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Surface Damage on Si Substrates Caused by Reactive Sputter Etching

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Surface damage on silicon substrates caused by RSE has been investigated. Defects are classified into four categories in order of destruction, namely, precipitates surrounded by elastic strain field, surface roughness pattern, polycrystalline and amorphous silicon, and no defects, based on the results of TEM and RHEED observation. In particular, precipitates which reach a depth more than 500 Å were found to cause OSF. The surface damage consists of contamination (C, F, O) layer, C and defect mixed layer, and defect layer in order from the top. The degree of these defects and contaminations expand with increasing power density and etching duration. RSE conditions, where no defects are formed, were determined, *e.g.*, within 1 minute at 0.4 W cm^{-2}.

§1. Introduction

Dry etching for semiconductor device fabrication has been developed to realize fine line resolution, cleanliness, low-cost and process brevity.[1] Reactive sputter etching (RSE), using RF sputtering configuration, is effective for the selective etching of Al[2] and SiO_2[3], while plasma etching is used to remove polycrystalline Si and Si_3N_4 films. Since RSE is suitable for good pattern delineation,[4] this method will be adopted for all dry etching process.

RSE utilizes not only the chemical effects of reactive ions but also the physical effects of ion bombardment.[5] The radiation damage thickness at silicon substrate surface, caused by Ar^+ ion bombardment during ion etching of SiO_2 films at energy bellow 1 keV, is 50–100 Å.[6] In the case of RSE, ions (CF_x^+, CCl_x^+) also impinge on the surface at several hundreds of eV, therefore surface damage may be formed. Damage is expected to consist of defects due to ion bombardment and contaminations due to decomposed etching gas, and can be cause of electrical characteristic deterioration. However, very few studies on surface damage caused by RSE have been reported.

In the present paper, the surface damaged layer on silicon substrates caused by over-etching of RSE after removal of SiO_2 films [illegible] tron microscopy (TEM), reflection high energy electron diffraction (RHEED), oxidation Sirtl (OS) check and Auger electron spectroscopy (AES). Based on the obtained results, the recommended RSE conditions where no defects were formed on silicon substrates were proposed.

§2. Experimental Procedures

Experiments were carried out using a diode RF sputter etching apparatus with a 100 mm^{ϕ} target. The (100) and (110) surface silicon wafers with no SiO_2 films were reactive-sputter-etched. Then, crystal structures and contaminations in the surface damaged layer were investigated by TEM, RHEED, OS check and AES. Since etching gas, gas pressure, power density, etching duration and target materials were considered to influence the surface damage, RSE conditions were set as shown in Table I. C_2F_6 gas was used as etching gas, because active species for SiO_2 were CF_3^+ ions[7] and C_2F_6 gives more CF_3^+ ions, compared with CF_4.[8] Ar, C_2H_4 and O_2, respectively, were mixed with C_2F_6 in order to extract sputtering effects, increase etching selectivity for SiO_2/Si[9] and make faster etch rate by raising chemical effects.[10] Gas pressure was set at 0.04 Torr. Power densities were set from 0.13 to 1.3 W cm^{-2}. Etching durations were [illegible]

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Table I. RSE conditions.

Etching gas	Pressure [Torr]	Power Density [W cm^{-2}]	Etching duration [sec]
C_2F_6	0.04	0.13, 0.25, 0.6, 1.0, 1.3	5, 15, 30, 60, 120, 180, 300
C_2F_6+Ar	0.04	1.0	300
$C_2F_6+C_2H_4$	0.04	1.0	180
$C_2F_6+O_2$	0.04	1.0	180

the lower electrode was a carbon plate. Although iron and teflon plates were also used as targets, no particular difference in surface damage could be recognized.

Samples for TEM observation were prepared by RSE of silicon thin films, which were made by conventional thinning technique using $HF+HNO_3+CH_3COOH$ solution, as shown in Fig. 1. The same surface damage was observed on the substrates regardless of the samples used. One was made by chemical back etching after RSE of silicon wafer. The other was ready for RSE of silicon thin film.

