Removal of Post Etch/Ash Residue on an Aluminum Patterned Wafer Using Supercritical CO_2 Mixtures with Co-solvents and Surfactants: the Removal of Post Etch/Ash Residue on an Aluminum Patterned Wafer

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ABSTRACT

The supercritical CO_2 (sc-CO_2) mixture and the sc-CO_2-based Photoresist(PR) stripping(SCPS) process were applied to the removal of the post etch/ash PR residue on aluminum patterned wafers and the results were observed by scanning of electron microscope(SEM). In the case of MDII wafers, the carbonized PR was able to be effectively removed without pre-stripping by oxygen plasma ashing by using sc-CO_2 mixture containing the optimum formulated additives at the proper pressure and temperature, and the same result was also able to be obtained in the case of HDII wafer. It was found that the efficiency of SCPS of ion implanted wafer improved as the temperature of SCPS was high, so a very large amount of MEA in the sc-CO_2 mixture could be reduced if the temperature could be increased at condition that a process permits, and the ion implanted photoresist(IIP) on the wafer was able to be removed completely without pre-treatment of plasma ashing by using the only 1 step SCPS process. By using SCPS process, PR polymers formed on sidewalls of metal conductive layers such as aluminum films, titanium and titanium nitride films by dry etching and ashing processes were removed effectively with the minimization of the corrosion of the metal conductive layers.

Key Words : SCORR, sc-CO_2, Additive, Homogeneous and transparent phase, Etch, Ash, PR

1. Introduction

The research on the semiconductor wafer cleaning by using CO_2-based supercritical fluids started by Rubin et al. [1,2] of Los Alamos National Laboratory (LANL) in end of the 1990s. This technology called supercritical carbon dioxide resist removal (SCORR) was studied for the removal of hard-baked PR at the beginning [1]. Until now, various studies have been performed about the removal of PR on post-metal etch/ash wafer, ion implanted wafer, and so on [2,9]. the sc-CO_2-based PR stripping (SCPS) process, which is generally called a SCORR, was needed as a new technology to replace the the conventional water-based stripping process as described in the previous paper [10]. The previous paper is about the chemicals to be used in the SCPS process, and this study relates to the results of applying the cleaning solution to actual wafer cleaning.

The post-etch / ash residue on the aluminum patterned wafer was removed using sc-CO_2 mixture with co-solvent and surfactant under SCPS process conditions and investigated the results using scanning of electron microscope (SEM).

2. Experimental

2.1. Materials and analyses

Post aluminum etch/ash wafer was used as a test sample

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which was supplied by National Nanofab Center (NNFC) in Korea and others are described in the previous paper [10]. The five kinds of PR removers were prepared as shown in Table 1.

Table 1. Additives which were formulated by the recipe of mixing surfactant and co-solvents so as to make it possible to form HTP by mixing with sc-CO_2 at the temperature range from 40 to 80°C

Additive 1 : SMS50L - 7.1wt%, Ethanol - 10.4wt%, PFOA - 82.5wt%,
Additive 2 : MEA - 2.5wt%, 1M2P - 1.7wt%, Ethanol - 13.1wt%, PFOA - 82.7wt%,
Additive 3 : MEA - 4.9wt%, 1M2P - 1.2wt%, Ethanol - 9.5wt%, PFOA - 84.4wt%,
Additive 4 : SMS50L - 6.1wt%, Ethanol - 7.4wt%, RM 258 - 86.5wt%
Additive 5 : SMS50L - 7.1wt%, Ethanol - 10.4wt%, PFHA - 82.5wt%,

The PR removers in Table 2 are sc-CO_2 mixtures including the five kinds of additives in Table 1.

Table 2. PR removers which were formulated by mixing additive and sc-CO_2 to remove post etch/ash residues on aluminum patterned wafers while maintaining HTP at the temperature range from 40 to 80°C

PR remover 1.		
	Additive 1 in Table 1	: 13.6vol%
	sc-CO_2	: 86.4vol%
PR remover 2.		
	Additive 2 in Table 1	: 13.6vol%
	sc-CO_2	: 86.4vol%
PR remover 3.		
	Additive 3 in Table 1	: 18.2vol%
	sc-CO_2	: 81.8vol%
PR remover 4.		
	Additive 4 in Table 1	: 17.1vol% (12vol%)
	sc-CO_2	: 82.9vol% (88vol%)
PR remover 5.		
	Additive 5 in Table 1	: 13.6vol%
	sc-CO_2	: 86.4vol%

