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Method to improve chemical-mechanical-planarization polishing rate of low-*k* methyl-silsesquiazane for ultralarge scale integrated interconnect application*

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In this work, characteristics of low-*k* methyl-silsesquiazane (MSZ) for the chemical-mechanical-planarization (CMP) process using oxygen plasma pretreatment were investigated in detail. The low-dielectric-constant (low-*k*) MSZ was prepared by a spin-on deposition process. The resultant wafers were followed by an oxygen (O_2) plasma treatment. After oxygen plasma treatment, the CMP process was implemented. Electrical and material analyses were utilized to explore the characteristics of post-CMP MSZ. Experimental results showed that the polish rate of MSZ film with O_2 plasma pretreatment was increased as much as two times in magnitude, as compared to that of the MSZ without O_2 plasma pretreatment. In addition, the post-CMP MSZ exhibited superior electrical properties. These results clearly indicated that the modification surfaces that resulted from O_2-plasma treatment facilitated CMP MSZ. After CMP polishing, the MSZ film still maintained low-*k* quality.
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I. INTRODUCTION

As integrated circuit dimensions continue to shrink, highly packed multilevel interconnections with low-resistance metal and low-dielectric constant materials have attracted much attention as a method for increased ultralarge scale integrated (ULSI) circuits operating speed.[1,2] Because continued miniaturization of device dimensions and the related need to interconnect an increasing number of devices on a chip is a trend in ULSI technology, this has led to building multilevel interconnections on planarized levels.[3,4] Obviously, surface planarization is a key technology during the manufacture of multilevel interconnects.[5–7] Because the chemical-mechanical-planarization (CMP) process satisfies the requirement of global topography planarization during integrated circuit fabrication, this method has been introduced to form interconnections between devices and between devices and outside.[8,9] In the development of CMP low-*k* dielectrics, Forester *et al.*[10] found that the polish rate of alkyl siloxane-based spin-on glass (SOG) was lower than that of plasma enhanced chemical vapor deposition oxide or thermal oxide using only conventional silica-based slurry. When using conventional oxide slurries, the polish rate of alkyl siloxane-based SOG is dependent on the organic content. A higher Si–R/Si–O ratio in the SOG films induces a lower hydrolysis reaction rate, leading to a lower polish rate. Several reports[11,12] indicate that the use of alkaline cerium oxide-based slurry and the introduction of additives could greatly improve the removal rate for organic spin-on materials. However, before adopting consumables into production, much experimental work should be completed to qualify these consumables.

In this study, we propose oxygen plasma pretreatment on low-*k* methyl-silsesquiazane (MSZ) film to improve the pol-

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ish rate of CMP MSZ film. The low-*k* MSZ film is provided by Clariant Corp. in Japan and is one of methylsilsesquioxane-like organic polymers derived from MSZ precursor solution. Moreover, the investigation of post-CMP characteristics such as electrical performance and desorption of constitution water also were emphasized.

II. EXPERIMENT

The substrates used in this study were 150 mm *p*-type (11–25 Ω cm) single-crystal silicon wafers with (100) orientation. Before film deposition, Si wafers were boiled in $H_2SO_4+H_2O_2$ solution and heated to 120 °C for 20 min to remove particles on the surfaces. Then, these wafers were spin coated with a MSZ solution at a spin speed of 2000 rpm for 30 s on a model 100CB spin coater. This was followed by a series of sequential thermal baking steps on the hot plate at 150 and 280 °C for 3 min. The wafers coated with MSZ precursor solution then received a hydration treatment. The wafers were left in a clean room for 48 h and the precursor structure of MSZ films will be transformed to methylsilsesquiazane through hydrolysis and condensation process, as follows:

Hydrolysis reactions:

$$\equiv\text{Si–NH–Si}\equiv_{(s)}+\text{H}_2\text{O}_{(g)}\rightarrow\equiv\text{Si–NH}_{2(s)}+\text{HO–Si}\equiv_{(s)}$$

$$\equiv\text{Si–NH}_{2(s)}+\text{H}_2\text{O}_{(g)}\rightarrow\equiv\text{Si–OH}_{(s)}+\text{NH}_{3(g)}\,.$$

