

Dissolution of copper and copper oxide in aqueous solution containing amine or carboxylic acid

Cheon Kwang Ko* and Won Gyu Lee**,*†

*Gangwon Institute for Regional Program Evaluation, 1, Kangwondaehak-gil, Chuncheon, Gangwon 24341, Korea

**Division of Chemical Engineering and Bioengineering, Kangwon National University,
1, Kangwondaehak-gil, Chuncheon, Gangwon 24341, Korea

(Received 10 February 2022 • Revised 27 April 2022 • Accepted 6 June 2022)

Abstract—Using a component having an amine group ($-NH_2$) or a carboxyl group ($-COOH$) for a cleaning solution, the etching rates of copper oxide and copper were analyzed by measuring the solubility of copper to evaluate the etch residue removal properties. Based on this, it was attempted to establish the basis of a cleaning process for removing etch residues in the copper back end of line (BEOL) process. In addition, the etch rate and surface structure change of fluorine-doped fluorosilicate glass (FSG), Black Diamond (BD), and methyl group-doped organosilicate glass (OSG), which are low-k dielectric materials, were analyzed. The copper oxide etching rate of the component having an amine group showed a tendency to increase as the basicity of the solution increased. Also, the solubility of copper oxide in the amine solution decreased with the increase of the carbon length in the amine molecular structure. The solution having a carboxyl group compared to the amine group has a high etching rate for the low-k dielectric material. The amine component showed reactivity only in the basic region and, on the contrary, the carboxyl group component is reactive only in the acidic region.

Keywords: Cleaning Solution, Post Etch Residue, Amine, Carboxylic Acid, Copper Interconnection

INTRODUCTION

As the degree of integration of semiconductor devices increases, a multilayer interconnection structure using a low-resistance Cu/low-k dielectric material has been introduced to cope with high current density and fast response speed. The semiconductor Back End of Line (BEOL) process, represented by Cu dual damascene, consists of a series of steps that repeatedly perform patterning and deposition to form interconnection [1]. For patterning of low-k dielectric forming an interlayer insulating film, fluorine carbon gas (CF_4 , C_4F_8 , CHF_3 , etc.) is mixed with Ar, N_2 , or O_2 to form an interconnection structure through anisotropic etching in a plasma state. Electrical properties required for low-k dielectric materials include a low dielectric constant (k) of 3.0 or less, low leakage current (about 10^{-8} A/cm²), high breakdown voltage (>2 MV/cm²), high crack resistance, excellent adhesion to heterogeneous thin films, strong resistance to heat cycling, high thermal conductivity, small surface roughness, and excellent mechanical strength are required [2-4]. In the dual damascene structure, after dielectric etching processes, photoresist residues and etching residues such as copper oxide are formed on the sidewalls and surfaces of the pattern [5,6].

The main contaminants to be removed after etching in the BEOL process are photoresist deteriorated/cured by the etching process, organic compounds remaining by hybrid polymerization of etching gas and photoresist residues, and metal-organic polymers con-

taining nonvolatile CuO_x and metal halides [7]. These etch residues consist of high molecular weight organic materials, inorganic materials such as copper oxide or copper fluoride, and materials containing Si from the interlayer insulating film [5]. In general, residues are removed through a wet cleaning process. Recently, research on the cleaning process using O_3 has been actively conducted. Ozone water has strong oxidizing power, so it is expected to replace hydrogen peroxide in the RCA cleaning process. This ozone can be mixed with various acidic substances to remove organic and metal contaminants as well as particles [8-10].

In addition, a semi-aqueous fluoride (SFA) solution has been proposed as a wet cleaning agent, and the SFA cleaning solution consists of water, an organic solvent, fluoride, and a corrosion inhibitor [11,12]. Although these cleaners effectively remove etch residues, they have disadvantages in that they affect the structural change of low-k dielectric materials, reduction of critical dimension (CD) of interconnection, corrosion of metal layers, and dielectric constant of interlayer insulating layers. To overcome the problems that occur when removing the etch residue, a material having an amine group and a carboxyl group that forms a chelate with copper oxide among the etch residue components is applied as a major additive to the cleaning solution [13,14].

In this study, using a component having an amine group ($-NH_2$) and a carboxyl group ($-COOH$) as a cleaning solution component, the etching rates of copper oxide and copper were analyzed by measuring the solubility of copper ions to evaluate the etch residue removal characteristics. The suitability was analyzed by measuring the rate of change of the roughness caused by the contact of the cleaning solution component with the copper surface. To investigate the

†To whom correspondence should be addressed.

E-mail: wglee@kangwon.ac.kr

Copyright by The Korean Institute of Chemical Engineers.

Table 1. List of amines and carboxylic acids used in this study

Chemicals	
Amines	mono-ethanol amine (MEA), di-ethanol amine (DEA) tri-ethanol amine (TEA), ethylene diamine (EDA) methyl amine (MA), ethyl amine (EA), propyl amine (PA)
Carboxylic acids	formic acid (FA), acetic acid (AA), propionic acid (PAC) oxalic acid (OA), malonic acid (MAC), succinic acid (SA) lactic acid (LA), tartaric acid (TA), citric acid (CA)

effect of each component on the low-k dielectric material, physical and chemical analyses were evaluated using the etch rate and FT-IR. For the characteristics of the cleaning solution, the etching rate of residue, the compatibility with a copper surface, and the physical and chemical compatibility with low-k dielectric materials were analyzed for the etch residues generated in the Cu BEOL process. It was attempted to establish the basis of a cleaning process for removing etch residues in the Cu BEOL process including components having an amine group and a carboxyl group.

