Double Exposure Stabilization of Positive Photoresist

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Synopsis

Positive photoresists appeared to be the most promising material in VLSI microfabrication for ten or more years from now. Thus, processing know-how needs to be accumulated continuously. This work deals with thermal characteristics of positive photoresist. The following facts were declared experimentally. The quinone diazide, photosensitizer, was thermally decomposed at around 140°C to release N_2. Simultaneously the surface layer of resist film was changed into innert state, called as 'husk', with low gas permeability and high chemical resistance. These thermal changes in resist film affect the photoresist to SiO_2 adhesion. In this work a noble process, named double exposure stabilization, is developed to get sufficient chemical resistance and good adhesion simultaneously.

INTRODUCTION

The last few years of semiconductor industry have been actual mass production of VLSIs, such as 64K bit dynamic RAMs accomplished with 3-μm lithography technology. In comparison with 5-μm technology, 3-μm photolithography features the use of positive photoresists rather than negative photoresists. As is well known, the main reason why positive photoresists were adopted for 3-μm lithography was their capability of high resolution. It has been reported that positive photoresists are capable of delineating as fine as 1-μm geometories when used in combination with 10-to-1 projection aligners.[1] Such progress in photolithography seems to have prolonged its life with regards to VLSI technology, negating the expectation that photolithography would be exchanged for electron beam or X-ray lithography in the *near* future. Considering this situation, characterization and control of the positive photoresists are important subject for VLSI processing technology. For example, from the viewpoint of practical use, thermal stability and plasma resistance of resist materials are important criteria in addition to resolution and sensitivity. In fact, Hiraoka and Pacansky[2] proposed a novel method to improve the plasma resistance of photo- and electron beam resists by exposing short wavelength (200–250 nm) ultraviolet light, that is, deep UV hardening.

EXPERIMENTAL

Resist Processing

Commercially available positive photoresists, which are composed of phenol novolak resin and photosensitive quinone diazide, were tested here.

Resist film, typically 1 μm thick, was exposed by an Hg lamp through a photomask. Spray developement with organic alkaline aqueous solution followed. Baking was carried out in thermostatted N_2 ambient for typically 20 min.

SiO$_2$ Wet Etching

It is well known that, in the wet etching process, resist baking conditions affect the cross-sectional shape of the substrate film after etching. In this study, SiO$_2$ films of 1 μm thickness were etched to form a line of 5-μm width with HF–NH$_4$F buffer solution, after various baking treatments. The cross-sectional shape of the etched SiO$_2$ film was observed by a scanning electron microscope. The etch factor (EF), which represents the cross-sectional shape of etched SiO$_2$ film, was defined by the ratio of the etched depth y to the extent of undercut x, as shown in Figure 1. The x and y values were measured in the photographs. By definition, the poorer the adhesion between resist and SiO$_2$, the smaller the etch factor.

IR Spectroscopy

After various baking treatments at temperatures ranging from 100°C to 300°C, IR spectra were measured in the investigation of the chemical change in the resist film. The spectrometer used was FTC-20 Fourier transform infrared spectrophotometer from DIGILAB Co. The resists were coated on the Si wafer, and baked under each condition; then transmition spectra were measured by the differential mode. The reference was a clean Si wafer.

Observation by Scanning Electron Microscope

A Hitachi MSM-2 SEM was used to observe the cross-sectional shape of the patterned photoresist and etched SiO$_2$ films. Wafers were cleaved along the crystal orientation for observation. To prevent surface charge ups, thin aluminum film was deposited on the sample with great care being taken that the patterned shape not be deformed.