Condensation reactions:

$$\equiv\text{Si–OH}_{(s)}+\text{HO–Si}\equiv_{(s)}\rightarrow\equiv\text{Si–O–Si}\equiv_{(s)}+\text{H}_2\text{O}_{(g)}\,.$$

Afterward, the resultant wafers were thermally cured in a quartz furnace at 400 °C for 30 min under N_2 ambient. The final MSZ films (called as-cured MSZ, marked as sample STD) were formed to a thickness of 400 nm. The final structure is shown in Fig. 1.

After film formation, the as-cured MSZ was treated with O_2 plasma for 60 s prior to the CMP process (marked as sample O). The O_2 plasma was operated at a pressure of 650 mTorr and with an oxygen gas flow rate of 900 sccm. A radio frequency power of 110 W was applied to the upper electrode. Next, the wafers were placed on the grounded bottom electrode, which can be rotated for improving uniformity. The wafers had a substrate temperature up to 250 °C. Then the CMP process was applied to the plasma-treated MSZ films for 2 min. These post-CMP MSZ films were marked as "sample C." The CMP experiment was carried out on an IPEC/Westech 372M CMP processor with a Rodel IC 1400 pad on the primary polishing platen and Rodel Politex Regular embossed pad on the final buffering platen. A Rodel R200-T3 carrier film was used to provide a buffer between the carrier and wafer. A single 6 in. wafer was mounted on a template assembly. During the polishing experiment, the slurry was commercial CABOT™ SS-25 diluted by deionized water with the ratio of 1:1, which is typically used to polish SiO_2. The resultant solution *p*H value is in the range of 10–11. The polishing parameters, such as down force, backpressure, platen and carrier rotation speeds, and slurry flow rate, were set to be 3, 2, 50, 60 rev/min, and 150 ml/min, respectively. By means of light interference effects in films, the thickness of all MSZ films in this experiment was measured using an N&K 1200 analyzer. The structure properties of the MSZ films were studied using Fourier-transform infrared spectroscopy (FTIR). The infrared spectrometry was performed from 4000 to 400 cm^{-1} using a Bio-Red QS300 FTIR spectrometer calibrated to an unpatterned wafer and their data were collected in the absorbance mode for studying the chemical structure of films. The surface morphologies of the polished films were investigated by atomic-force microscopy (AFM). Thermal desorption spectroscopy (TDS) was carried out to monitor the desorbed elements from post-CMP MSZ films during the high temperature process. In the duration of TDS analysis, samples were heated from room temperature to 600 °C at a rate of 20 °C/min in a vacuum chamber. In addition, the outgassing species were collected through the mass spectrometer. In this work, M/e (mass-to charge ratio)=18 peak attributed to H_2O was monitored. Electrical characteristics of post-CMP MSZ films were performed on the metal–insulator–semiconductor capacitor with metallic–aluminum deposition as the top electrode and backside electrode. Leakage current–voltage ($I-V$) and capacitance–voltage characteristics were also used to analyze the leakage current behaviors and measure the dielectric constants of post-CMP MSZ films, respectively. In addition, $I-V$ measurements were also conducted for these specimens at different stable temperatures during the temperature rising and cooling procedures to evaluate the practicability of im-

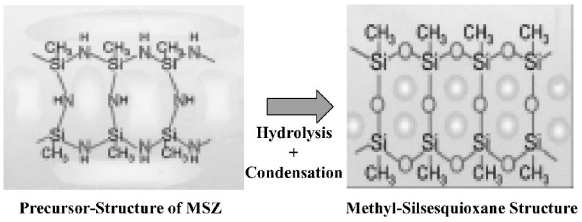

FIG. 1. Formation mechanism diagram of MSZ films.

