

Multiple Surfaces Pretreatments of SiO₂-based Dielectric Layers for Electroless Plating of Copper

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ABSTRACT

In this work, comparative study of surface treatments of non-porous (HOSP) and nanoporous (Black Diamond II; DB II) SiO₂-based dielectric layers by vacuum plasma of gaseous mixture (N₂/H₂) is made. Fourier transform infrared x-ray spectroscopy indicates that, for HOSP, properly adjusting the operating power supply and shifting the gas mixture toward the N₂ dominant regime cause the N₂/H₂ plasma to outperform the commonly used NH₃ and N₂ plasma sources with respect to protecting the films against O₂ plasma damage. However, The BD II containing porosity is very sensitive to plasma exposure, and thus a much less dosage has already induced a heavier removal of carbonaceous species and cross-linking of the nanoporous film, sharply degrading the film's dielectric constant (k) and insulating capacity. Using multiple surface pretreatments to modify the DB II ends up with a resolution of the above-mentioned issue. The hydrophobic DB II becomes hydrophilic after the plasma pretreatment. In contrast to the pristine hydrophobic counterpart, the plasma-pretreated BD II with water-wetted surface anchors a high-quality self-assembled monolayer (SAM). The roles of the SAM, in terms of facilitating electroless plating of Cu films and improving the process/material integration of nanoporous DB II and Cu, will be presented.

Keywords: dielectric layer, self-assembled monolayer

1 INTRODUCTION

The next generation integrated-circuit fabrication process has several issues concerning the degradation of low-k inter-metal dielectrics (IMDs) by processing steps such as oxygen plasma, which causes a removal of aryl and alkyl side

chains particularly from nanoporous IMDs, leading to a decay of the dielectric properties and reduced thermal stability [1]. These process-induced problems are viewed as obstacles to integrating low-k IMDs into the copper-wiring process, and thus have been investigated extensively in recent years [2–4].

Developing a barrier-free scheme is important as the feature size of integrated-circuits scales down to less than 45 nm. Indeed, most works have used a single reactive gas, usually NH₃, N₂O, N₂, or H₂, to generate surface pre-treating plasma for a variety of low-k IMDs [5,6]. This study addresses the feasibility of using mixed gases (N₂/H₂) to generate plasma for surface treatments of both traditional (non-porous) and nanoporous IMD. First, optimum plasma conditions will be found for hybrid organic siloxane polymer (HOSP), and then the effect of such as plasma treatment on the dielectric properties of nanoporous IMD (Black Diamond II; BD II) will be evaluated and compared with that of HOSP.

2 EXPERIMENTAL DETAILS

Both HOSP and BD II were coated on silicon wafers by sol-gel and chemical vapor deposition, respectively. The dielectric samples were then put in a vacuum glow-discharge reactor under a base pressure of 10⁻¹ Pa or less, and treated by plasma generated around the substrate holder connected to a radio-frequency generator. The plasma sources were gaseous H₂, N₂, or various N₂/H₂ mixtures, separately admitted to the reactor by a mass flow controller.

For the HOSP samples, the plasma pretreatments were performed at an overall pressure of 50 Pa and with a power supply from 50 to 150 W for duration ranging from 1 to 12 min. Dielectric characterization was performed at 1 MHz by capacitance measurements of metal-insulator-semiconductor

(MIS) capacitors. An Al film was deposited on the back side of the Si wafer to improve back contact. Variation of the intensity of the Si-CH₃ stretching peak at 1270 cm⁻¹, and network Si-O (1040 cm⁻¹) and caged Si-O (1125 cm⁻¹) peaks in the Fourier transform infrared (FTIR) spectra, as well as dielectric constant and leakage current measurements, were used to evaluate the capacity of various N₂/H₂ plasma pretreated films against O₂ plasma damage. From these analyses, the optimum plasma condition for surface passivation was found. This plasma condition was then used to treat the BD II, subsequently followed by evaluations of dielectric properties and bonding structures. These evaluations allowed the plasma dosage to be suitably adjusted for passivation of the SAM-coated BD II. The SAM material was octadecyltrichlorosilane (OTS).