EXPERIMENTAL

The cleaning solution for removing the etching residue is composed of a component for removing organic matter, a component for removing metal impurities, a component for suppressing corrosion of the metal surface, a component for adjusting the pH of the cleaning solution, and ultrapure water. To evaluate the removal characteristics of etching residues and compatibility with Cu/low-k-based process materials, a single component was prepared at 10 wt%, and the pH was adjusted from 2 to 12 using HClO_4 and KOH. Table 1 shows the amines and carboxylic acids used as single components.

Using an electrolytic plating method, a copper thin film deposited on a Si wafer to a thickness of 500 nm was used as a substrate for evaluating the copper etching rate and surface compatibility of a single component. After washing with acetone for 30 seconds, rinsing with ultrapure water for 30 seconds, and drying with nitrogen gas, it was used to evaluate the roughness of the copper surface. To evaluate the etching characteristics of copper oxide, it was oxidized at 300 °C for 10 minutes to form a copper oxide film with a thickness of 200 nm.

To measure the etch rate of a single-component low-k dielectric material, fluorine-doped FSG (fluorosilicate glass), BD (Black Diamond™), and methyl group-doped OSG (organosilicate glass) were provided and used with the help of a Korean semiconductor device maker. The thickness of the FSG, BD, and OSG is 790 nm, 540 nm, and 740 nm, respectively.

Solubility was measured using an inductively coupled plasma spectrometer (ICP, OPTIMA 7300DV, Perkin Elmer) to analyze the etching characteristics of the etching residues of the cleaning components. Copper surface properties were analyzed using atomic force microscopy (AFM, NanoScope Multimode, Digital Instruments). To analyze the effect of the cleaning solution on the low-k dielectric, the thickness of the low-k thin film before and after the cleaning was measured at a 70° angle using a spectroscopic ellipsometer (Nano View, SE MG1000-V). In addition, Fourier trans-

form infrared spectrometry (FT-IR, ABB, FTLA 2000) was used to evaluate the chemical change of the low-k thin film surface.

RESULTS AND DISCUSSION

1. Evaluation of Copper Cleaning Suitability of Amines and Carboxylic Acids

According to the solution treatment, the change and rate of change in the roughness of the copper surface were calculated using Eqs. (1) and (2) below.

$$\begin{aligned} \text{Change in surface roughness } (\Delta\text{RMS}) \\ = \text{Surface roughness after solution treatment} \\ - \text{Surface roughness of standard sample} \end{aligned} \quad (1)$$

$$\begin{aligned} \text{Surface roughness change rate } (\%) \\ = \Delta\text{RMS} / \text{Surface roughness of standard sample} \end{aligned} \quad (2)$$

First, the change in the roughness of the copper surface treated

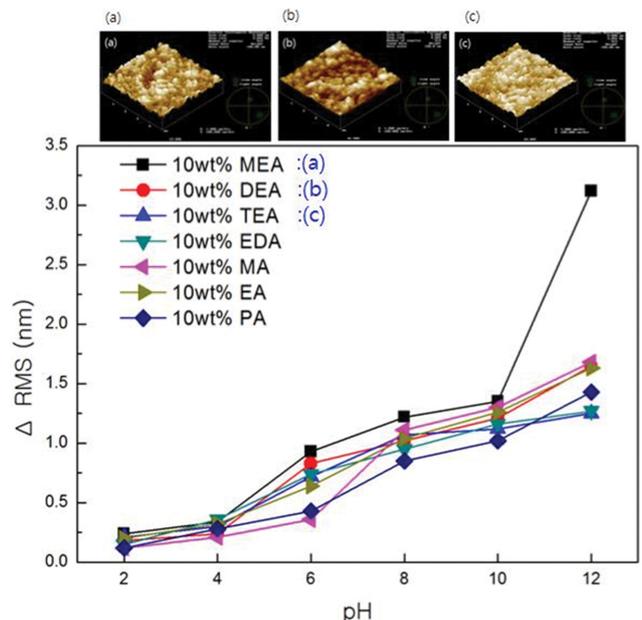


Fig. 1. Changes in copper surface roughness and surface morphology according to pH variation in 10 wt% amine solutions, which was measured at 25 °C for 1 minute. The AFM results on the graph show the surface shape after surface treatment with (a) mono-ethanol amine (MEA), (b) di-ethanol amine (DEA), and (c) tri-ethanol amine (TEA).

with a solution containing an amine component was measured and shown in Fig. 1. A copper thin film having an initial surface roughness of 13.849 nm was used. As shown in Table 1, each 10 wt% aqueous solution was prepared as a single amine component, and the pH of each solution was adjusted from 2 to 12 using HClO_4 and KOH . The surface roughness was a condition of maintaining 10 ml of each solution at 25 °C. and supporting copper oxide for 1 minute. HClO_4 and KOH used to adjust the pH of the solution have an etching rate of copper and copper oxides of 0.1 Å/min or less and do not affect the etching evaluation of the copper and copper oxides of the solution used in this study [15].