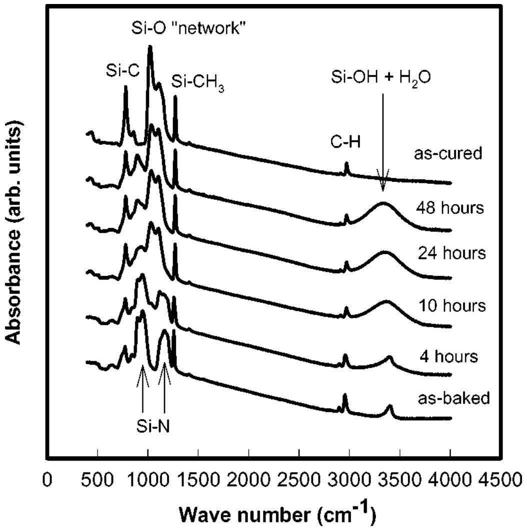

FIG. 2. FTIR spectra of MSZ during formation procedure.

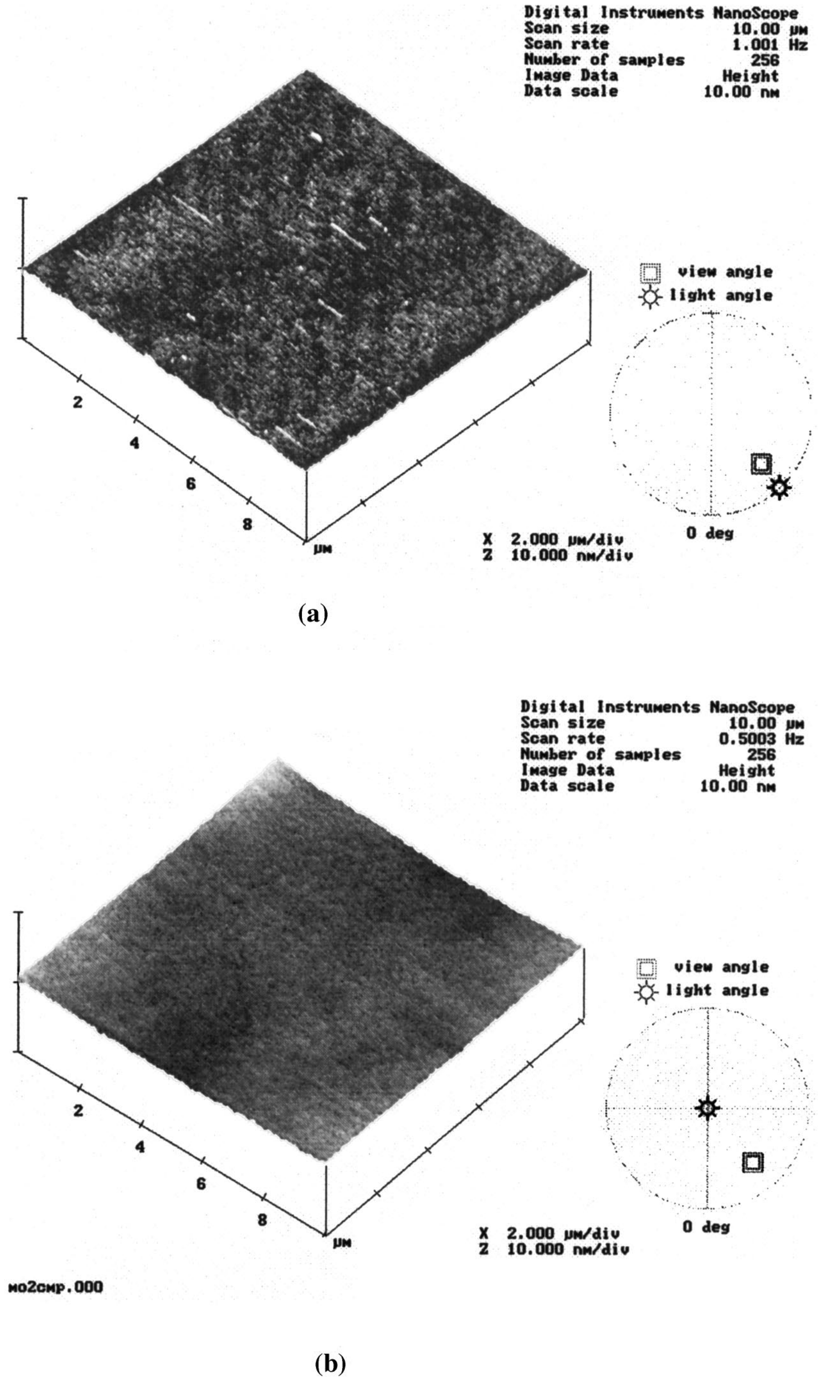

FIG. 3. AFM micrographs of 60 s O_2 plasma-treated MSZ films (a) without CMP process (b) with CMP process.

proving the polishing rate of MSZ films with O_2 plasma pretreatment for the CMP process.

III. RESULTS AND DISCUSSION

For the applications for multilevel interconnects, low-*k* dielectrics must be carefully characterized for their material and electrical properties. Figure 2 represents the FTIR spectra of MSZ films during formation