3 RESULTS AND DISCUSSION

Figure 1(a) is the FTIR spectrum for as-cured HOSP, and spectra (b) and (c) are associated respectively with the as-cured HOSP after H₂ and N₂ plasma treatments (100 W/9 min). Comparing (a) and (b) shows that the H₂ plasma treatment markedly reduces the intensities of the Si-C (1270 cm⁻¹) and Si-H (2250 cm⁻¹) bonds. This H₂ plasma treatment also partially converts the caged Si-O to network Si-O.

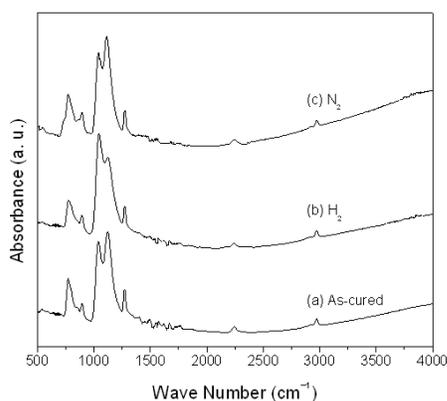


Fig. 1. FTIR spectra for (a) as-cured and (b) H₂ and (c) N₂ plasma treated HOSP films.

FTIR analysis (spectra not shown) revealed that O₂ plasma behaviors similarly to H₂ plasma in terms of bond damage. O₂ plasma removes the CH₃ chains, leaving behind

active sites to which adjacent O-Si-O backbones can bond. Accordingly, the plasma-treated HOSP becomes more like silicon dioxide than the as-cured counterparts, eventually causing a sharp rise in k value exceeding 4. However, the films after the exposure of N₂ plasma suffer a slight reduction in the number of Si-C bonds, while the conversion of the caged to network structure is not observed [see 1(c)], suggesting that the N₂ plasma treatment removes methyl groups, but is hard to disrupt the caged Si-O.

Figure 2 shows that varying the plasma gaseous compositions from 100% H₂, N₂/H₂ mixtures to 100% N₂ alters the degree of the bond-structure disruption (and hence increase in k values) of the HOSP films. The data points (filled circles) in Fig. 2 are the results obtained for plasma treatment at 100 W for 9 min, while the other set of data points are the results for less energy input (50 W/6 min). According to Fig. 2, the H₂ plasma transforms part of the caged Si-O to network Si-O, thereby causing a sharp increase (by 50% of the as-cured level) in the network/caged Si-O peak ratio (denoted as I_{N/C}). These changes establish that the H₂ plasma indeed is most efficient among all the plasma-generating gaseous sources in opening up caged Si-O. The plasma generated by gradually adding N₂ to the H₂ gas, and particularly for N₂ flow rates exceeding 60%, tends to retard the disruption of the caged Si-O. Consequently, the film treated by the N₂ dominant plasma gives an I_{N/C} value close to that of as-cured films.

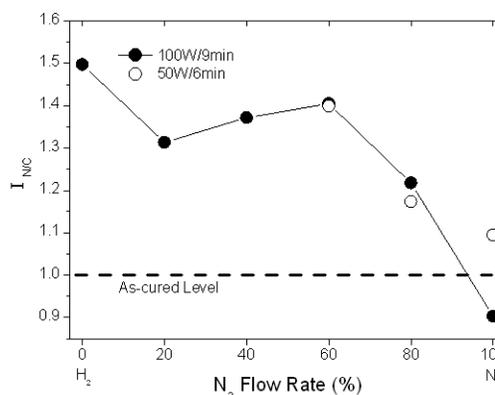


Fig. 2. Network/caged Si-O peak ratios for a series of FTIR spectra from HOSP films receiving various plasma treatments.

Figure 3 shows the values of $I_{N/C}$ for the as-cured and N_2/H_2 plasma-treated HOSP films that have been post-treated by O_2 plasma (150 W/5 min). The as-cured film is heavily damaged by the O_2 plasma. Pretreatment with the plasma comprising either pure N_2 or 60% N_2 –40% H_2 is not working in terms of protecting the bonds against O_2 plasma exposure. Thus, these films are still severely damaged by the O_2 plasma, and yield a sharp increase in $I_{N/C}$. However, the films, pre-treated by the 80% N_2 –20% H_2 plasma under the power/energy input of 50 W/6 min resists against the O_2 plasma attack, hence maintaining an $I_{N/C}$ level comparable to that of the as-cured HOSP.