Chemical Resistance

A nitric acid soaking test was performed to evaluate the chemical resistance of baked resist films. Resist patterns 1 mm square and 1 μm thick were formed on the Si wafer, then baked at various temperatures for 20 min. After soaking in the nitric acid aqueous solution at room temperature,
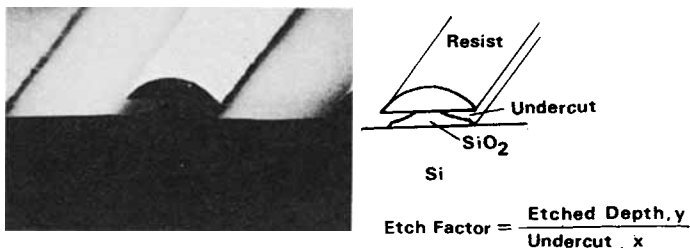

$$\text{Etch Factor} = \frac{\text{Etched Depth}, y}{\text{Undercut}, x}$$

Fig. 1.   Cross-sectional shape of wet-etched SiO$_2$ film, and definition for etch factor (EF).

samples were carefully observed to evaluate the time when the resist patterns started to lift from the substrate surface.

Gas Adsorption

A Kr gas adsorption measurement was carried out to evaluate the porosity of the resist film, after various baking treatments. The gas adsorption apparatus was a home made one equipped with a capacitance manometer. The gas adsorption isotherms were measured at 77 K, the boiling point of liquid nitrogen, and analyzed with the BET theory.[3] The BET monolayer volumes V_m were calculated to estimate porosity. A larger V_m value corresponds to a more porous structure.

RESULTS AND DISCUSSION

Change in Resist Characteristics Due to Baking

Some remarkable experimental results were demonstrated here. Figure 2 is the top view of the resist spot on a Si wafer after 200°C baking. Since a resist droplet of about 0.5 mL was applied and spontanously spread, the thickness of the resist film is considered to be of the order of several 100 microns. The circles observed in the resist layer are part of the spherelike foam. This phenomenon implies that some gaseous substance was evolved and trapped inside the resist.

Figure 3 shows the cross-sectional shape of the resist line, 5 μm wide and 1 μm thick, after baking at various temperatures. The round image for the 160°C baked pattern indicates that the resist film was melted once and then reformed.

The third phenomenon is the most serious factor affecting resist material in practical use. In Figure 4, the temperature dependence of the etch factor (EF) is shown. On the top of this figure, three photographs are shown. They
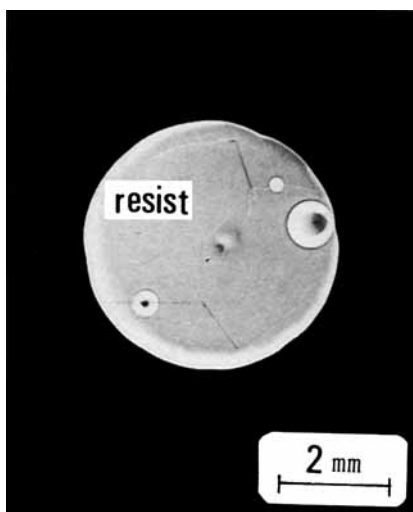

Fig. 2.   Top view of thick positive photoresist film baked at 200°C.
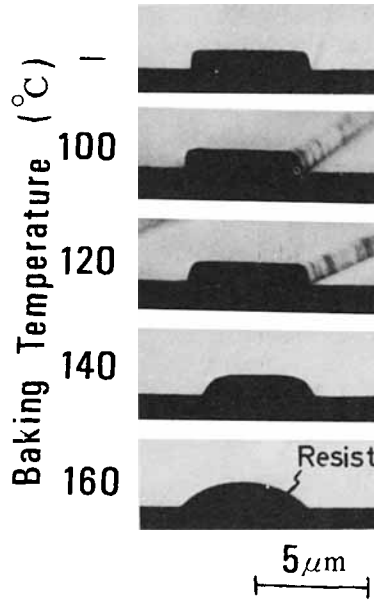
Fig. 3. Cross-sectional shapes of resist patterns baked at various temperatures. The pattern is 5 μm wide and 1 μm thick.

are the three representative cross-sectional shapes of SiO$_2$ film, which were put through the wet etching after baking at the indicated temperatures. The abrupt decrease in EF value at 140°C results in a difference in the SiO$_2$ cross-section producing isotropic and two-step bevel shapes.

Based on these phenomena, a speculation was made concerning the baking process.