processes. After 10 h of hydration reaction proceeded in a clean room, it was observed that the Si–N peaks almost disappeared, while the Si–O network-like bonds and Si–OH bonds grew gradually. This was due to the hydrolysis process. This result implied that the hydrolysis and condensation process occurred simul-

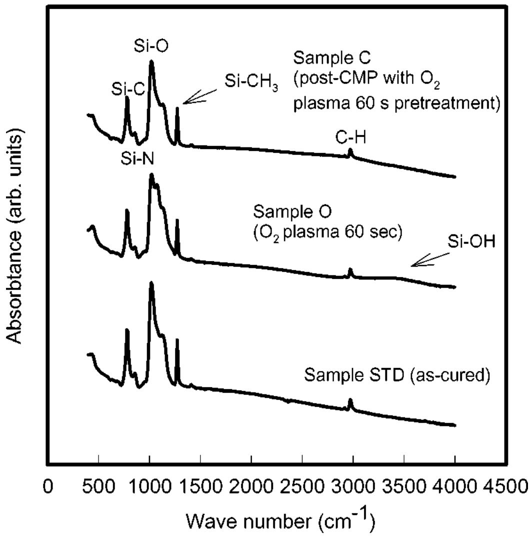

FIG. 4. FTIR spectra of O_2 plasma-treated MSZ films before and after CMP process.

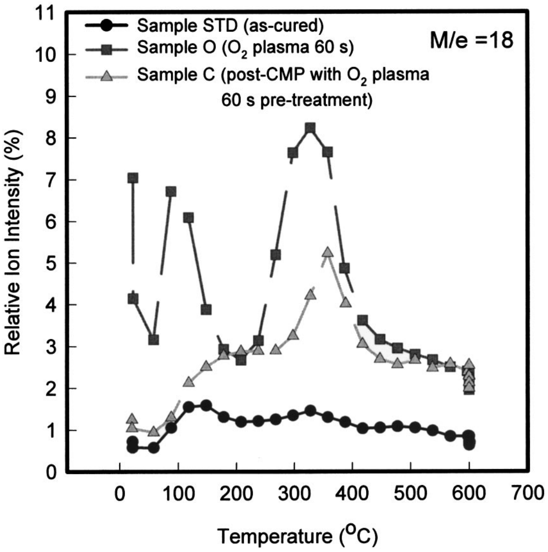

FIG. 5. Moisture-desorption spectra of O_2 plasma-treated MSZ films before and after CMP process.