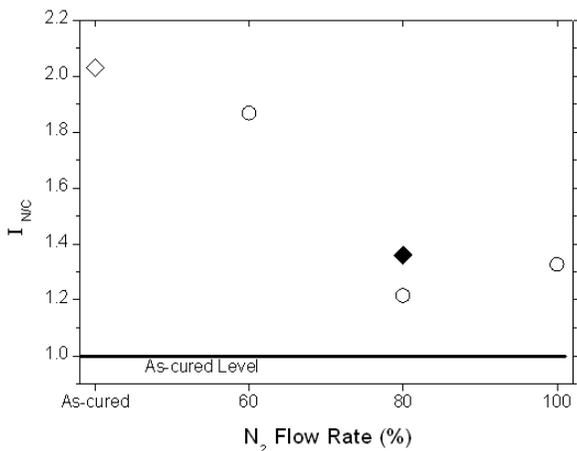


Fig. 3. Values of $I_{N/C}$ for the as-cured and plasma-treated HOSP films subsequently exposed to O_2 plasma.

Figure 4 displays the variation of leakage current density against electric field for various MIS capacitors. Comparing plots (a) and (b) reveals that treating the as-cured films with the O_2 plasma causes a sharp rise in leakage values by more than two orders. Notably, the O_2 plasma exposure also causes an increase in k value to 3.2, consistent with a loss of the methyl side chains and the caged Si-O, as revealed by FTIR. After treatment by the N_2 dominant plasma, the films can be exposed to the identical O_2 plasma without suffering decays in k and leakage current [plot (c)]. Notably, comparing plots (c) and (d) reveals that N_2/H_2 outperforms the commonly used NH_3 , regarding the suppression of leakage current against the O_2 plasma post-treatment. However, as illustrated by plot (e),

pretreatment with either excess power or energy cannot preserve the bond structure and dielectric properties against O_2 plasma exposure.

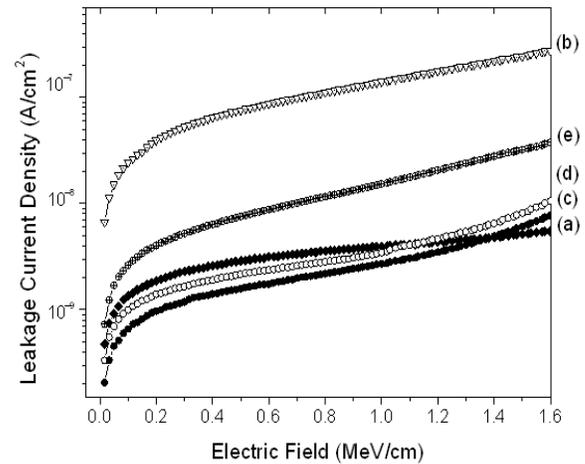


Fig. 4. Leakage current density as a function of electric field for (a) as-cured films that subsequently treated by various plasmas of (b) O_2 , (c) 80% N_2 –20% H_2 (50 W/6 min) + O_2 , (d) NH_3 (50 W/6 min) + O_2 , and (e) 80% N_2 –20% H_2 (100 W/3 min) + O_2 .

This study has shown that H_2 plasma tends to remove the caged Si-O and CH_3 chains, creating surface active sites (dangling bonds) that are readily terminated by the reactive nitrogen species. The roles of H and N species determined herein relate closely to the finding for plasma etching of low- k films [7,8]. Those studies showed that H radicals/ions are responsible for the etching, while the nitrogen neutral radicals assist anisotropic etching by forming a nitride protective layer on the sidewall. Herein, the competition between nitridation and etching to suppress the degradation of HOSP is optimized at an N_2/H_2 flow ratio of 80% to 20% and an energy input of 300 W-min (50W/6 min). Under this condition, spectra of x-ray absorption fine structure taken using a synchrotron light source revealed a significant signal corresponding to covalently bonded nitrogen (spectra not shown). This finding suggests that nitrogen atoms are implanted into the HOSP film and form a thin Si-N surface layer.

