleaning for organic material (PMMA) removal was carried out in a load-locked reactor equipped with a UV lamp and PBN heater. UV-excited O_2/H_2 gas phase cleaning removes PMMA better at lower process pressure with higher content of H_2. Higher etch rate of PMMA with UV/H_2 than UV/O_2 can be explained by lower UV absorption by H_2, where decomposition of PMMA by UV is rate-controlling step. In our experimental conditions, etching of PMMA at the substrate temperature between 75℃ and 125℃ had activation energy of about 5.86 kcal/mol indicating etching was controlled by surface reaction. Above the 180℃, PMMA removal reaction was governed by a supply of reaction gas rather than by substrate temperature.

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