taneously during the period. In the periods ranging from 10 to 48 h, the condensation process resulted in a network-like structure through the bulk MSZ film. Next, the water content was eliminated and the standard MSZ film was obtained after thermal curing in a furnace. AFM images of O_2 plasma-treated MSZ films before and after CMP process are shown in Figs. 3(a) and 3(b), respectively. The roughness (R_a) of MSZ films with O_2 plasma treatment was 0.341 nm, while the R_a value of O_2 plasma-treated MSZ after being subjected to a CMP process was reduced to 0.227 nm. In addition, the CMP polish rate of MSZ with O_2 plasma pretreatment was increased as much as twice in magnitudes compared to MSZ without O_2 plasma treatment (the average polishing rate of MSZ is increasing from 16 to 35 nm/min). The results indicated that the removal rate of MSZ can be improved by O_2 plasma treatment, even with SS-25 slurry used typically. Figure 4 shows FTIR spectra of O_2 plasma-treated MSZ films before and after the CMP process. Prior to the CMP process, both intensities of Si–OH and H_2O groups (at 993 and 3400 cm^{-1}) increased, whereas the intensities of C–H (2974 cm^{-1}) and $Si–CH_3$ (at 781 and 1273 cm^{-1}) groups decreased when MSZ film underwent O_2 plasma treatment. Moreover, the peak of the Si–O bond at 1070 cm^{-1} was slightly formed in O_2 plasma-treated MSZ. After the CMP process, however, all intensities of functional groups in MSZ films maintained a high level again. These observed phenomena are clearly interpreted as follows.

The decomposition of functional groups in MSZ films, due to O_2 plasma pretreatment, would lead to forming Si–OH bonds, which easily induced moisture uptake and modified the MSZ surfaces from hydrophobic into hydrophilic ones. It was believed that oxygen radicals generated from O_2 plasma could react with a large amount of $Si–CH_3$ groups on MSZ films, which caused the decreasing intensities of Si–C and C–H groups. Hence, the oxidation reaction would convert $Si–CH_3$ groups into Si–OH groups via the following processes:

$$\equiv \mathrm{Si{-}CH}_{3(s)} + 2\mathrm{O}_{2(g)} \rightarrow \equiv \mathrm{Si{-}OH}_{(s)} + \mathrm{CO}_{2(g)} + \mathrm{H}_2\mathrm{O}_{(g)}\,.$$

Because the Si–OH group was hydrophilic, it was easy to induce moisture uptake. As a result, after the MSZ film underwent O_2 plasma treatment, the intensities of the Si–OH and H_2O signals would increase. In addition, a partial amount of Si–OH groups might react with each other via a dehydration reaction during O_2 plasma treatment

$$\equiv \mathrm{Si{-}OH}_{(s)} + \mathrm{HO{-}Si}\equiv_{(s)} \rightarrow \equiv \mathrm{Si{-}O{-}Si}\equiv_{(s)} + \mathrm{H}_2\mathrm{O}_{(g)}\,.$$

The intensity of the absorption band (at 1070 cm^{-1}), which was characteristic for the Si–O–Si vibration in silica, was thereby increased. The hydrophilic surfaces consisting of oxide facilitated CMP of MSZ films and a rapid CMP polish rate was obtained, just with only the conventionally used CMP oxide slurry CABOT™ SS-25. The hydrophilic Si–OH bonds would be removed after the CMP process. Thus, Si–OH bonds disappeared in FTIR spectra. After the removal of the oxide layer on the surface of O_2 plasma-treated MSZ, organic function groups such as Si–C and C–H bonds maintained a high level of peak intensity.

The temperature dependence of moisture desorption is shown in Fig. 5. After being subjected to the O_2 plasma treatment, the moisture content of MSZ film was increased, while it decreased after the CMP process. This was consistent with our inference that oxide layers on MSZ surfaces could induce moisture and be easily polished away just with oxide slurry used typically. Once the surface oxide layers were absent, the surfaces of MSZ would return to being hydrophobic-like, resulting in less moisture content. Furthermore, the electrical characteristics were investigated to evaluate the impacts of the CMP process on MSZ films. Figures 6(a) and 6(b) show the leakage current and dielectric constant of O_2 plasma-treated MSZ before and after the CMP process. The electrical properties of MSZ with O_2 plasma treatment were degraded. After the CMP process, however, the leakage current and dielectric constant of MSZ