The results presented so far have shown that treating the HOSP films with the optimum N_2/H_2 plasma results in the formation of a surface nitride layer, which works effectively in

maintaining the dielectric properties and suppressing the etching of low-k films against O₂ plasma. The optimum energy source is ~300 W-min. However, BD II having a porous structure is seriously damaged by this level of energy input. Indeed, BD II is degraded both in bond structures and dielectric properties even with much smaller energy levels of a few W-min. For example, treating with 10-W for 20 seconds causes the marked rise of leakage current level from 10⁻¹⁰ to 10⁻⁷ MV/cm, in stark contrast to that of the HOSP counterpart shown in Fig. 4.

Another problem for nanoporous IMD is the difficulty of electroless plating. First, proper pore-sealing is required to avoid the penetration/absorption of the plating solution to the bulk film. Otherwise, the absorbed solution would downgrade the insulating capacity. Second, we have found that catalytic seeds cannot be densely and evenly grown on the surface using the seeding process presented previously [9]. As demonstrated by the SEM micrograph on the left of Fig. 5, this ends up with a scarce deposition of poor-quality electroless films. We first sought solutions by using OTS-SAM to passivate the BD II surface. The OTS-coated, hydrophobic BD II became hydrophilic after the brief exposure of plasma for few seconds (Water contact angle was initially 110°, and became under 15° after plasma exposure.) As evidenced from the SEM micrograph on the right of Fig. 5, Cu films were uniformly deposited on the multiple-treated BD II by electroless plating. The role of the SAM in terms of protecting the nanoporous IMD against plasma damage is currently under investigation.

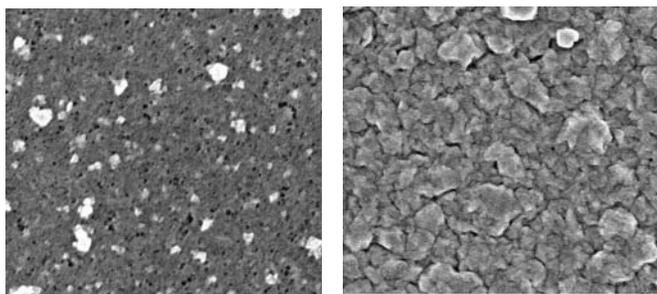


Fig. 5. SEM micrographs of Cu deposits grown on as-deposited (left) and (b) OTS-coated (right) BD II films. The magnification was $\times 50,000$.

CONCLUSIONS

This study has demonstrated that treating spin-coated HOSP films with O₂ or H₂ plasma clearly disrupts the low-polarized molecular bonds. The destructive behavior is associated with a decay of dielectric properties. N₂/H₂ plasma, discharged from N₂ dominant source, with energy input of ~300 W-min is effective in protecting the HOSP films against O₂ plasma damage. However, nanoporous IMD examined herein, i.e., CVD-BD II, is readily damaged by the optimum plasma source (80% N₂-60% H₂) even with an energy input of a few W-min. Coating an SAM on BD II allows Cu films with good morphology to be uniformly deposited by electroless plating. The function of the SAM for the nanoporous layers against plasma damage is currently under examined.

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REFERENCES

- [1] H. Yamamoto, K. Takeda, K. Ishikawa, M. Ito, M. Sekine, M. Hori, T. Kaminatsui, H. Hayashi, I. Sakai, T. Ohiwa, *J. Appl. Phys.*, 109, 084112 (2011).
- [2] K. L. Fang, B. Y. Tsui, *J. Electrochem. Soc.*, 152, G766 (2005)
- [3] I. Fisher, M. Eizenberg, *Thin Solid Films*, 516, 4111 (2008).
- [4] P. I. Wang, J. S. Juneja, Y. Ou, T. M. Lu, G. S. Spencer, *J. Electrochem. Soc.*, 155, H53 (2008).
- [5] J. J. Kim, H. H. Park, S. H. Hyun, *Thin Solid Film*, 377-378, 525 (2000)
- [6] Y. C. Quan, S. Yeo, C. Shim, J. Yang, *J. Appl. Phys.*, 89, 1402 (2001).
- [7] Y. Morikawa, S. Yasunami, W. Chen, T. Hayashi, T. Uchida, *J. Vac. Sci. Technol. A*, 19, 1747 (2001).
- [8] H. Nagai, S. Takashima, M. Hiramatsu, M. Hori, T. Goto, *J. Appl. Phys.*, 91, 2615 (2002).
- [9] G. S. Chen, S. T. Chen, Y. L. Lu, *Electrochem. Commun.*, 9, 2764 (2007)