Speculations Concerning Resist Baking

As a result of baking of the resist film, nitrogen gas was released through thermal decomposition of the diazide group. At the same time, the resist melted and reformed, to result in a surface layer with low gas permeability.
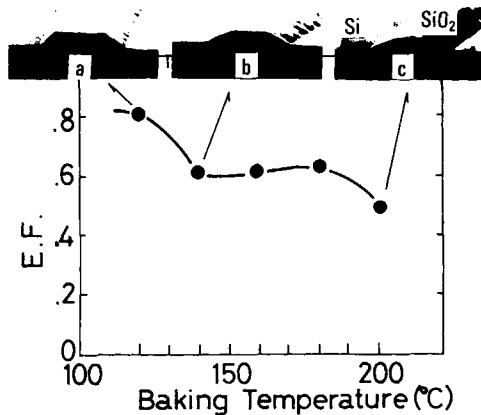

Fig. 4. Etch factor vs. baking temperature. Three representative cross-sectional shapes of SiO$_2$ film, which were etched after baked at 120°C, 140°C, and 200°C, respectively, are shown.
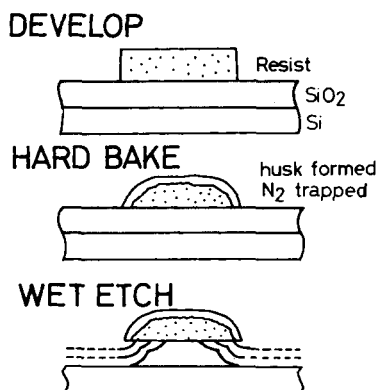
DEVELOP

HARD BAKE   husk formed
                   N$_2$ trapped

WET ETCH

Fig. 5.   Speculated model for the resist baking and SiO$_2$ wet-etching process.

Hereafter we call such surface layers "husks." In consequence, N$_2$ was trapped inside the husk, as symbolically depicted in Figure 5. An extreme case is the foam in Figure 2. Furthermore, trapped N$_2$ makes photoresist adhesion to SiO$_2$ poor, resulting in a two-step bevel shape during SiO$_2$ wet etching, as demonstrated by photographs (b) and (c) in Figure 4. Photograph (a), however, of the same figure, baked at 120°C, does not show the two-step bevel, but a normal isotropically etched shape, indicating good adhesion between the SiO$_2$ and resist film. Thus, it is speculated that N$_2$ from the diazide group is trapped inside the resist layer by baking at temperatures higher than 140°C.

Experimental Verification

Infrared Spectroscopy. A series of IR spectra in Figure 6 indicates the thermal decomposition of the diazide group. The absorption at 2120 cm^{-1} is considered to be assigned to the—N $\equiv$ N group by analogy with the fact[4]
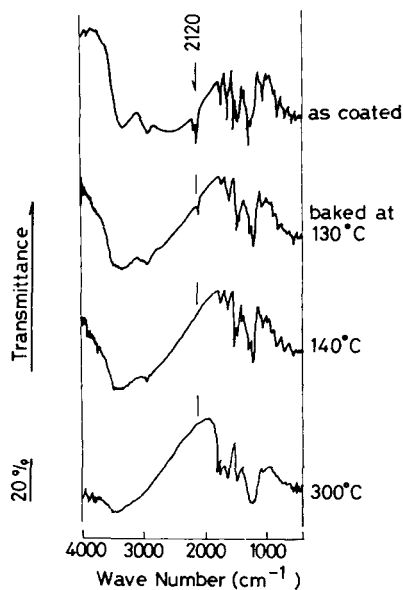

Fig. 6.   IR spectra of positive photoresist baked at various temperatures.
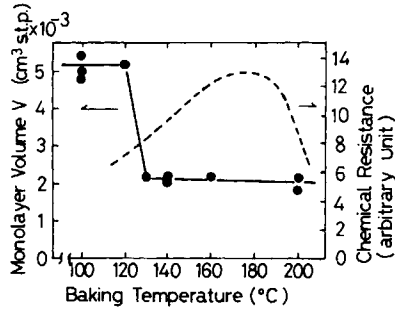
Fig. 7. Porosity and chemical resistance for positive photoresist.

that diazonium salt has an absorption at 2050–2035 and the azide group does so at 2095–2160 cm^{-1}. As shown in Figure 6, by 140°C baking, the absorption at 2120 cm^{-1} completely disappears, whereas after 130°C baking absorption is still observed.

