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UV Resist-Stripping for High-Speed and Damage-Free Process

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Fundamental characteristics of resist stripping in oxygen atmosphere under direct ultraviolet irradiation were investigated. The UV resist stripping rate showed a gradual decrease with the lapse of time. A practical rate was obtained at substrate temperatures around 120°C or below under oxygen pressure of 6.6×10^4 Pa, flow rate of 50 l/min, and UV irradiation energy density of 2.4 W/cm^2. After stripping, contaminants and residues which affect the device characteristics were removed by ultrasonic cleaning in diluted HCl solution. The UV irradiation induced damage was not serious and was annealed out during stripping at substrate temperature higher than 150°C.

1. Introduction

Semiconductor processing technologies which utilize both the high reactivity and directionality of charged particles such as reactive ion etching have become indispensable to the fabrication of microelectronic devices requiring fine-line lithography. However, for practical application of those processing technologies, some attention must be paid to the deleterious effects of surface contamination[1,2] and radiation induced damage[3-5] essentially incidental to them. Those drawbacks become more remarkable and serious together with the increasing necessity for thinner film processing in VLSI.

In the process of resist stripping by oxygen plasma, problems mentioned above are brought about as well, and it is not easy to find a solution because of complicated reaction mechanisms. Ultraviolet (UV) radiation was shown to be an effective method of dissolving hydrocarbons adsorbed on the surfaces[6,7] and photoresist.[8] These UV radiation induced reactions are simpler than those of plasma and therefore UV radiation may be a promising candidate for resist stripping. This paper describes the basic characteristics of resist stripping by direct irradiation of UV to the resist under controlled conditions as compared with conventional oxygen plasma stripping.

2. Experimental apparatus

A schematic diagram of the experimental apparatus is shown in Figure 1. The ultraviolet light source is an electrodeless lamp filled with argon gas and mercury. It is energized by 2.45 GHz microwave generated by a magnetron. The UV light was introduced to the sample in the chamber by reflection from a UV mirror. The UV mirror selectively reflects wavelengths from 200 to 300 nm in normal incidence. The shorter wavelength portion is used to dissolve the oxygen molecules and wavelength around 260 nm is effective for dissolving ozone generated as a result of secondary reaction of atomic oxygen. The scissions of polymer chains, which play an important role in resist stripping, are also brought about in this wavelength range.

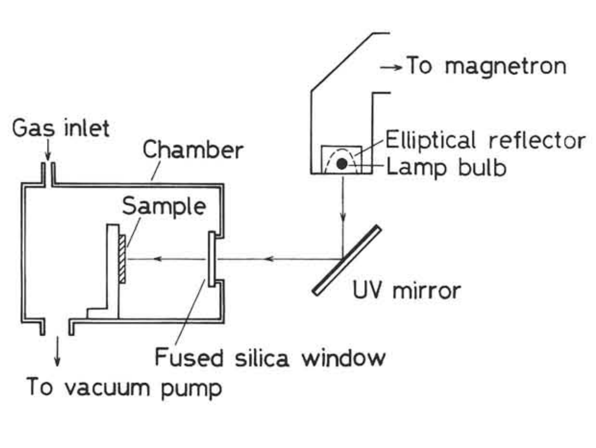

Fig.1 Schematic of UV stripping apparatus.

This UV irradiation system allowed free control of the substrate temperature by resistance heating. The temperature rise of the substrate by UV irradiation for 20 min was less than 5°C. The UV energy incident to the sample was 2.4 W/cm^2. The pressure and flow rate of oxygen were fixed at 6.6×10^4 Pa and 50 l/min, respectively.

3. Experimental results

3-1 UV resist stripping rate

Resists are subjected to various processings before stripping, and therefore, the detailed characteristics of polymers as a stripping object may be changed. Here, we concentrated on the UV stripping of typical electron beam and photo resists of positive and negative types processed under the conditions shown in Table 1. Figure 2 shows the residual resist thickness with the lapse of time in the UV stripping. We used OMR photoresist spin coated on the whole Si substrate surface to 0.59 µm initial thickness. The substrate temperature was 120°C. The stripping rate decreased gradually with time. This is quite different from oxygen plasma stripping, where the stripping rate does not depend on time when the substrate temperature is kept constant. The stripping rate also decreased in a similar manner for the other resists at each substrate temperature. The difference in time dependence between plasma and UV stripping rate can be attributed to the stripping mechanisms. In plasma stripping, various reactions caused by the impact of charged particles over a wide energy range as well as UV irradiation, proceed at the same time. On the other hand, in UV stripping, only limited reactions induced by UV irradiation can contribute. Therefore in this case, as the stripping proceeds, that part of stripping with a comparatively slow reaction relatively increases, resulting in a decrease in

Table 1. Conditions of resist treatment for the UV stripping.