When treated with 10 wt% MEA solution at pH 12, the change in surface roughness was 3.1 nm, and the rate of change of surface roughness was 22.5%, showing a relatively large change. Copper treated with MEA, DEA, MA, EA, and PA solutions at pH 12 showed a surface change rate of over 10%. The AFM result of the MEA solution with a copper etching rate of 4.8 Å/min at pH 12 shows that a specific region is intensively etched rather than uniformly etched on the copper surface. It is shown that ΔRMS according to the treatment of the copper surface with an amine solution increases with pH. There is a report that copper oxide is removed from a solution containing an amine component through complex formation with copper ions [16,17]. The MEA, DEA, and TEA solutions exhibited copper oxide etching rates of 50, 31, and 25 Å/min at pH 12, and the MA, EA, and PA solutions exhibited 48, 35, and 33 Å/min at pH 12. The amine solution shows an increase of etch rate for copper oxide as the pH increases. The selectivity of copper oxide was calculated from Eq. (3) using the etching rate of copper oxide and the etching rate of copper.

$$\begin{aligned} &\text{Selectivity of copper oxide} \\ &= \text{Etching rate of copper oxide} / \text{Etching rate of copper} \end{aligned} \quad (3)$$

The MEA, DEA, and TEA solutions exhibited copper etching rates of 4.6, 3.4, and 2.8 Å/min at pH 12, and copper oxide selec-

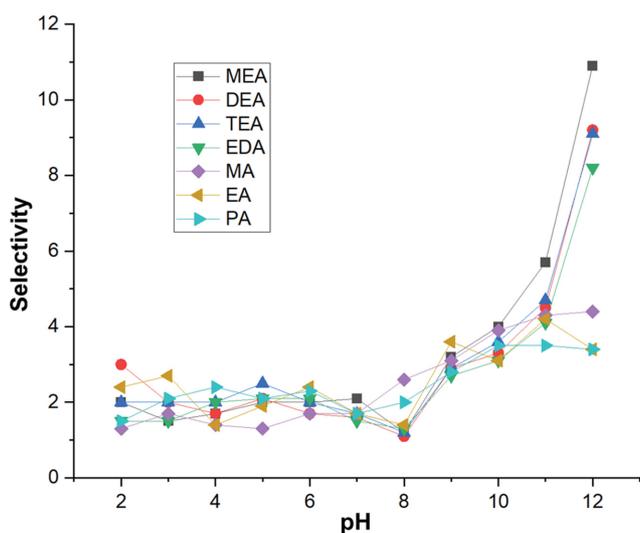


Fig. 2. Comparison of calculated selectivity (copper etch rate/copper oxide etch rate) according to pH variation in 10 wt% amine solutions. The etch rate was measured at 25 °C for 10 minutes.

tivity of 10.9, 9.2, and 9.1. It was reported that the Cu complex is formed in the form [18] and that EDA forms a Cu complex in the form of CuEn^{2+} and EuEn_2^{2+} [19,20]. The MA, EA, and PA solutions at pH 12 exhibited a copper etch rate of 11.1, 10.3, and 9.8 Å/min, and the selectivity of 4.4, 3.4, and 3.4, respectively. The etching rate of copper oxide does not show a significant change according to the number of amine groups, but it is affected by the nitrogen-substituted component of the amine group and the length of the carbon chain. As the pH increased in all amine solutions, the selectivity of copper oxide increased significantly with the increase of the etch rate. There was almost no change in selectivity up to pH 8, but a linear increase in the pH range above that was shown in Fig. 2.

Fig. 3 shows the change in copper surface roughness caused by the carboxylic acid solution shown in Table 1. The copper thin film sample used had a surface roughness of 11.403 nm. The change in surface roughness was 1.57 nm at pH 4 with a MAC solution of 10 wt% at pH 4, and the change rate was the largest at 13.7%. 10 wt% of PAC showed more than 10% change in surface roughness in the range of lower than pH 7. The OA, LA, and CA solutions exhibited 0.82, 0.87, and 0.82 nm changes in surface roughness at pH 2, and showed the surface roughness change rate of 7.2, 7.6, and 5.3%, respectively. The carboxyl group effectively formed a complex with copper ions [21,22]. The solution with 10 wt% carboxylic acid was adjusted to pH from 2 to 12 using HClO_4 and KOH . Among them, the pH was adjusted by preparing 5 wt% of SA. 10 ml of each solution was maintained at 25 °C, and the Si wafer with the copper oxide film on the surface was dipped for 1 minute. Fig. 4 shows the selectivity using the measured copper oxide and copper etch rates. In terms of selectivity, CA and AA, which have rela-