"Husk" Existence. Two experimental results which throw light on the existence of the husk are shown in Figure 7. As is well known, novolak resin is so fragile that it is difficult to form thin film with it for conventional gas permeability measurements. Thus, the physical adsorption amount of the inert gas, in this study Kr, was measured to evaluate the porosity of the resist film after various baking treatments. For the left-hand ordinate in Figure 7, the BET monolayer volumes V_m were plotted against the baking temperature. The larger V_m values indicate a more porous and highly gas permeable structure of the resist film, and vice versa. An abrupt decrease in V_m value is observed at a baking temperature of 140°C, by a factor of 2/5 compared to those baked at lower temperatures. From this result, the husk is concluded to be formed by baking at temperatures higher than 140°C.

Chemical resistance in the resist film which was evaluated by the nitric acid soaking test is shown in Figure 7 as the right-hand ordinate. Monotonous increase in resistance with baking temperature was observed up to 180°C, followed by a decrease. Such behavior is consistent with formation of the husk by 140°C baking, and thermal degradation of novolak resin at higher temperatures.

Evaluation of the "Husk's" Thickness. As was shown in Figure 1, a unique two-step bevel shape was found in the SiO$_2$ wet etching. It was speculated in the previous section that this was caused by the nitrogen
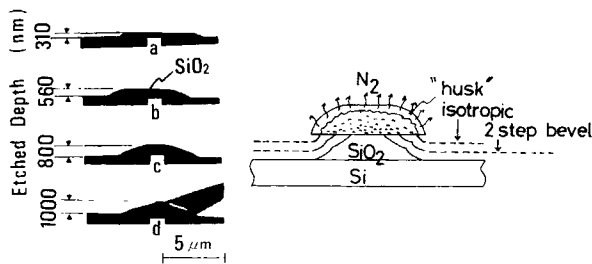

Fig. 8. Time progress with SiO$_2$ wet-etching.

Flood Exposure

N_2 diffuses outside

Hard Baking(husk formed)

N_2 trapped inside

no N_2 trapped

Wet Etching

poor adhesion

2 step bevel

good adhesion

isotropic etch

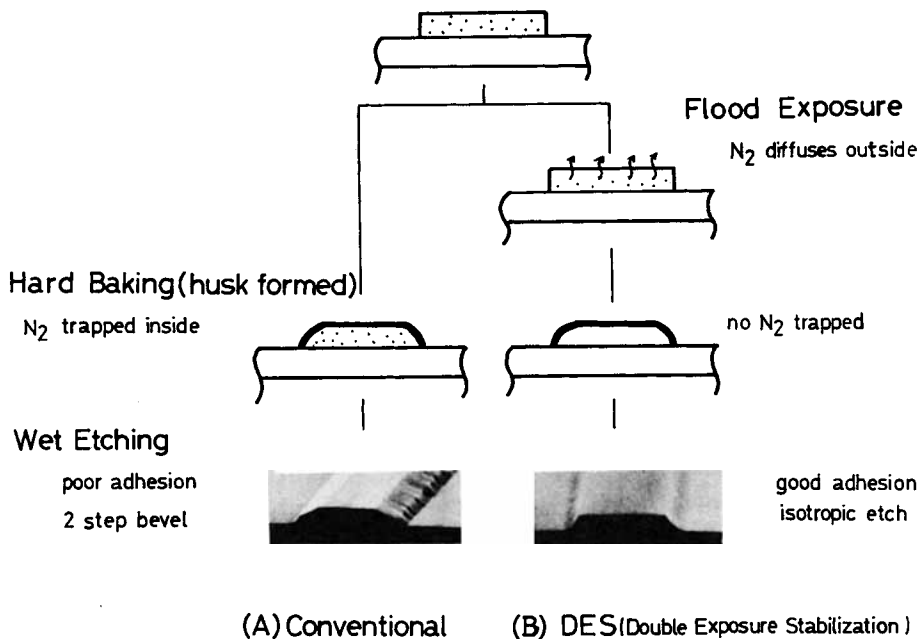(A) Conventional   (B) DES (Double Exposure Stabilization)

