Changing Behavior of Residue during Dry Etching in Multilayer Resist Process

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The behavior of residue formation during the oxygen-reactive ion etching (RIE) in the multi-layer resist process is studied. The mechanism for the formation of residue and the method used to remove residue are studied. The needle-like residue generated during the under-layer etching process is completely removed by covering the electrode target of the RIE apparatus with polyethylene terephthalate or RIE with O₂/CF₄ mixture gas. The mechanism for formation of residue is as follows: silicon containing compounds were deposited on the under-layer by sputtering of the upper resist and electrode target with oxygen ion generated in O₂-RIE process.

Keywords: Multilayer resist, Etching, Mechanism, Residue, Silicone resist

1. Introduction

As critical images used in ULSI production approach the sub-100 nm size, fabrication of thin-imaging layers and anti-reflection from the substrate become more desirable as a means of improving process latitude. In particular, the multilayer resist processes can divide the thin imaging layer and thick anti-reflective under-layer, resulting in an improvement of resolution and dry-etching resistance. This process has been studied very extensively because of minimal influence from the surface heterogeneity of a multi-wiring substrate compared with a single-layer resist. The bi-layer resist process [1-5] with silicon-containing resist as the upper-layer is loaded in the lowest steps in the multilayer resist process and has a significant improvement effect. Consequently, demand is high for introduction of the resist process. However, in actual cases, there are unresolved problems about the formation of residue in the etching process [6, 7]. The removal of residue is required in order to improve the reliability of the product and the process. In this study, the etching residue formed in a bi-layer resist process using a silicon-containing resist is investigated. The method of residual removal is examined. The mechanism for residue formation is also discussed.

2. Experimental

The conditions of the negative bi-layer resist

process using silylated polymethylsilsesquioxane (PMSS [8]) for the Al wiring is shown in Table 1. PMSS is used at Mw=3.7E4 and Mw/Mn=1.4. The lower-layer resist consists of chloromethyl polystyrene (CMS). In order to prevent sputtering the electrode target covered with PET film in the reactive ion etching (RIE) apparatus as a result of a decrease in residue during etching, the experiment was carried out at total O₂ pressure of 20 mTorr, frequency of 13.56 MHz, O₂ flow rate of 20 sccm, and r.f. power of 0.16 W/cm² using a Anelva DEM-451 RIE apparatus. Secondary ion mass spectroscopy (SIMS) measurement was done for detecting positive secondary ions using a Hitachi IMA-3 secondary ion mass spectrometer at the measuring conditions of O₂ ion source and accelerating voltage of 20 kV. Auger electron spectroscopy (AES) measurement was done using a JEOL JAMP-30 scanning auger microprobe device under the following conditions: accelerating voltage of 5 kV, electron current of 5.5E-4 A, measuring time of 4.6 min, and a scanning time of 5. Melting point of the resin was measured using a Kofler company WEM-type hot bench. Infrared spectra of the resin films were analyzed using a JEOL (JIR-100) FT reflective infrared spectrometer.

Table 1. Bi-layer resist process for Al wiring

Process	Conditions
Al coating	0.9 μm
Lower resist coating	CMS, 2 μm
UV curing	170°C, 180 sec
Upper resist coating	PMSS, 0.2 μm
Pre baking	80°C, 100 sec
EB exposure	30 kV
Post exposure bake	100°C, 60 sec
Development	Organic solvents
Lower resist etching	Oxygen-RIE
Al etching	Chlorine-RIE
Resist removal	Fluoride-RIE

3. Results and Discussion

3.1 Mechanism of formation residue

3.1.1 Analysis of aluminum etching residue

Clarifying the reason for residue formation by aluminum etching, SEM images in each step of the process of bi-layer resist are shown in Fig. 1. The granule residue was formed on the ground of the oxidized film surface after aluminum etching of the patterned bi-layer resist as a masking agent.

Figure 1. Bi-layer resist process and residue

The composition of residue is analyzed to study the formation mechanism of the residue. The results of SIMS measurements of the surface of untreated oxidized film (reference) and oxidized film with residue formed by aluminum etching is shown in Table 2. These spectra are the elements

with higher intensity than the reference by normalizing the peaks of obtained spectra with that of a Si peak. The contents of titanium, copper, and silicon in the compounds increased by aluminum etching, as shown in Table 2. Titanium-containing and copper-containing compounds likely turned into residue because they have a slower etching rate than aluminum. For titanium and copper elements, wiring materials were the multi-layer structures of Al, TiN, Al-Cu. These residues were not formed using a conventional single-layer resist under the same etching conditions but they increased the amount of silicon-containing compounds in the residue component. Consequently, the residue was formed with some change in the silicon-containing resist of the upper-layer.