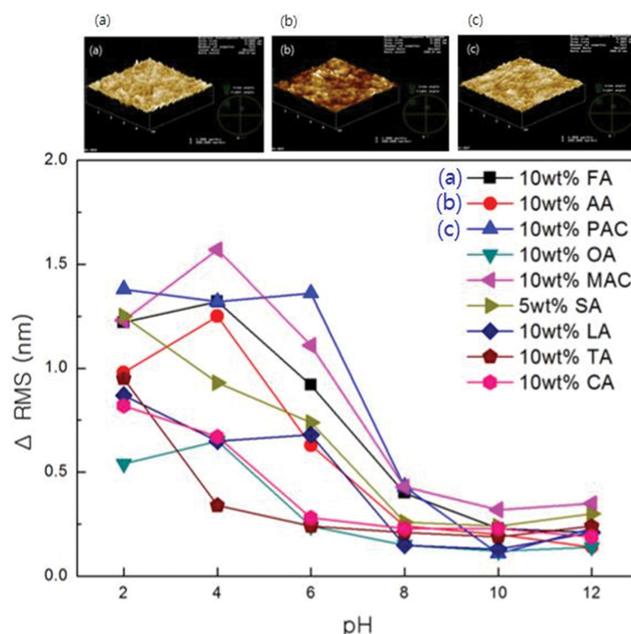


Fig. 3. Changes in copper surface roughness and surface morphology according to pH variation in 10 wt% carboxylic acid solutions (cf. 5 wt% succinic acid), which was measured at 25 °C for 1 minute. The AFM results on the graph show the surface shape after surface treatment with (a) formic acid (FA), (b) acetic acid (AA), and (c) propionic acid (PAC).

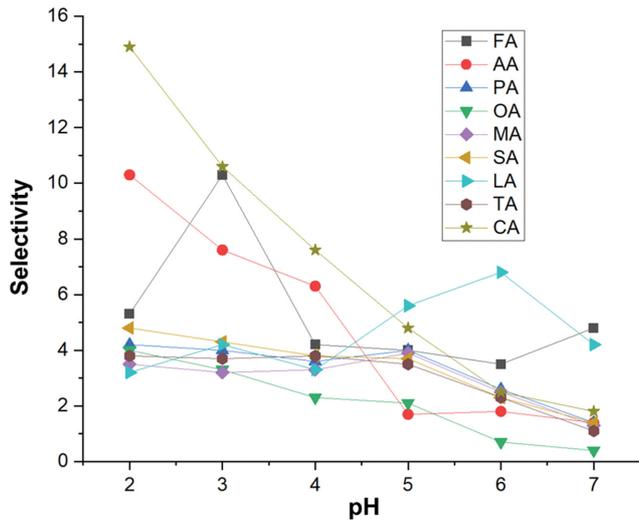


Fig. 4. Comparison of calculated selectivity (copper etch rate/copper oxide etch rate) according to pH variation in 10 wt% carboxylic acid solutions (cf. 5 wt% succinic acid). The etch rate was measured at 25 °C for 1 minute.

tively high copper oxide etching rates, showed results of 14.9 and 10.3 at pH 2. LA, which had the highest copper oxide etching rate, also exhibited a selectivity of 3.2 because the copper etching rate was also high. In the case of CA, the maximum value changes

depending on the pH, and since it contains three carboxyl groups, it is interpreted that the complex form with copper ions changes whenever one hydrogen atom is lost. That is, it forms a complex with copper ions in the form of $-\text{COO}^-$, $-\text{COO}^{2-}$, $-\text{COO}^{3-}$ [23,24].

As dicarboxylic acid components, OA and MAC of 10 wt% are 1.11 M, 0.96 M, and an etching rate of 32.1 and 15.8 Å/min at pH 2 is shown so that a shorter carbon length is advantageous for copper oxide removal. However, at pH 2, 10 wt% MAC and 5 wt% SA showed 0.96 M and 0.42 M, respectively, and it can be confirmed that the carbon length does not affect the removal of the etch residue like the monocarboxylic group above. The etching rates of LA and TA having carboxyl and ethanol groups were measured, and the etching rates of CA having three carboxyl groups were measured for copper oxide. As can be seen from the results, the etching rate of carboxylic acid for copper oxide was 10 Å/min up to pH 5, and it was found that there was almost no removing power for copper oxide in neutral and basic regions. OA and TA having a carboxyl group and an ethanol group exhibit an etching rate of 8 Å/min at pH 3 and 5.2 Å/min at pH 2. CA having three carboxyl groups exhibits an etching rate of 2.8 Å/min at pH 3, and it is the most stable against copper etching together with PAC.

2. Compatibility Evaluation with Low-k Dielectric Materials

To evaluate the suitability of the Cu/low-k dielectric-based BEOL process of components having an amine group and a carboxyl group, the etching rates of FSG, OSG, and BD, which are low-k dielectric materials, were measured and listed in Table 2. To evaluate the

Table 2. Etch rate (Å/min) of low-k dielectric materials (OSG, FSG, BD) according to pH in amine solutions of 10 wt%, which was measured at 25 °C for 10 minutes