Fig. 9.   Flow for conventional (A) and DES (B) processes.

trapped inside the husk. Time progress for the SiO_2 wet etching process was analyzed in detail to estimate the thickness of the husk. After baking at 160°C, four SiO_2 films were etched to different depths. The shapes of cross-sections of them are shown in Figure 8. A clear difference can be recognized between photographs (a) and (b). This corresponding to etching at 310 and 560 nm depth, respectively. Namely, a two-step bevel shape is observed when SiO_2 was etched deeper than 310 nm. Thus, the thickness of the husk is considered to be at least 310 nm.

Double Exposure Stabilization

The basic idea behind the double exposure stabilization, or DES, process is that, to avoid nitrogen trapping, the diazide groups should be decomposed by ultraviolet irradiation rather than baking. The practical flow of the process is illustrated in Figure 9. Resist patterns were formed through conventional exposure and development treatments. At this stage, the husk did not form, because the resist was baked only at a low temperature of around 90°C. Inside the resist pattern, diazide groups were still contained unchanged. According to the conventional process, high temperature baking is applied to get the chemical resistance. In the DES process, prior to such hard baking, wafers were exposed to UV irradiation to eliminate the N_2 outside the resist layer. Typical exposure time was 30 s, which was about triple of that for conventinal patterning. To get sufficient chemical resistance, resist patterns were baked at high temperature, for example, higher than 140°C. Since no diazide group was contained in the resist patterns, N_2 trapping could not occur. Thus, good adhesion between SiO_2 and the resist was maintained.
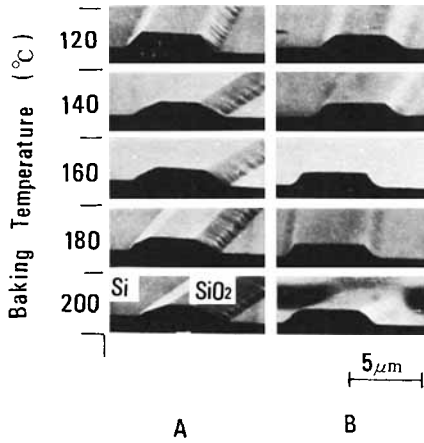
Fig. 10. Cross-sectional shape of etched SiO₂ film from (A) conventional and (B) DES processes.

In Figure 10, cross-sectional shapes of etched SiO_2 films are shown to clarify the difference between the DES and conventional processes. As was mentioned, conventional process baking at temperatures higher than 140°C produce two-step bevel shapes, whereas the DES process, as shown in the column (b), results in isotropically etched shapes throughout the temperature range studied. Figure 11 is a plot of the etch factor (EF) vs. the baking temperature. As expected from the photographs in Figure 10, with the DES process the EF value increases, with baking temperature, up to 180°C. The decrease in EF at 200°C baking is considered to be due to thermal degradation, as was mentioned in the previous section.

CONCLUSION

The novolak type positive photoresists need to be baked at higher temperatures around 140°C to get sufficient chemical resistance. When this is done, quinone diazide is thermally decomposed and release N_2. This nitrogen
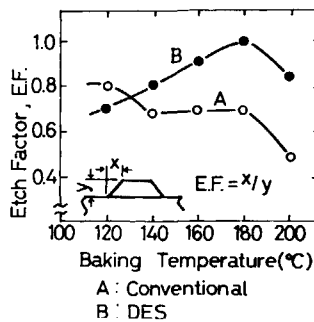

Fig. 11. Etch factor vs. baking temperature in conventional (A) and DES (B) processes. Remarkable difference in EF value is observed at 140°C.

is trapped inside the resist layer and makes resist to substrate adhesion poor. To avoid such adverse effect of trapped nitrogen, the diazide is photochemically decomposed prior to hard baking. In consequence, both the chemical resistance and adhesion are filled simultaneously. This process was named as double exposure stabilization.

References

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4. K. Nakanishi, P. H. Solomon, and N. Furutachi, *Infrared Absorption Spectroscopy,* Nankodo, Tokyo, 1978, p. 26.