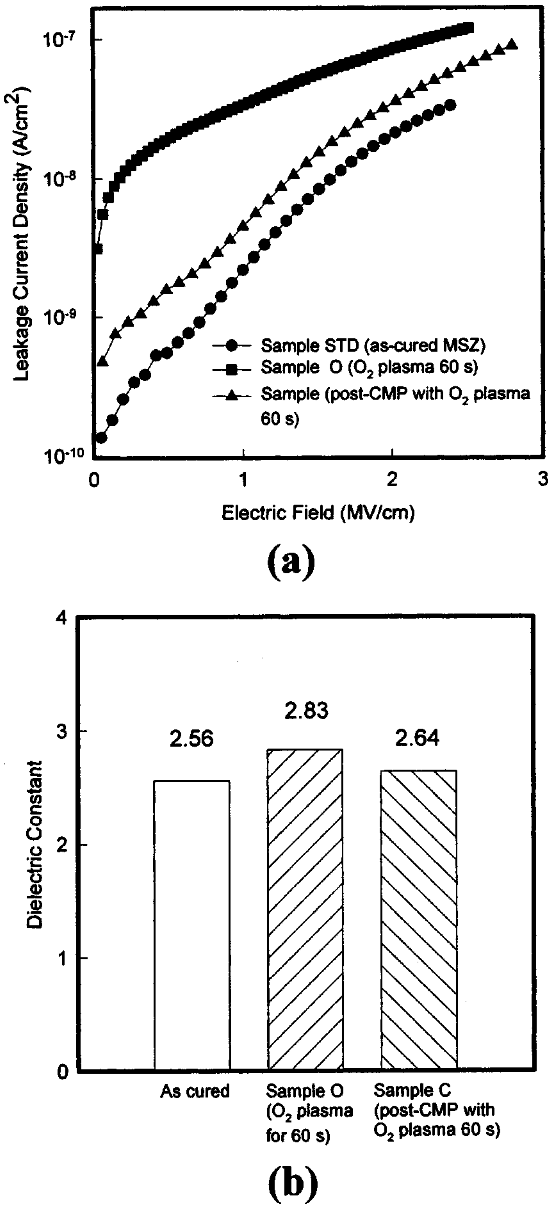

FIG. 6. Dielectric properties of O_2 plasma-treated MSZ before and after CMP process (a) leakage-current density of MSZ films as a function of electrical field. (b) Variation in dielectric constant of O_2 plasma-treated MSZ films.

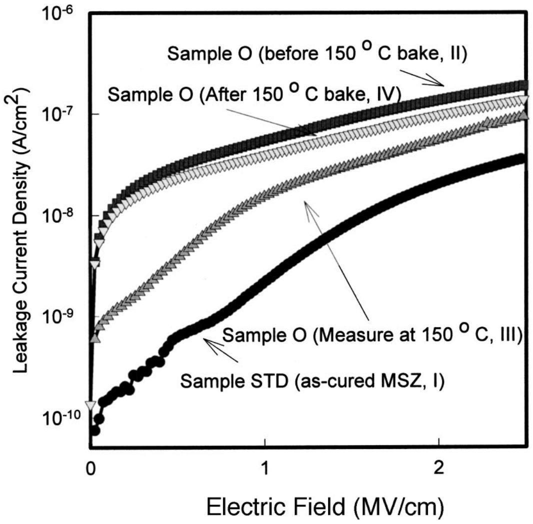

FIG. 7. Leakage-current density of sample O before and after the 150 °C bake [curve I, sample STD measured at 25 °C; curve II, sample O measured at 25 °C (before 150 °C bake); curve III, sample O measured at 150 °C; curve IV, sample O measured at 25 °C (after 150 °C bake)].