2.2. SCPS Process

This process system was largely classified into pressurizing process, stripping process, rinsing process, and drying process. The first two-part process are described in the previous paper [10]. In this study, there is provided a cleaning process comprising : loading a wafer piece (1.0cm×2.7cm) in a high pressure cleaner (28㎖); injecting CO_2 (greater than 99.99%) having lower pressure than supercritical cleaning pressure into the high pressure cleaner; cleaning the wafer by injecting a supercritical homogeneous transparent phase mixture in which a cleaning additive and supercritical CO_2 are mixed, into the high pressure cleaner under a supercritical cleaning pressure; rinsing the wafer by injecting a supercritical rinsing mixture in which a rinsing additive and supercritical CO_2 are mixed, into the high pressure cleaner; and separating CO_2 from a mixture discharged from the high pressure cleaner.

The supercritical cleaning pressure is 130 to 300 bar, and the injecting of CO_2 having lower pressure than supercritical cleaning pressure into the high pressure cleaner comprises injecting CO_2 having pressure lower than the supercritical cleaning pressure by 10 to 50 bar into the high pressure cleaner.

The supercritical HTP mixture in which the cleaning additive and the supercritical CO_2 are mixed may be formed using a mixing effect by a large pressure difference between CO_2 having higher pressure than the supercritical cleaning pressure and the cleaning additive having atmospheric pressure or low pressure less than 10 bar.

The supercritical HTP mixture may be formed using a mixing effect by a large pressure difference by injecting CO_2 having higher pressure than the supercritical cleaning pressure into the cleaning additive having low pressure.

After the rising of the wafer piece by using a supercritical rinsing mixture by mixing the rinsing additive and the supercritical CO_2, the wafer piece was rinsed the wafer using supercritical CO_2.

After discharging CO_2 completely from the high pressure cleaner, the cleaned wafer piece was unloaded and the surface of the wafer piece was examined by SEM.

3. Results and discussion

3.1. The removal of post etch/ash residues on aluminum patterned wafers

The goal of this experiment is to remove the dense and carbonized PR, known as the crust, on the MDII wafer. The MDII wafers were made by Arsenic ion implantation at a dosage of $5E^{13}$ atoms/cm^2 at 60 keV. Actually, it has been known it is difficult to remove the ion implanted PR in semiconductor manufacturing Fab., so two step processes were needed for removing it.

At the first step, most of the PR is pre-stripped by oxygen plasma ashing, but the popped PR residue still remains. At the second step, the popped PR residue is removed completely by post wet-stripping. It still had the limit to penetrate the wet chemicals with DIW(de-ionized water) into the very fine structure, and the dielectric material on wafers can be damaged during plasma ashing [5,7,8]. Therefore, the sc-CO_2 based PR stripping(SCPS) technology is applied as non-ashing method which is desirable at 65nm technology and below. Two kinds of wafers were used for the experiment of SCPS, the one was pre-stripped by plasma ashing, the other was not pre-stripped. In this experiment, it was found that 1 step stripping process, by using sc-CO_2 mixture, could be effectively removed the IIP. Table 3 shows the experimental conditions for SCPS of the MDII wafers. The process of SCPS was carried out continuously from pressurizing step to vent step according to the whole procedure presented in Table 2. The Exp.1 in Table 2 is the experimental condition for SCPS of pre-stripped MDII wafer by plasma ashing, and the other is the experimental conditions for SCPS of the MDII wafer without pre-treatment of plasma ashing.

Fig. 1 shows the reference SEM images of pre-stripped MDII wafer by plasma ashing before SCPS. The state of contaminated surface on wafer can be seen by the top view of the SEM images. The popped PR residue still remained on the wafer even after plasma ashing process, as shown in Fig. 1.

Fig. 2. shows the result of SCPS of pre-stripped MDII wafer shown in Fig. 1 at the condition of Exp. 1 in Table 2. The popped PR residue existed on the wafer was removed after SCPS, as shown in Fig. 5.

From Exp. 1, it was found that the small amount of 3.6 vol% additive in sc-CO_2 mixture was enough for removing the popped PR residue on pre-stripped MDII wafer.