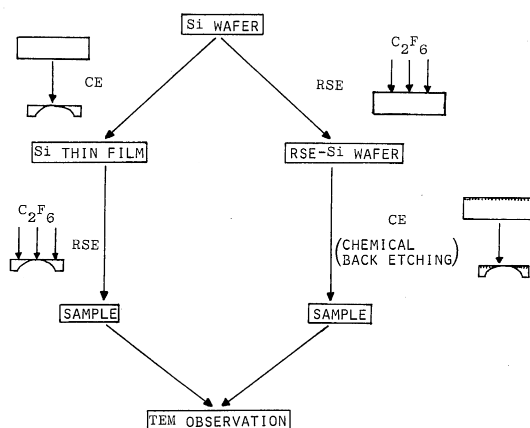

Fig. 1. TEM observation samples.

§3. Results and Discussion

Defects on silicon substrates caused by RSE are described in §3.1. Section 3.2 deals with gas mixing effects on defects and §3.3 with OS check results. Section 3.4 describes contamination in surface damaged layer. Finally RSE conditions are discussed in §3.5.

3.1 *Defects caused by RSE*

The dependence of surface damage structure on etching conditions, that is, power density, etching duration, C_2F_6 pressure and target materials, was investigated. The defects formed in RSE for long duration at high power density were found by TEM observation to be precipitates surrounded by elastic strain field. They existed on {111} planes along ⟨011⟩ directions taken from (100) direction, as shown in Fig. 2(a). These defects proved to be formed on silicon substrates regardless of gas pressure and target materials. Figure 3(a) shows the defects which were formed using CF_4 gas and iron target at 0.04 Torr. Figure 3(b) shows the defects formed using C_2F_6 gas and teflon target at 0.1 Torr. On the other hand, surface roughness pattern was formed under RSE conditions at lower power density, as shown in Fig. 2(b). In these cases no defects were observed on the TEM samples without RSE.

structure depends especially on power density and etching duration. Then, the dependence of damage structure on these parameters was investigated by TEM at a C_2F_6 pressure of 0.04 Torr with a carbon target. The tendency of damage formation conditions is summarized as follows. (1) Precipitates surrounded by elastic strain field are formed with RSE for more than 1 minute at more than 1 W cm^{-2}. (2) No defects are observed within 15 seconds at 1 W cm^{-2} or within 5 minutes at 0.25 W·cm^{-2}. (3) Surface roughness pattern is formed under intermediate conditions. Figures 2(a)–(c) show typical TEM images of these defects. More detailed results will be described in §3.5 using Fig. 13 which will be drawn up based on RHEED observation and OS check in addition to TEM observation.

Since precipitates existed on {111} planes, (110) surface silicon filmes were used in order to make clear TEM image. Figure 4 shows a dark field TEM image of this defect using (2$\bar{2}$2) spot. This defect proved to be interstitial type inclusion, because the image changed from light to dark before and behind the defect along the direction of reciprocal lattice vector.[11)]

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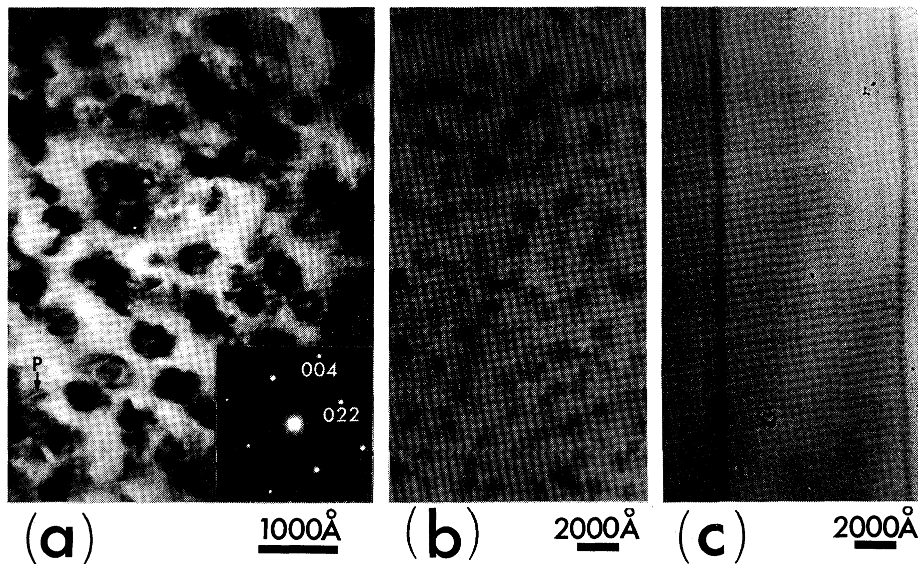