Resist	Baking temperature (°C)	Baking time (min)
PMMA	150	30
CMS	100	30
AZ	120	15
OMR	150	15

stripping rate with time. Figure 3 shows the substrate temperature dependence of stripping rate for the resists listed in Table 1. The stripping rate is defined as the average rate until the resist thickness decreases to half of the initial thickness. The decrease in resist thickness without UV irradiation was negligible compared with the decrease with UV irradiation at each substrate temperature. The stripping rate increased drastically with substrate temperature just as it does in plasma stripping. Except AZ1350J, the practical

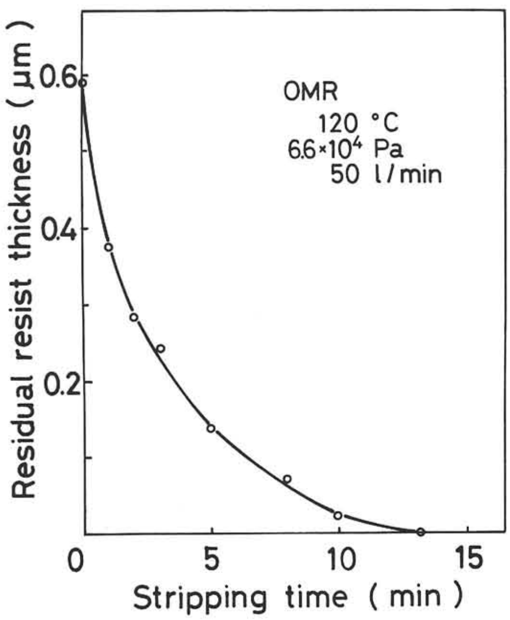

Fig.2 Time dependence of resist thickness in UV stripping. OMR resist was stripped at 120°C.

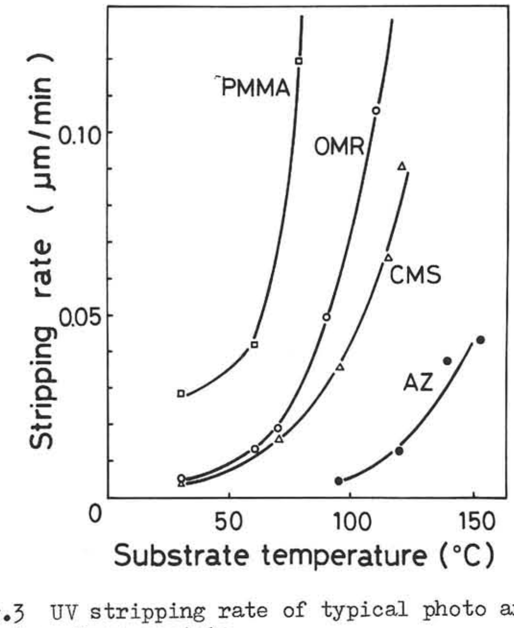

Fig.3 UV stripping rate of typical photo and electron beam resists.

stripping rate was obtained around 120°C or below.

3-2 Residues and contaminants after UV stripping

Surface layer contamination which affects the operation of devices was evaluated by the flat band voltage shift of MOS capacitor. The substrates used were Si (100) wafer of 1 Ω cm with 52 nm wet SiO_2 oxidized at 1000°C followed by annealing for 20 min in N_2. The PMMA was coated to 720 nm thickness on SiO_2 and baked under the conditions shown in Table 1. The sample thus prepared was UV-stripped for 8 min at a substrate temperature of 150°C. After the resist stripping, ultrasonic cleaning treatment was done for some samples in diluted HCl solution for 10 min. The Al electrode 400 µm in diameter was then evaporated followed by 400°C annealing for 20 min in the forming gas. Bias-temperature (B-T) stress was done on samples without resist stripping process (reference sample) as well as those with and without ultrasonic cleaning after resist stripping. The condition of B-T stress was +5V on the gate at 200°C for 20 min. The results of high frequency capacitance-voltage (C-V) measurements are shown in Figure 4. The flat band voltage shift in reference samples was less than 0.2V. Flat band voltage shift in samples with and without ultrasonic cleaning after stripping was about 0.2V and 2.4V, respectively. According to the report on oxygen plasma stripping, ultrasonic cleaning did not remove the contaminants effectively[9] and this was partly attributed to the knock-on effect of ions impinging on the sample.[10]