		Etch rate (Å/min)										
		pH 2	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10	pH 11	pH 12
MEA	OSG	0	0	0	0	0	0	0	0	0	0	0.18
	FSG	0	0	0	0	0	0	0.7	0.6	1.23	1.11	1.39
	BD	0	0	0	0	0	0	0	0	0	0	0
DEA	OSG	0	0	0	0	0	0	0	0	0	0	0
	FSG	0	0	0	0	0	0	0	0.45	1.42	1.37	1.62
	BD	0	0	0	0	0	0	0	0	0.24	0	0.27
TEA	OSG	0	0	0	0	0	0	0	0	0	0	0
	FSG	0	0	0	0	0	0	0	0.23	0.71	1.47	1.32
	BD	0	0	0	0	0	0	0	0	0.19	0.21	0.2
EDA	OSG	0	0	0	0	0	0	0	0.24	0.27	0.23	0.19
	FSG	0	0	0	0	0	0	0	0.34	0.67	1.91	1.79
	BD	0	0	0	0	0	0	0	0.31	0.87	1.48	1.31
MA	OSG	0	0	0	0	0	0	0	0	0	0	0.24
	FSG	0	0	0	0	0	0	0	0	0	0.97	1.12
	BD	0	0	0	0	0	0	0	0.24	0.61	0.77	1.1
EA	OSG	0	0	0	0	0	0	0	0	0	0	0
	FSG	0	0	0	0	0	0	0	0.31	0.75	0.95	1.32
	BD	0	0	0	0	0	0	0	0	0.23	0	0.42
PA	OSG	0	0	0	0	0	0	0	0	0	0	0
	FSG	0	0	0	0	0	0	0.37	0.62	1.99	1.62	1.48
	BD	0	0	0	0	0	0	0	0	0.19	0.21	0.71

suitability for the single-wafer tool process, each low-k dielectric material was surface-treated with a 10 wt% solution of amines and carboxylic acids listed in Table 1 at 25 °C for 10 minutes.

The etching rate of the low-k dielectric material of the MEA solution was 1.39 Å/min for FSG and 0.18 Å/min for OSG at pH 12. BD had no thickness change due to the MEA solution. No change in OSG thickness was observed at pH 11 or lower, no thickness change was observed in FSG at pH 7 or lower, and BD was not etched by MEA. The DEA solution exhibited an FSG etching rate of 1.62 Å/min at pH 12 and no thickness change due to etching at pH 8 or less. BD showed etching rates of 0.24 and 0.27 Å/min at pH 10 and 12, and no change in thickness was observed at other pHs. In addition, in the case of OSG, there was no change in thickness over the entire pH range. The etching rate of FSG was observed from 1.47 Å/min to 0.23 Å/min in the TEA solution in which three ethanol groups were substituted for the nitrogen of the amine group. In the case of BD, the etching rate changed from 0.19 Å/min to 0.21 Å/min, but in the case of OSG, there was no change in thickness.

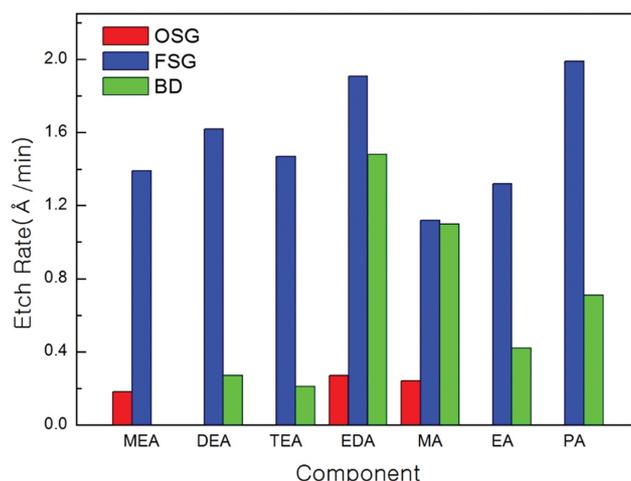


Fig. 5. Maximum etch rates, measured at 25 °C for 10 minutes, of low-k dielectric materials (OSG, FGS, BD) treated in various 10 wt% amine solutions, which were chosen over all pH ranges.

Table 3. Etch rate (Å/min) of low-k dielectric materials (OSG, FSG, BD) according to pH in carboxylic acid solutions of 10 wt% (in the case of succinic acid, 5 wt%), which was measured at 25 °C for 10 minutes

		Etch rate (Å/min)										
		pH 2	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10	pH 11	pH 12
FA	OSG	0.57	0.61	0.37	0.34	0	0	0	0	0	0	0
	FSG	2.37	1.54	2.34	1.2	0.42	0	0	0	0	0	0
	BD	0	0.32	0.74	0	0.24	0	0	0	0	0	0
AA	OSG	0	0	0	0	0	0	0	0	0	0	0
	FSG	1.01	2.67	2.31	0.24	0	0	0	0	0	0	0
	BD	0.78	0.37	0.46	0	0	0	0	0	0	0	0
PAC	OSG	1.34	2.31	1.45	0.64	0	0	0	0	0	0	0
	FSG	3.24	2.34	2.74	1.20	0.37	0.45	0	0	0	0	0
	BD	0.97	0.64	0.32	0.41	0.27	0	0	0	0	0	0
OA	OSG	0.32	0.75	0.36	0.21	0.31	0	0	0	0	0	0
	FSG	1.26	1.37	1.64	1.02	0.36	0	0	0	0	0	0
	BD	1.42	1.18	1.24	0.49	0	0	0	0	0	0	0
MAC	OSG	0.96	0.42	0.71	0.31	0.2	0	0	0	0	0	0
	FSG	3.1	1.24	1.38	0.67	0	0	0	0	0	0	0
	BD	0.97	0.37	0.62	0	0	0	0	0	0	0	0
SA	OSG	0	0.21	0	0.43	0	0	0	0	0	0	0
	FSG	1.83	1.93	1.37	1.42	0	0	0	0	0	0	0
	BD	0	0	0	0	0	0	0	0	0	0	0
LA	OSG	1.06	1.32	0.46	0.53	0.21	0	0	0	0	0	0
	FSG	0.81	1.01	1.25	0.27	0	0	0	0	0	0	0
	BD	0	0.37	0.28	0.2	0.17	0	0	0	0	0	0
TA	OSG	0	0	0	0	0	0	0	0	0	0	0
	FSG	1.72	1.55	2.76	0.66	0.31	0.2	0	0	0	0	0
	BD	1.25	0.85	0.92	0.47	0.24	0	0	0	0	0	0
CA	OSG	0.31	0.35	0.37	0.28	0.19	0	0	0	0	0	0
	FSG	2.77	2.81	2.17	1.34	0.62	0.2	0	0	0	0	0
	BD	1.8	1.74	1.24	1.35	0.42	0.71	0	0	0	0	0