Fig. 2. TEM bright field images of (100) silicon films: (a) Precipitates surrounded by elastic strain field, RSE for 3 minutes at 1 W cm^{-2}. P shows a precipitate. (b) Surface roughness pattern, RSE for 3 minutes at 0.6 W cm^{-2}. (c) No defects, RSE for 3 minutes at 0.25 W cm^{-2}.

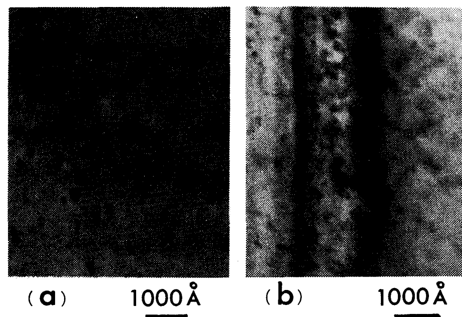

Fig. 3. TEM bright field images of surface damage under various RSE conditions: (a) CF_4, 0.04 Torr, 1.3 W cm^{-2}, 3 min, iron target. (b) C_2F_6, 0.1 Torr, 1.3 W cm^{-2}, 3 min, teflon target.

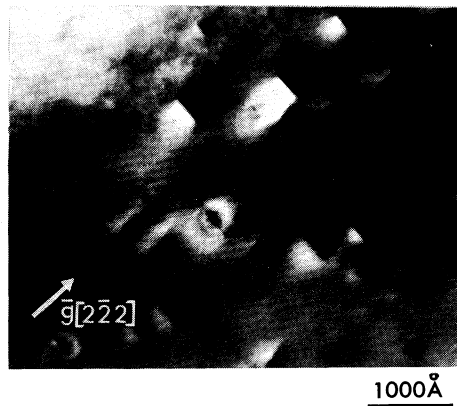

Fig. 4. TEM dark field image of (110) silicon film using (2$\bar{2}\bar{2}$) spot. RSE for 3 minute at 1 W cm^{-2}.

that the region containing these defects remains single crystal. Then, the damage structure in the extreme surface region was investigated by means of RHEED. The observation was carried out at a pressure of 10^{-6} Torr and with an accerating voltage of 200 kV. Samples were washed with HF solution and rinsed with H_2O after RSE. After this treatment, carbon contaminations on the surface was washed away, which was ascertaind by AES analysis.

Figures 5(a)–(d) show RHEED patterns of reactive-sputter-etched (110) silicon surface. Under RSE conditions where precipitates and surface roughness pattern were observed, polycrystalline silicon ring pattern and amor-

phous silicon halo pattern occurred, as shown in Fig. 5(a) and (b). Even under RSE conditions where no defects were observed by TEM, a small amount of polycrystalline silicon was formed, as shown in Fig. 5(c). The strongest polycrystalline silicon ring pattern occurred at 0.6 W cm^{-2}. Over 0.6 W cm^{-2}, the amorphous silicon halo pattern grew stronger and the polycrystalline ring pattern became weaker. The single crystal silicon rod pattern changed to a round, ring and halo pattern with increasing power density and etching duration, which indicates that the substrate surface became

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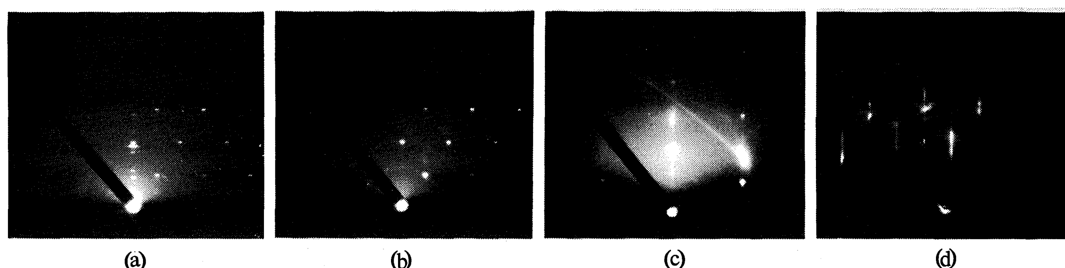