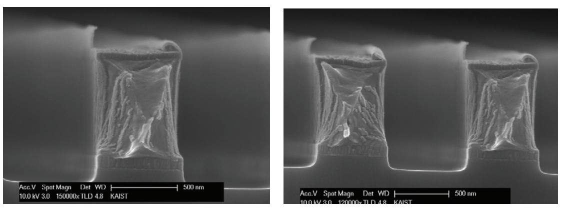

Fig. 1. Reference SEM images of post aluminum etch/ash wafer.

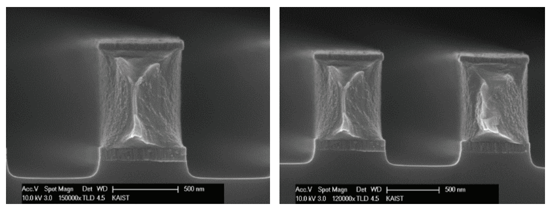

Fig. 2. The result of SCPS at the condition of Exp.1 in Table 2.

Table 3. The experimental conditions for SCPS of post aluminum etch/ash wafer

<table>
<tr><th>Exp.</th><th colspan="2">Stripping Condition</th><th>Additive formulation</th><th>The composition of additive in sc-CO_2 mixture (vol%)</th></tr>
<tr><td>1</td><td colspan="2">49°C, 153bar, 3min</td><td>Additive 1 in Table 1</td><td>3.6%</td></tr>
<tr><td>2</td><td colspan="2">52°C, 152bar, 3min</td><td>Additive 2 in Table 1</td><td>3.6%</td></tr>
<tr><td colspan="5">Whole Procedure : Preheating →Pressurizing→Stripping→Rinsing flow 1 (sc-CO_2+Ethanol)
→Rinsing flow 2 (sc-CO_2)→Vent (sc-CO_2 →gas-CO_2→atmosphere)</td></tr>
<tr><td colspan="2"></td><td colspan="2">Exp.1</td><td>Exp.2</td></tr>
<tr><td colspan="2">Preheating</td><td colspan="2">Reactor to 49°C</td><td>Reactor to 52°C</td></tr>
<tr><td colspan="2">Pressurizing</td><td colspan="2">Reactor to 115bar,
Line mixer to 165bar</td><td>Reactor to 120bar,
Line mixer to 157bar</td></tr>
<tr><td colspan="2">Stripping
(3min)</td><td colspan="2">49°C, 153bar,
static stirrer mixing</td><td>52°C, 152bar,
static stirrer mixing</td></tr>
<tr><td colspan="2">Rinsing flow 1
(2min)</td><td colspan="2">sc-CO_2(200cc/min),
Ethanol(30cc/min),
pressure variation(160~180bar) at 40°C</td><td>sc-CO_2(200cc/min),
Ethanol(40cc/min),
pressure variation(160~175bar) at 40°C</td></tr>
<tr><td colspan="2">Rinsing flow 2
(2min)</td><td colspan="2">sc-CO_2(300cc/min),
pressure variation(160~180bar) at 40°C</td><td>sc-CO_2(300cc/min),
pressure variation(160~175bar) at 40°C</td></tr>
<tr><td colspan="2">Vent(2min)</td><td colspan="2">temperature variation(34~41°C)</td><td>temperature variation(39~41°C)</td></tr>
</table>

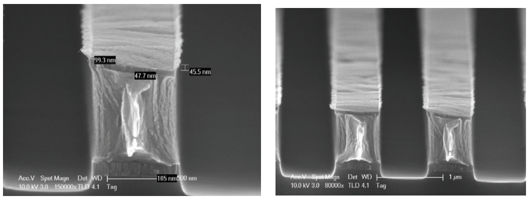

Fig. 3. The result of SCPS at the condition of Exp.1 in Table 2.

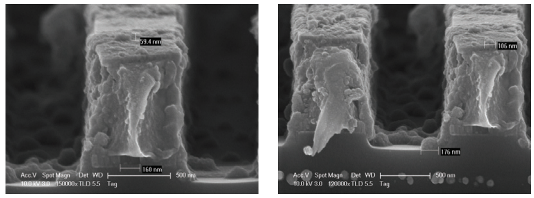

Fig. 4. The result of SCPS at the condition of Exp.2 in Table 2.