Figure 2. Generating behavior of residue A**Table 2. SIMS results of Al residue sample**

Mass	Ion	Intensity	
		Reference	Sample
10	SiH	4.1E-4	8.1E-4
14	Si	1.9E-2	4.8E-2
18	O	2.0E-4	7.7E-4
30	Si (CO)	3.8E-1	9.0E-1
48	Ti (SiO)	1.8E-4	3.0E-3
63	Cu (TiO, SiO ₂)	6.7E-4	1.2E-3
65	Cu (TiO, SiO ₂)	4.6E-4	7.6E-4

3.1.2 Development residue (residue A)

The granulated residue was observed after the development of silicon containing resist on the upper layer and needle-like residue was formed after oxygen-reactive ion etching (O₂-RIE) of the lower layer (Fig. 1). We expected that the development residue on the upper layer (residue A) was transferred to form needle-like residue on O₂-RIE treatment (residue B) and subsequently formation of aluminum etching residue (residue C) was more influenced by transformation of the needle-like residue. Therefore, we first studied the formation of

development residue of the upper layer.

The SEM images of formation of development residue of the upper layer are shown in Fig. 2. A significant amount of residue was formed at a narrow place close to the pattern and few particles were formed far from the pattern. The amount of residue near the pattern became larger with an increase in exposure dose and the shape of the residue was similarly large at a part of the pattern for lack of exposure (Fig. 3). From the result, the residue near the pattern was formed by the proximity effect on exposure of the electron beam. The amount of formed residue far from the pattern depended on the reciprocal molecular weight of PMSS, that is, the lower molecular weight of the resist, the more residue was formed. The relationship between the molecular-weight distribution and the softening temperature of PMSS in this study shows that the residue contained the compounds melted at a post-exposure bake (PEB) temperature of 100°C, as shown in Fig. 4. Consequently, the residue was formed as small particles, which were unresolved in a developer after the reaction of unstable unsilylated silanol groups with each other.

Figure 3. Upper resist profile with unsuitable dose

Figure 4. Relationship between molecular weight and softening temperature of PMSS

Figure 5. Generating behavior of residue B

Figure 6 Change in residue B during O₂-RIE with time

3.1.3 Etching residue on lower layer (residue B)

The situation of formed residue after O₂-RIE of lower-layer resist is shown in Fig. 5. The residue was not formed at a narrow place near the pattern but a number of large needle-like particles were formed far from the pattern. This behavior is different from the situation of development residue formed on the upper layer. The change in residue during O₂-RIE with time is shown in Fig. 6. Small particles of development residue on the upper-layer resist were observed in the initial stage of the etching. Furthermore, the amount of particle residue decreased at the narrow place with etching time and increased at locations far from the pattern. As a result, we suggest that the upper-layer residue was removed to form new residue on the lower layer by sputtering during O₂-RIE. The changes in the generated situation with etching overtime of O₂-RIE and r.f. power are shown in Figs. 7 and 8. The particle of residue became large with increasing etching overtime from 0, 20 to 50% at r.f. power of 300 W, and at 150% it turned into the pillar-like particles which were grown around needle like residue during etching. In Fig. 8, the formation

density of residue increased with increasing r.f. power from 100, 300 to 450 W at a constant (20%) of etching overtime. At 600 W the residual particle became small but the formation density was extremely high. Consequently, the characteristics of the etching residue on the lower layer depends on the overtime on O₂-RIE and r.f. power.

Figure 7. Change in residue B with overtime of O₂-RIE

Figure 8. Change in residue B with r. f. power of O₂-RIE

The residue on the lower layer by etching was observed on the tri-layer resist as shown in Fig. 9. The residue of the tri-layer resist occurred at the same place of bi-layer resist and did not occur at a narrow place. The shape of the tri-layer resist is the same needle as that of the bi-layer resist but the particle size is one-tenth that of the bi-layer resist. The residue of tri-layer resist in O₂-RIE with time is shown in Fig. 10. The residue was not formed while

the upper-layer resist remained in the initial stage of etching (a). However, a small amount of residue began to form when the poly-siloxane layer as the intermediate layer appeared after the complete etching of the upper-layer resist (b), and then the residual particles gradually became bigger (c,d). As a result, it is noted that the lower-layer etching residue is exposed during O₂-RIE of poly-siloxane.