were recovered significantly. In order to explore the leakage behaviors of MSZ films with O_2 plasma pretreatment before and after CMP process, we tried to conduct $I-V$ measurement at different temperatures during the temperature rising and cooling procedure. Figure 7 shows the leakage current density of sample O and sample STD measured at 25 °C (curves I, II, and IV) and 150 °C (curve III), respectively. Owing to O_2 plasma treatment, the leakage current of sample O is larger than that of sample STD. The O_2 plasma could modify the surface of MSZ film, leading to formation of defects and inducing moisture uptake. Both the hydrophilic defects and the defect-induced moisture often result in an increase of leakage current. In order to recognize the effect of moisture uptake on the O_2 plasma-treated MSZ film, leakage-current measurement is performed before and after the 150 °C bake. In comparison with sample STD, after O_2 plasma ashing, the leakage current density increases about 1–2 orders of magnitude due to defects-induced moisture uptake, as shown for sample O (curve II). After the 150 °C baking process (curve III), an amount of water molecules are desorbed from the sample O so that the leakage current of the sample O (measured at the 150 °C baking temperature) decreases about one order of magnitude. Nevertheless, when the measured temperature of sample O is cooling from 150 to 25 °C, the leakage current of sample O increases significantly again (curve IV), which results from the moisture reuptake during the temperature-cooling processing. In addition, the moisture reuptake may be due to the remainder of hydrophilic defects caused by O_2 plasma damage in the surface of the MSZ film. Figure 8 shows the leakage current density of sample C and sample STD measured at 25 °C (curves I, II, and IV) and 150 °C (curve III), respectively. Because the modification surface layer of O_2 plasma-treated MSZ was polished away by the CMP process, the leakage current of sample C (curves II and IV) was close to that of as-cured MSZ film (curve I) at 25 °C. Moreover, the leakage current of sample C (curve III) increased by one order of magnitude compared to that of the as-cured MSZ film (curve I) at 150 °C. This indicates that the leakage current mechanism could be dominated by a thermionic field emission procedure at the high temperature $I-V$ measured condition. Our results reveal that the hydrophilic surface layer made due to the O_2 plasma treatment would result in the increase of leakage current of MSZ film. However, the leakage current of O_2 plasma-treated MSZ could be recovered after polishing the most of hydrophilic layer by CMP process. These electrical results were consistent with aforementioned FTIR and TDS analysis data.

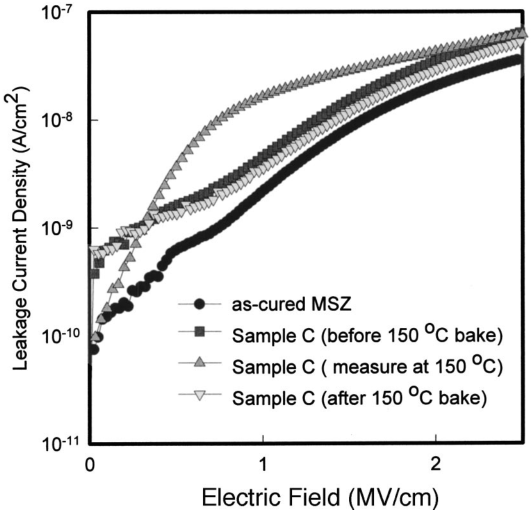

FIG. 8. Leakage-current density of sample C before and after the 150 °C bake [curve I, sample STD measured at 25 °C; curve II, sample C measured at 25 °C (before 150 °C bake); curve III, sample C measured at 150 °C; curve IV, sample C measured at 25 °C (after 150 °C bake)].

IV. CONCLUSIONS

In this study, we have proposed an effective method to improve the CMP polish rate of organic MSZ films. The oxygen plasma was used to make the surface of the MSZ film more hydrophilic and to facilitate the CMP of MSZ films. As a result, the polish rate of O_2 plasma-treated MSZ was as large as twice the magnitude of MSZ without O_2 plasma pretreatment. In addition, the electrical properties of O_2 plasma-treated MSZ films could be recovered almost to a similar state as the as-cured MSZ after CMP process. This indicated that most of damage surfaces of O_2 plasma-treated MSZ films could be removed during the CMP process. Also, the dielectric properties of MSZ could maintain the low-*k* quality. The results were consistent with those of material analyses. Therefore, O_2 plasma pretreatment will be a promising method to increase the polish rate of organic MSZ films.

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