Fig. 5. RHEED patterns of reactive-sputter-etched (110) silicon wafers: (a) RSE for 3 minutes at 1 W cm^{-2}. (b) RSE for 3 minutes at 0.6 W cm^{-2}. (c) RSE for 3 minutes at 0.25 W cm^{-2}. (d) RSE for 3 minutes at 0.13 W cm^{-2}.

destroyed. In etching for 1 minute at 0.25 W· cm^{-2} or up to 5 minutes at 0.13 W cm^{-2}, no defects were observed.

3.2 *Gas-mixing effects on surface damage*

RSE is a technique to etch materials both by sputtering effects and by chemical effects. Then, Ar, C_2H_4 and O_2 gases were added to C_2F_6 in order to investigate the influence of the two effects on surface damage. Figures 6(a)–(d) show the dependence of surface damage on Ar ratio in the Ar+C_2F_6 mixed gas. The surface destraction enlarged with increasing the Ar ratio, that is, ring patterns appered in addition to the single crystal silicon (100) pattern in selected area electron diffraction. They correspond, as shown in Table II, to polycrystalline silicon and β-silicon carbide (zinc blende type). Polycrystallization of silicon substrate surface is enhanced with increasing Ar sputtering effects, while polycrystalline silicon was observed only by RHEED on the silicon surface etched with the pure C_2F_6. Therefore, the polycrystallization is thought to be taken place by ion bombardment effects. In the case of C_2F_6, the momentum given to the surface by CF_x^+ ions could be consumed in the chemical reaction. Accordingly, the ion bombardment

Table II. Spacing of lattice planes for polycrystalline Si and β-SiC in the experiment and ASTM card.

	ASTM card			Experiment		Error [%]
	d [A]	I/I$_0$	hkl	d [A]	Intensity	
Si	3.14	100	111	3.21	s[a]	+2.2
	1.92	60	220	2.02	w[b]	+5.2
	1.64	35	311	1.67	m[c]	+1.8
β-SiC	2.51	100	111	2.48	s	−1.2
	2.17	20	200	2.17	m	0.0
	1.54	63	220	1.48	w	−3.9
	1.31	50	311	1.34	w	+2.3

[a]Strong, [b]Weak, [c]Medium.

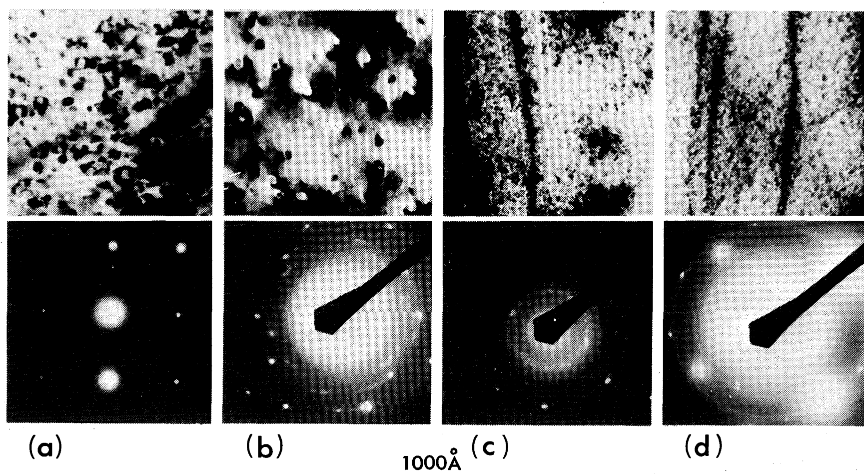

Fig. 6. TEM images and their selected area diffraction patterns of (100) silicon films using C_2F_6+Ar mixed gas. RSE for 5 minutes at 1 W cm^{-2}: (a) C_2F_6+Ar(0%). (b) C_2F_6+

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effects would be reduced comparing with the case of Ar ion etching. SF_6 gas is considered to have larger momentum than C_2F_6, because the ion species would be SF_y^+ which has a larger mass number than CF_x^+. The experimental result shown in Fig. 7 that the similar damage to Fig. 6(d) was observed on the substrate etched with SF_6 consists with the above explanation. Thus, the defects caused by RSE are found to be determined by the balance between the ion momentum and the chemical reactivity of ions.