Figure 9. Generating behavior of residue B by tri-layer resist

Figure 10. Change in residue B of tri-layer resist during O₂-RIE with time

The etching of the lower layer in the bi-layer resist was carried out with various pattern areas of upper PMSS in order to investigate the residue on the lower-layer, that is, in variation of poly-siloxane amount exposed during O₂-RIE. The generated situation of the residue in the etching process is shown in Fig. 11. The residue clearly increased as the pattern area of the upper-layer resist increased from 3, 37 to 71%. Furthermore, the residue was slightly less formed at the pattern area of 0% (i.e. in O₂-RIE process using only the lower-layer resist applied on the substrate). In order to explain the reason, the surface analysis of lower-layer residue in etching was carried out. The AES charts of the aluminum surface of formed needle-like residue after O₂-RIE as well as the untreated aluminum surface (reference) are shown in Fig. 12. The silicon peak was observed on an aluminum surface

formed on residue but not on a reference.

Figure 11. Change in residue B with pattern area of PMSS

Figure 12. AES results of residue B sample

Table 3. SIMS results

Mass	Ion	Intensity		
		Reference	Sample 1 (w/o PMSS)	Sample 2 (w PMSS)
29	Si	4.0E-5	2.7E-4	3.0E-4

Figure 13. Effect of PET cover for residue B

Table 3 shows the results of the analysis of silicon by SIMS. The intensity of silicon increased on an aluminum surface by O_2 -RIE treatment without upper PMSS resist. Furthermore, the silicon intensity increased when the PMSS resist was present. Consequently, the mechanism for

formation of residue on the lower-layer resist on etching suggests the following: the residue is formed by sputtering of the upper Si-containing resist and quartz electrode target in RIE apparatus with oxygen ion generated on O_2 -RIE.

Figure 14. Effect of PET cover during O_2 -RIE with time

3.2 Removal method of residue B

3.2.1 Electrode cover with polyethylene telephlate (PET)

The quartz electrode target in the RIE apparatus was covered with a PET film in order to prevent spattering the quartz as the amount of the residue on etching is decreased. Figure 13 shows the SEM image of a bi-layer resist pattern using quartz target with and without the PET cover in O_2 -RIE treatment. The quartz target with the PET cover is effective at removing the needle-like residue. Figure 14 illustrates the change in SEM image of substrate using quartz target with PET on O_2 -RIE with time. Small particles like the development residue were observed on a lower resist layer in the initial stage of etching with the same results of the quartz target (Fig. 6), and the amount of the residue decreased with the etching and then finally disappeared. Figure 15 shows the IR spectra of the upper PMSS after O_2 -RIE treatment using a quartz target with and without a PET cover in comparison before RIE. Since the peak of an -Si-O-Si- bond group at between 1000 and 1100 cm^{-1} functions as a main structure of an -Si-O-Si- of a ladder-type molecule of PMSS for the quartz target, the PET cover is significantly changed. This change is caused by etching in comparison with the quartz target

without the PET cover and reference. Figure 16 shows the O₂-RIE rate of PMSS using the quartz target with and without the PET cover. The etching rate of PMSS with PET cover was faster than that without PET cover. The film thickness measurement showed that the PET cover was adequately etched after the etching process. Based on the result, the mechanism of residue reduction was not covered by the quartz target in RIE with PET but the silicon containing residue was removed in reaction of silicon with the gases evolved from PET on etching.

Figure 15 IR spectra of PMSS

Figure 16 O₂-RIE rate of PMSS

3.2.2 RIE with O₂/CF₄ mixture gas

CF₄ is used as an agent of plasma etching of SiO₂.

The etching reaction proceeds as follows:

This reaction is applied to the removal of silicon as a component of the residue on etching while adding CF₄ into O₂ gas on RIE. The O₂ addition varied, ranging between 0, 25, 50, and 100 sccm, in order to evaluate the influence on the pattern size effect by etching. The shift of size with the added amount is

shown in Table 4. The pattern disappeared at 100 sccm of CF₄ on etching and there was a large shift of the pattern size at 50 sccm. On the other hand, the size at the additional amount of 25 sccm is close to that at 0 sccm. Figure 17 shows the patterns of the resist at the added amount of CF₄ at 25 sccm.