Table 4. The experimental condition for SCPS of the HDII wafer

Exp.	Stripping Condition	Additive formulation	The composition of additive in sc-CO_2 mixture(vol%)
3	62°C, 217bar, 3min	Additive 2 in Table 1	13.6%
4	52°C, 147bar, 3min	Additive 3 in Table 1	18.2%
5	63°C, 197bar, 3min	Additive 3 in Table 1	3.6%
Whole Procedure : Preheating →Pressurizing→Stripping→Rinsing flow 1(sc-CO_2+Ethanol) →Rinsing flow 2(sc-CO_2)→Vent(sc-CO_2 →gas-CO_2→atmosphere)			

	Exp.3	Exp.4	Exp.5
Preheating	Reactor to 62°C	Reactor to 52°C	Reactor to 63°C
Pressurizing	Reactor to 180bar, Line mixer to 230bar	Reactor to 120bar, Line mixer to 150bar	Reactor to 180bar, Line mixer to 205bar
Stripping (3min)	62°C, 217bar, static stirrer mixing	52°C, 147bar, static stirrer mixing	63°C, 197bar, static stirrer mixing
Rinsing flow 1 (2min)	sc-CO_2(200cc/min), Ethanol(40cc/min), pressure variation(178~198bar) at 45°C	sc-CO_2(200cc/min), Ethanol(40cc/min), pressure variation(132~146bar) at 38°C	sc-CO_2(200cc/min), Ethanol(40cc/min), pressure variation(170~190bar) at 43°C
Rinsing flow 2 (2min)	sc-CO_2(300cc/min), pressure variation(181~204bar) at 45°C	sc-CO_2(300cc/min), pressure variation(138~148bar) at 38°C	sc-CO_2(300cc/min), pressure variation(177~200bar) at 41°C
Vent(2min)	temperature variation(52~62°C)	temperature variation(35~38°C)	temperature variation(43~45°C)

Fig. 3 shows the reference SEM images of the MDII wafer without pre-treatment of plasma ashing before SCPS. The state of contaminated surface on wafer can be seen by the top view and vertical view of the SEM images. The opaque white dots on wafer are IIP.

Fig. 4. shows the result of SCPS of MDII wafer without pre-treatment of plasma ashing at the condition of Exp.2 in Table 3. The opaque white dots which were considered as the IIP on the wafer were removed as shown by the top view of the SEM images in Fig. 7.

From Exp.2, it was found that the same small amount of additive in sc-CO_2 mixture as that of Exp.1 was needed for removing the ion implanted carbonized PR on wafer, although plasma ashing was not performed on the IIP on the MDII wafer before SCPS, and the IIP was able to be removed completely even without pre-treatment of plasma ashing by using the SCPS process of only 1 step.

3.2 The removal of the PR on the high dose ion implanted (HDII) wafer

Generally, the HDII wafers have the dosage levels of greater than 1E15 atoms/cm^2, and less than 100 keV implant energy [3].

The HDII wafer used in this experiment was made by Arsenic ion implantation at a dosage of 5E15 atoms/cm^2(high dose) at 60 keV. It was known that the removal of the high dose IIP is more difficult than that of the medium dose IIP.

The experimental condition was presented in Table 4.

The process of SCPS was carried out continuously from pressurizing step to vent step, similarly to the case of the

MDII wafers.

Fig. 5 shows the reference SEM images of the HDII wafer without pre-treatment of plasma ashing before SCPS. The opaque white dots on the HDII wafer is considered as the high dose IIP like the MDII wafer reviewed in the above statement. The more opaque white dots on the HDII wafer than them on the MDII wafer can be seen in Fig. 5.

Fig.6 shows the result of SCPS of HDII wafer without pre-treatment of plasma ashing at the condition of Exp.3 in Table 4. The high dose IIP with opaque white dots existed on the wafer was removed as shown in Fig.6.

The efficiency of SCPS increase with the amount of cleaning additive in PR Removers, the amount of MEA in cleaning additive and the temperature of SCPS.

Although the temperature and pressure of SCPS were high(62°C, 217bar), the large portion(13.6vol%) of cleaning additive in PR Remover 2 was needed to remove the IIP on the HDII wafer perfectly because the amount of MEA in cleaning additive was small.

In the case of Exp.4 presented in Table 4, the temperature and pressure were 52°C and 147bar respectively, and the amount of MEA in PR Remover 3 was increased to about twice.

Fig.7 shows the good result of SCPS about Exp.4, but the amount of cleaning additive in the PR Remover 3 was increased to 18.2vol%, which is larger than that of Exp.3 because temperature is lower than that of Exp.3.

In the case of Exp.5, the PR Remover 3 was used like the case of Exp.4, but the temperature and pressure were increased to 63°C, 197bar respectively.