Among the components having an amine group, the MA solution exhibited FSG and BD etch rates of 1.12 and 1.1 Å/min at pH 12, and the etch rates decreased as the pH decreased. The PA solution exhibited the largest FSG etching rate among components having an amine group at 1.99 Å/min at pH 10.

A 10 wt% single-component cleaning solution having an amine group was prepared and the etching rates of low-k dielectric materials were measured from pH 2 to 12. The maximum etching rates for low-k dielectric materials were compared and shown in Fig. 5. Among the low-k dielectric materials, FSG showed a decrease in thickness of more than 1 Å in the component having an amine group used in this study. OSG showed a decrease in thickness only in MEA, EDA, and MA solutions, and showed an etching rate of 0.19–1.48 Å/min at pH 9 or higher. A component having an amine group dissolves in water to exhibit basic properties. As shown in the above copper oxide removal characteristics, the etching of the low-k dielectric material is promoted by activation in the base region where the original characteristics of the component having an amine group appear.

Table 3 shows the results of preparing a 10 wt% single-component cleaning solution having a carboxyl group and shows the etching rate through the thickness change of the low-k dielectric material. In the FA solution at 25 °C for 10 minutes, the FSG reveals a thickness reduction of 2.37 Å at pH 2 and 0.42 Å at pH 6. It shows a tendency to decrease from pH 2 to 6. However, at pH 7 or higher, pH variation did not affect the change in the thickness of low-k dielectric films. The PAC solution shows an FSG etching result of 3.24 Å/min at pH 2, and the etching rate tends to decrease as the pH increases. At pH 2, a decrease in thickness for BD occurred by 0.97 Å, and at pH 6, a decrease of 0.27 Å was observed. OSG showed an etching rate of 2.31 Å/min at pH 3. When PAC was used, the thickness reduction did not occur for the low-k dielectric material at pH 8.

The etching rate of the low-k dielectric materials was measured using an OA solution, which is a dicarboxylic acid having two carboxyl groups. OSG showed a result of 0.75 Å/min at pH 3, FSG was 1.64 Å/min at pH 4, and BD showed a result of 1.42 Å/min at pH 2. At pH 7 or higher, the thickness of the low-k dielectric material did not decrease. CA having three carboxyl groups showed the greatest decrease in the thickness of BD at pH 3 among components having carboxyl groups, and the value was 1.74 Å. In addition, the etching rate of FSG showed the maximum and 2.81 Å was obtained. For OSG, when the pH was 3, the etching rate was 0.37 Å/min. In LA and TA solutions having both carboxyl and ethanol groups, LA showed a maximum BD etch rate of 0.37 Å/min at pH 3, and the etch rate decreased as the pH increased. FSG showed a decrease in thickness of 1.25 Å at pH 4 and 1.32 Å at pH 3 of OSG, but there was no change at pH 7 or higher. In the case of the TA solution, the maximum etching rates were shown for FSG and BD at pH 2, and the values were 1.72 and 1.25 Å/min, respectively. At pH 7 or higher, BD was not etched at pH 8 or higher, and OSG was not etched in all pH ranges.

As in the copper oxide removal experiment, it was confirmed that the component having a carboxyl group was activated in the acidic region, and the same result was obtained for the low-k dielectric material [3,4]. A single component cleaning solution having a

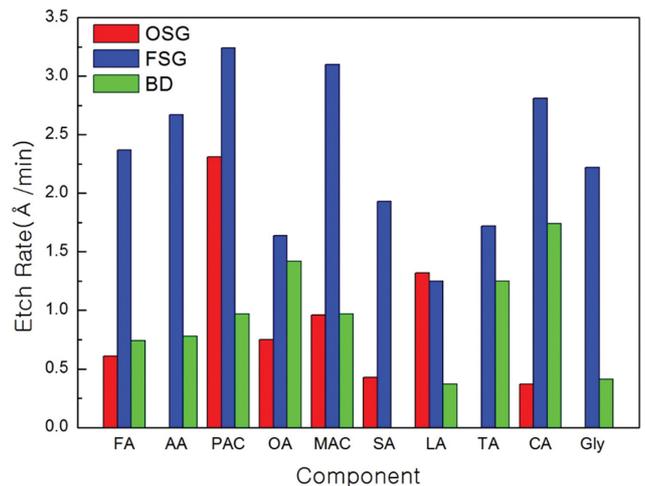


Fig. 6. Maximum etch rates, measured at 25 °C for 10 minutes, of low-k dielectric materials (OSG, FGS, BD) treated in various 10 wt% carboxylic acid solutions (cf. 5 wt% succinic acid), which were chosen over all pH ranges.