Table 4. Pattern width shift after RIE

		Pattern width after RIE (%)		
O ₂ /CF ₄ (sccm)		400/0	400/25	400/50
Center	Line	91.7	91.3	87.2
	Space	123.5	125.9	135.7
Edge	Line	91.2	90.5	85.6
	Space	123.9	126.7	136.3

Table 5. Pattern width shift after RIE

		Pattern width after RIE (%)		
O ₂ /CF ₄ (sccm)		400/0	400/25 ↓ 400/0	400/0 ↓ 400/25
Center	Line	91.7	91.6	91.8
	Space	123.5	125.0	125.3
Edge	Line	91.2	90.8	91.1
	Space	123.9	126.5	126.1

(a) O₂: 400 sccm(b) O₂: 400 + CF₄: 25 sccmFigure 17. Effect of CF₄ addition during O₂-RIE for residue B

The addition at a very small amount of CF₄ removed completely on the residue on etching of the lower-layer. The exposure of CF₄ at a shorter time is much more effective at decreasing the size of the pattern size shift. The situation of formation of the lower-layer residue on etching and the shift of the pattern is examined with the addition of CF₄ at 25 sccm in the initial or final stages of etching time. As a result, the shift of the pattern size is smaller than that at the addition of 25 sccm at a whole reaction

time in Table 5, and the effect of the pattern size shift was not observed with CF_4 addition. On the contrary, in Fig. 18, the amount of the residue with CF_4 addition in the initial stage remained small at the edge of the step, but it was completely removed in the final stage, resulting in the very effective removal of selectively added CF_4 . Figure 19 shows the Al wiring formed by masking of the bi-layer resist pattern which was removed by the lower-layer residue by the RIE with an O_2/CF_4 mixture gas. This Figure supports the removal of residue in aluminum etching as a problem.

Figure 18. Effect of CF_4 addition during O_2 -RIE for residue B

Figure 19. Effect of CF_4 addition during O_2 -RIE for residue C

4. Conclusion

The residue behavior during the aluminum wiring process using a multilayer resist is studied as follows:

- (1) The residue generated in aluminum etching using the bi-layer resist was an agglomeration of the silicon containing compound. The cause of the residue was due to transformation of the needle-like residue generated by O_2 -RIE of the under-layer.
- (2) The behavior of the development residue of the

upper-layer resist did not correspond to the place and situation of the formation of needle-like residue after O_2 -RIE of the lower-layer.

(3) The needle like residue was formed only after etching of the lower-layer, and increased proportionally as the area of the silicon containing upper-resist increased. As a result, the needle-like residue was generated by sputtering of the quartz target of O_2 -RIE apparatus and upper-layer resist with oxygen ion formed during O_2 -RIE.

(4) The needle-like residue are effectively removed by the methods involving the covering of the RIE apparatus with polyethylene terephthalate or RIE with O_2/CF_4 mixture gas, and the removal results in the elimination of the agglomerates of residue on aluminum wiring.

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References

1. B. J. Lin, Solid State Technol. 26, 5, p.105 (1983)
2. K. Watanabe, E. Yano, T. Namiki, Y. Yoneda, ACS Symposium Series, 537, 194 (1992)
3. W. Brunsvold, K. Stewart, P. Jagannathan, R. Sooriyakumaran, J. Parrill, K. P. Muller, H. Sachdev, Proc. of SPIE, Vol.1925, p.377 (1992)
4. R. Sooriyakumaran, D. F. Alexander, P. J. Brock, C. E. Larson, R. A. DiPietro, G. M. Wallraff, D. C. Hofer, D. J. Dawson, Proc. of SPIE, Vol.3999, p.1171 (2000)
5. J. Hatakeyama, T. Takeda, M. Nakashima, T. Kinsho, Y. Kawai, T. Ishihara, J. Photopolym. Sci. Technol., Vol.17, No. 4, p.519 (2004)
6. K. M. Kalpakjian, M. A. Lieberman, J. of Vac. Sci. Technol., 12, 3, 1351 (1994)
7. P. S. Nam, L. M. Ferreira, T. Y. Lee, K. N. Tu, J. of Vac. Sci. Technol., 18, 6, p.2780 (2000)
8. S. Fukuyama, Y. Yoneda, M. Myagawa, K. Nishii, U. S. Patent, 4657843 (1987)