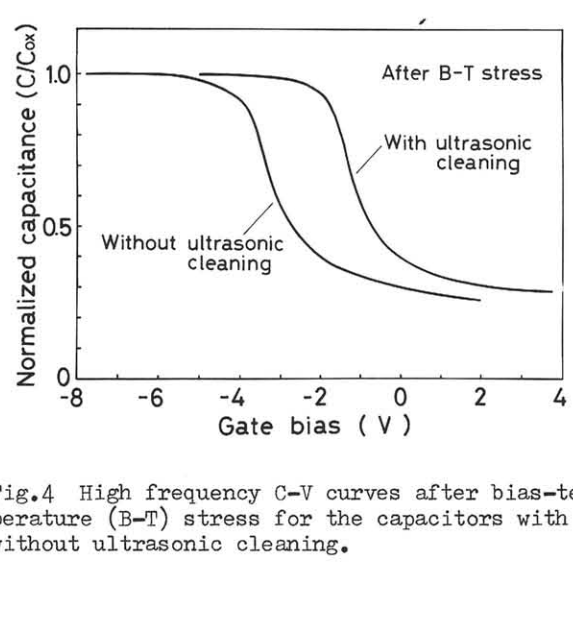

Fig.4 High frequency C-V curves after bias-temperature (B-T) stress for the capacitors with and without ultrasonic cleaning.

Thus, high temperature annealing in HCl atmosphere was needed to eliminate contaminants.[11] In UV stripping, residues and contaminants which affect the ion-drift type instability of MOS devices could be removed easily by ultrasonic cleaning. The results of Ion Micro Analysis also showed that the contaminants, which were mainly sodium and potassium and piled up near the surface layer, were removed to the level of the reference sample.

3-3 UV radiation damage

The effect of UV radiation on devices was evaluated in terms of breakdown voltages of radiation sensitive MOS diode. The gate was wet oxide 13 nm thick. After the Al electrode 400 µm in diameter was patterned by wet chemical etching using 600 nm thick OMR as the etching mask, the OMR was UV-stripped at 130°C for 30 min. The prolonged stripping time was to exaggerate the influence of the radiation on diodes. For comparison, oxygen plasma stripping was applied to some of the samples under the condition of 150 W, 130 Pa for 10 min. The breakdown voltage histograms are shown in Figure 5. The breakdown voltage was defined as the gate bias where leakage current reached 1 µA. The breakdown voltage histogram of

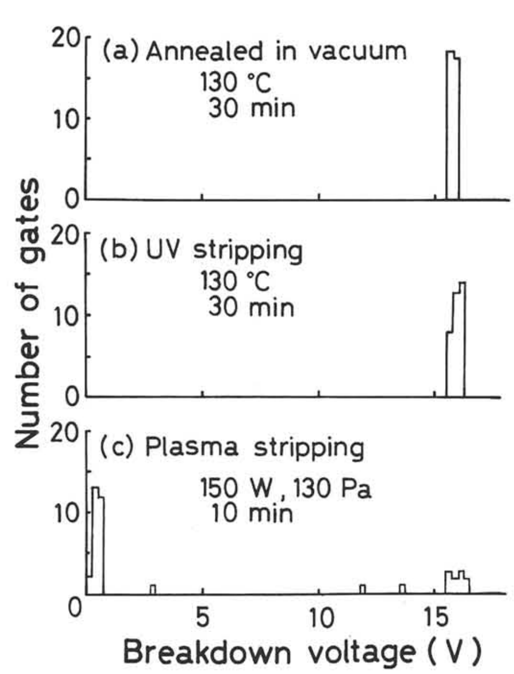

Fig.5 Dielectric breakdown histograms of diodes (a) after wet chemical stripping, (b) after UV stripping at 130°C for 30 min, (c) after oxygen plasma stripping at 150 W, 130 Pa for 10 min. Samples in (a) were annealed at 130°C for 30 min in a vacuum after stripping.

diodes after the wet chemical stripping is also shown. These diodes were annealed at 130°C for 30 min in a vacuum for reference. Degradation of breakdown voltages was not found in UV-stripped diodes. On the other hand, in a considerable fraction of the diodes, oxygen plasma stripping gave rise to serious damage which could not be annealed. This was caused by charging effect on the Al electrode[12-14] or local heating through ion impact. However, UV radiation is not completely free from damage to MOS diodes. About a quarter of the diodes irradiated with UV at room temperature in a vacuum for 30 min before Al gate metallization showed degraded breakdown voltages, while diodes UV-irradiated at 150°C showed little degradation.

4. Conclusion

Resist stripping by UV irradiation in an oxygen atmosphere had advantages over the conventional plasma stripping and showed promise for application to VLSI manufacturing in some steps. The distinctive features of UV stripping were ease of contaminant removal by ultrasonic cleaning and light radiation damage easily annealed during stripping as such a low temperature as 150°C. However, there remain problems of practical importance, that is, not all of the resist can be stripped at a reasonable rate and highly ion implanted resists show lowering of the stripping rate by more than an order of magnitude as compared with those subjected to baking only.

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