carboxyl group was prepared and the etching rates of low-k dielectric materials were measured from pH 2 to 12. Among the results, the maximum etching rates for low-k dielectric materials were compared in Fig. 6. The relatively low etching rates of OSG and BD can be interpreted as a result of low wettability contributed by the influence of carbon and methyl groups doped on the surface. It was found that the etching rate for the low-k dielectric material of the component having a carboxyl group was relatively high compared to the component having an amine group.

Due to the chemical and structural change of the surface of the low-k dielectric material, the dielectric constant changes. Each FT-IR analysis was performed to confirm the chemical and structural changes of these surfaces. Fig. 7 shows the FT-IR results before and after dipping treatment of FSG, OSG, and BD with a 10 wt% solution of single-component EDA and PAC at 25 °C for 10 minutes. The strong absorption bands between 800 cm⁻¹ and 1,400 cm⁻¹ are associated with the Si-O-Si (around 1,055 cm⁻¹) and Si-O-C (around 1,135 cm⁻¹) configurations. The absorption peak at 1,270 cm⁻¹ originates from the symmetrical deformation vibration of -CH₃ in Si-CH₃ [25]. As a result of the analysis, no significant chemical change was observed in FSG, OSG, and BD before and after dipping.

CONCLUSIONS

A solution containing a single component of amine and carboxylic acid was used to analyze the surface roughness of the cleaning process of copper, measure the etch selectivity for copper and copper oxide, and verify the etching rate and the surface morphology change of low-k dielectric materials such as FSG, OSG, and BD. The etching rate of copper oxide in the solution containing an amine group showed a tendency to increase as the basicity of the solution increased. The etching rate of copper oxide was shown in the order of MEA>DEA>TEA in the solution prepared at the same concentration in which the ethanol group was substituted for the