Fig.8 shows also the good result of SCPS like the result of Exp.5. In this case, the amount of cleaning additive in PR Remover 3 could be decreased to 3.6 vol% owing to the effect of temperature, it is considered that the stripping effect improves as the temperature increase.

From Exp.3, Exp.4 and Exp.5, it was found that the efficiency of SCPS of HDII wafer improved as the temperature of SCPS was high, so a very large amount of MEA in the PR Removers could be reduced if the temperature could be increased at condition that a process permits, and the high dose IIP on the HDII wafer was also able to be removed completely without pre-treatment of plasma ashing by using the only 1 step SCPS process, just as the SCPS result of MDII wafer.

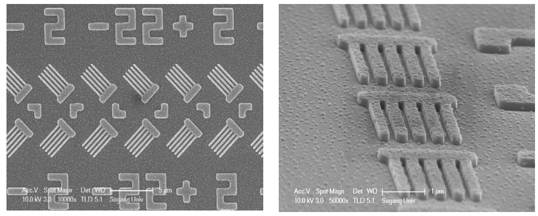

Fig. 5. Reference SEM images of the HDII wafer without pre-treatment of plasma ashing (before SCPS).

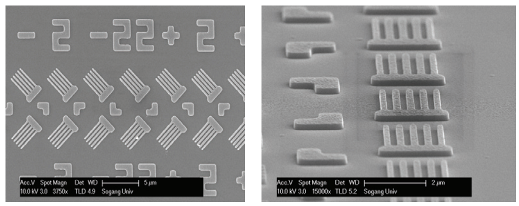

Fig. 6. The result of SCPS of HDII wafer without pre-treatment of plasma ashing at the condition of Exp.3 in Table 4.

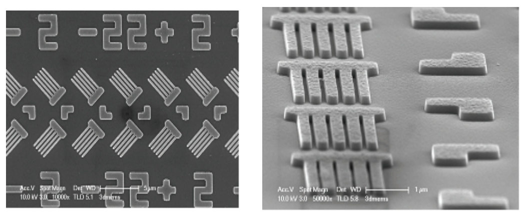

Fig. 7. The result of SCPS of HDII wafer without pre-treatment of plasma ashing at the condition of Exp.4 in Table 4.

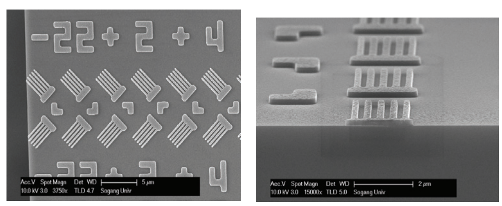

Fig. 8. The result of SCPS of HDII wafer without pre-treatment of plasma ashing at the condition of Exp.5 in Table 4.

4. Conclusions

In this study, the different additives in sc-CO_2 were formulated and used for removing IIP, and the relation between the effect and the formulation of additives in sc-CO_2 mixture on the removal of IIP was investigated. The following results were obtained by visual observation of the state of sc-CO_2 mixture and measuring the cloud points of it and the fine structure on the wafers after formulating the additive and removing the IIP on the ion implanted wafers by using sc-CO_2 mixture containing it.

Although the volume ratio between additive and sc-CO_2 in sc-CO_2 mixture varied, the cloud points of the sc-CO_2 mixture with it were almost same. The appropriate stripping pressure for the effective removal of the PR residue on the wafer while maintaining HTP was approximately 0.5Mpa larger than that of the cloud point measured at the stripping temperature from 40 to 80^oC. In the case of MDII wafers, the carbonized PR was able to be effectively removed without pre-stripping by oxygen plasma ashing by using sc-CO_2 mixture containing the optimum formulated additives at the proper pressure and temperature described above, and the same result was also able to be obtained in the case of HDII wafer.

It was found that the efficiency of SCPS of ion implanted wafer improved as the temperature of SCPS was high, so a very large amount of MEA in the sc-CO_2 mixture could be reduced if the temperature could be increased at condition that a process permits, and the IIP on the ion implanted wafer was able to be removed completely without pre-treatment of plasma ashing by using the only 1 step SCPS process.

By using SCPS, PR polymers formed on sidewalls of metal conductive layers such as aluminum films, titanium and titanium nitride films by dry etching and ashing processes were removed effectively with the minimization of the corrosion of the metal conductive layers.

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