Next, C_2H_4 and O_2, respectively, were added to C_2F_6 in order to increase the etching selectivity of SiO_2/Si and the etching rate of Si. In these cases, no gas-mixing effects on the defect could be observed either in the TEM images or in the selected area electron diffractions. This is explained as follows. When C_2H_4 is mixed with C_2F_6, chemical effects are reduced with decreasing free fluorine radicals. However, CF_x^+ would be still an attacked species on the substrates and the degree of defects would not be enlarged. When O_2 is mixed with C_2F_6, new fragment COF_x which has more momentum than CF_x^+ may be formed. In this case, since chemical effects would be also increased, the degree of defects would not be enlarged.

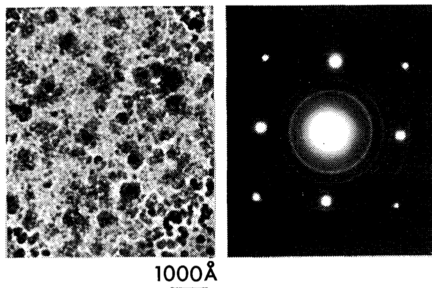

Fig. 7. TEM image and selected area diffraction pattern of (100) silicon film using SF_6 gas. RSE for 3 minutes at 1.3 W cm^{-2}.

3.3 *Defect enhancement by thermal oxidation*

OS check was carried out in order to investigate changes in the RSE-induced defects through device fabrication processes, especially thermal oxidation. Silicon wafers were reactive-sputter-etched under the conditions at which precipitates, surface roughness pattern, polycrystalline and amorphous silicon, and no defects were, respectively, formed. Then, they were oxidized at 1100°C for 2 hours in wet O_2. After oxide film was removed by the HF solution, the silicon surface was etched in a Wright etch solution for 1 minute. Figures 8(a) to (c) show oxidation induced stacking faults (OSF) and etch pits on the silicon surface. The relationship among OSF density, etch pit density and RSE conditions is shown in Table III. 10^5 cm^{-2} OSF were observed under the condi-

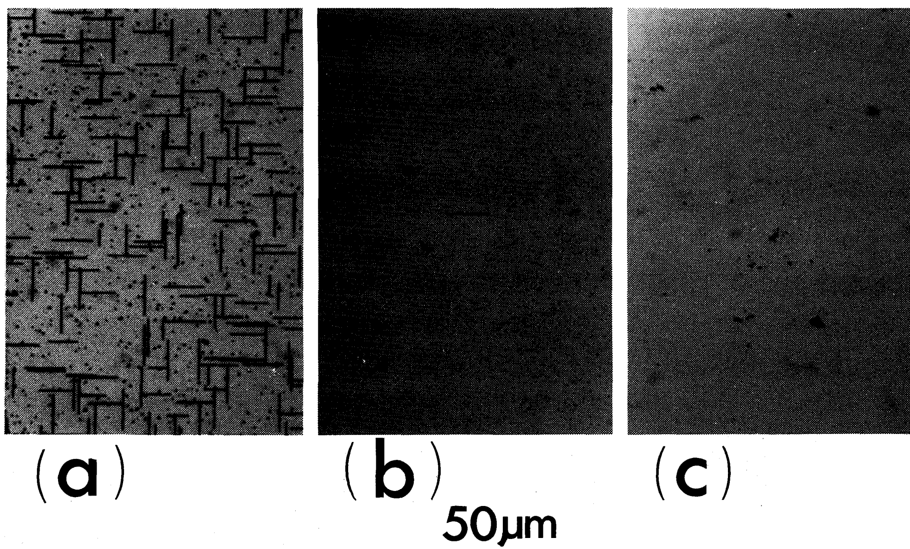

Fig. 8. Optical micrograph of (100) silicon wafers etched by Wright solution for 1 minute after thermal oxidation: (a) RSE for 3 minutes at 1 W cm^{-2}. (b) RSE for 3 minutes at

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