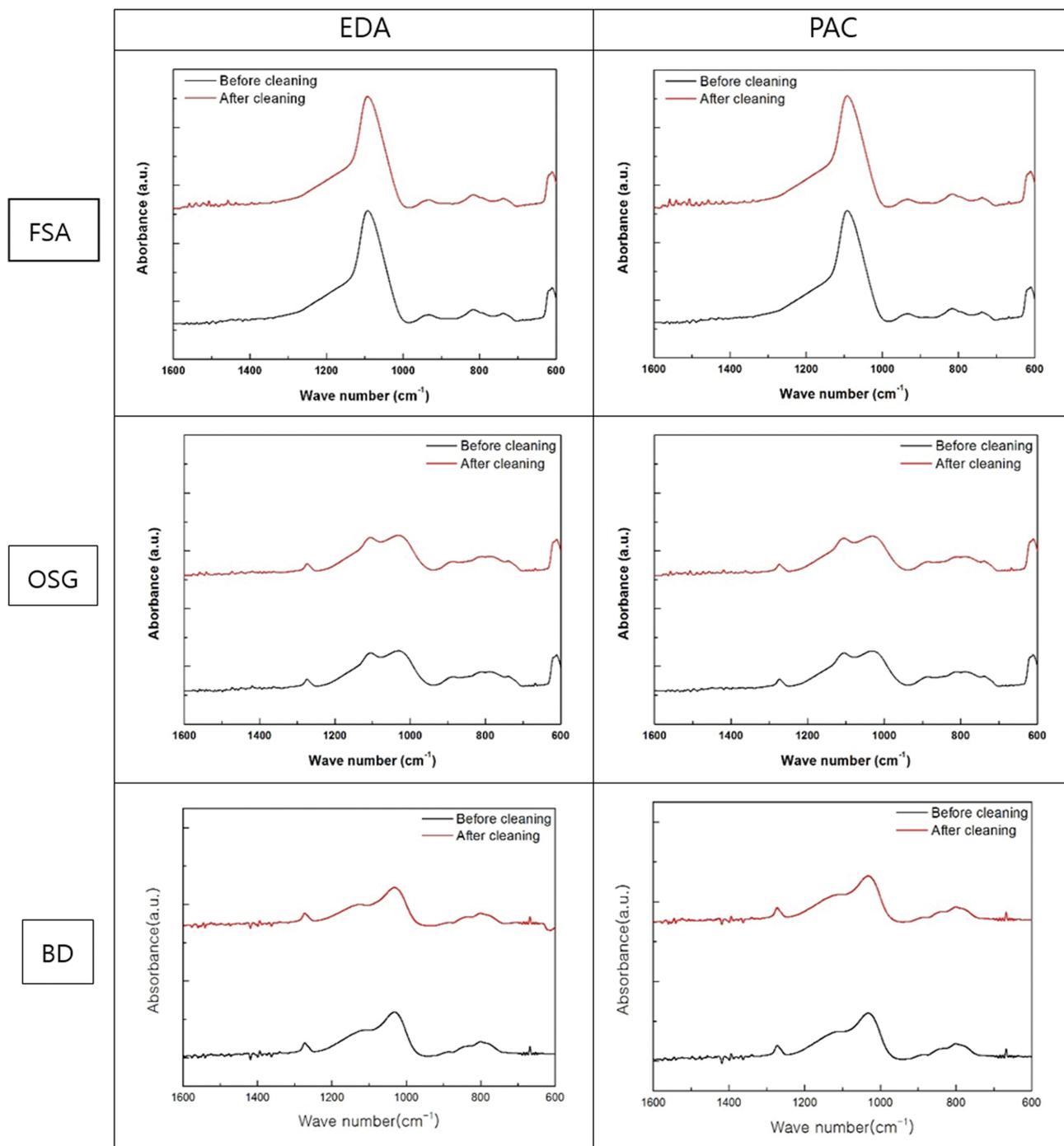


Fig. 7. Comparison of FTIR analysis results before and after low-k dielectric materials (OSG, FGS, BD) treated with 10 wt% ethylene diamine (EDA) and propionic acid (PAC) solutions at pH 8.

nitrogen of the amine group. Also, the solubility of copper oxide in the amine solution decreased with the increase of the carbon length in the amine molecular structure. It was found that the removal effect of the carboxylic acid solution on copper oxide was maintained in the acidic region, but there was almost no removing power on the copper oxide in the neutral and basic regions. A solution having a carboxyl group compared to an amine group had a high etching rate for the low-k dielectric material, and the amine

component was reactive only in the basic region and the carboxyl group component was reactive only in the acidic region.

ACKNOWLEDGEMENTS

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (Grant Number: 2019R1A2C1005445).

REFERENCES

1. M. A. Martinez, *Soild State Technol.*, **37**, 26 (1994).
2. D. Shamiryan, T. Abell, F. Lacopi and K. Maex, *Mater. Today*, **7**, 34 (2004).
3. Y. S. Zheng, Q. Guo, Y. J. Su and P. D. Foo, *Microelectron. J.*, **34**, 109 (2003).
4. D. Lu, R. Kumar, C. K. Chang, A. Y. Du and T. K. S. Wong, *Microelectron. Eng.*, **77**, 63 (2005).
5. Y. Wang, S. W. Graham, L. Chan and S. Loong, *J. Electrochem. Soc.*, **144**, 1522 (1997).
6. T. Maruyama, N. Fujiwara, K. Siozawa and M. Yoneda, *Jpn. J. Appl. Phys.*, **35**, 2463 (1996).
7. J. A. G. Baggerman, R. J. Visser and E. J. H. Collaert, *J. Appl. Phys.*, **75**, 758 (1994).
8. T. Ohmi, *J. Electrochem. Soc.*, **143**, 2957 (1996).
9. L. M. Loewenstein and P. W. Mertens, *J. Electrochem. Soc.*, **146**, 3886 (1999).
10. W. A. Cady and M. Varadarajan, *J. Electrochem. Soc.*, **143**, 2064 (1996).
11. K. A. Reinhardt and W. Kern, *Handbook of silicon wafer cleaning technology*, 3rd ed., Elsevier (2018).
12. N. Venkataraman and S. Raghavan, *Microelectron. Eng.*, **87**, 1689 (2010).
13. C. K. Ko and W. G. Lee, *Korean Chem. Eng. Res.*, **54**, 548 (2016).
14. C. K. Ko and W. G. Lee, *Korean Chem. Eng. Res.*, **59**, 632 (2021).
15. S. C. Sircar and D. R. Wiled, *J. Electrochem. Soc.*, **107**, 164 (1960).
16. S. Aksu and F. M. Doyle, *J. Electrochem. Soc.*, **149**, B340 (2002).
17. S. C. Sircar and D. R. Wiled, *J. Electrochem. Soc.*, **107**, 367 (1960).
18. M. K. Carter, E. Small, M. Cernat and B. Hansen, *J. Electrochem. Soc.*, **150**, B52 (2003).
19. Y. F. Wu and T. H. Tsai, *Microelect. Eng.*, **84**, 2790 (2007).
20. V. R. K. Gorantla, A. Babel, S. Pandija and S. V. Babu, *Electrochem. Solid-State Lett.*, **8**, G131 (2005).
21. V. Gorantla, D. Goia, E. Matijević and S. V. Babu, *J. Electrochem. Soc.*, **152**, G912 (2005).
22. S. Aksu and F. M. Doyle, *J. Electrochem. Soc.*, **149**, B340 (2002).
23. C. K. Ko and W. G. Lee, *Surf. Interface Anal.*, **44**, 94 (2012).
24. C. K. Ko and W. G. Lee, *Surf. Interface Anal.*, **42**, 1128 (2010).
25. Z. J. Ding, Y. P. Wang, W. J. Liu, S. J. Ding, M. R. Baklanov and D. W. Zhang, *J. Phys. D: Appl. Phys.*, **51**, 115103 (2018).