AIP | Journal of Applied Physics

Thermal stability enhancement of Cu/WN/SiOF/Si multilayers by post-plasma treatment of fluorine-doped silicon dioxide

Seoghyeong Lee, Dong Joon Kim, Sung-Hoon Yang, Jeongwon Park, Seil Sohn et al.

Citation: J. Appl. Phys. **85**, 473 (1999); doi: 10.1063/1.369410
View online: http://dx.doi.org/10.1063/1.369410
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v85/i1
Published by the American Institute of Physics.

JOURNAL OF APPLIED PHYSICS VOLUME 85, NUMBER 1 1 JANUARY 1999

Thermal stability enhancement of Cu/WN/SiOF/Si multilayers by post-plasma treatment of fluorine-doped silicon dioxide

Seoghyeong Lee, Dong Joon Kim, Sung-Hoon Yang, Jeongwon Park,
and Seil Sohn
Department of Metallurgical Engineering, Hanyang University, Seongdong-ku, Seoul 133-791, Korea

Kyunghui Oh
Reliability Technology Division, National institute of Technology and Quality, Kwacheon 427-010, Korea

Yong-Tae Kim
Semiconductor Materials Research Laboratory, Korea Institute of Science and Technology,
Seoul 136-791, Korea

Jung-Yeul Kim
Department of Semiconductor Engineering, Uiduk University, Kyungju 780-713, Korea

Geun-Young Yeom
Department of Material Science & Engineering, Sung Kyun Kwan University, Suwon 440-330, Korea

Jong-Wan Park[a)]
Department of Metallurgical Engineering, Hanyang University, Seongdong-ku, Seoul 133-791, Korea

(Received 14 July 1998; accepted for publication 12 September 1998)

The effect of a post-plasma treatment on the dielectric property and reliability of fluorine doped silicon oxide (SiOF) film was studied. Also, the thermal stability of the Cu/WN interconnect system with SiOF interlayer dielectrics was examined by rapid thermal annealing. The surface roughness of SiOF films increased with increasing plasma treatment power due to ion bombardment effect during the plasma treatment. As the plasma treatment power increased, the dielectric constant increased from 3.16 to 3.43, while the change in the relative dielectric constant of the plasma treated films decreased in magnitude after treatment at 100 °C for 30 min in boiling water. Furthermore, the chemical properties of the plasma treated SiOF layers near the top surface tend to resemble those of thermal oxides after plasma treatment with sufficient plasma power, apparently due to the reduction in the Si–F bonding in the films. In the case of a Cu/WN/SiOF/Si multilayer structure, surface oxidation and densification due to the plasma treatment seemed to play an important role in suppressing the interdiffusion between SiOF and metal interconnects. © *1999 American Institute of Physics.* [S0021-8979(98)02524-9]

I. INTRODUCTION

In multilevel interconnections, it has been predicted that RC delay of ultralarge scale integration (ULSI) circuits will limit operating speed of devices as parasitic resistance and capacitance increase. Propagation delays due to parasitic capacitance from interconnects are one of the main causes for reducing speed performance in advanced integrated circuits (ICs) as interconnect dimensions are scaled down.[1] In advanced logic devices, the stack of interlayer dielectrics (ILDs) has increased to eight or nine layers beyond the 0.07 μm technology.[2] On the other hand, high performance circuits are approaching speed limitations due to the interconnect dielectrics of conventional SiO_2-based materials, such as phosphosilicate glass (PSG), borophosphosilicate glass (BPSG), etc.[3] This is caused by large parasitic capacitance in the multilevel interconnections.[3–10] Therefore, it is necessary to reduce this parasitic capacitance to achieve high performance in ULSI circuits. One of the most effective ways to reduce the parasitic capacitance is using low dielectric constant materials for the interlayer dielectrics. The SiOF film is one of the realistic solutions for the low dielectric constant films in the ULSI multilevel interconnections. However, instability issued related to Si–F bonds must be overcome before process integration in multilevel interconnects. Also, in the subhalf micron region, it is necessary to reduce the resistivity of interconnection materials for implementation of new materials. Copper is a leading candidate because of its lower electrical resistivity and higher resistance to electromigration than aluminum. However, there are still many unsolved problems related with low dielectric constant ILDs, diffusion barrier, and damascene processes.[11]

The purpose of this research is to study the effect of post-plasma treatment on the reliability and dielectric properties of SiOF films. The reliability of the SiOF films in the Cu/WN/SiOF/Si multilayer structure was also studied.

II. EXPERIMENT

The SiOF films were deposited using an electron cyclotron resonance chemical vapor deposition (ECRCVD) system (AsTeX Model AX4505). Deposition of films was per-

---

[a)] Electronic mail: jwpark@email.hanyang.ac.kr

formed under predetermined conditions while the SiF_4/O_2 flow ratio in the feed mixture was varied.[4,5] The microwave power and substrate temperature during deposition were fixed at 700 W and 300 °C, respectively. The deposition time was adjusted to deposit films of appropriate thickness for analytical measurements. SiF_4 gas was introduced into the reaction chamber, while O_2 and Ar gases were introduced into the plasma generation chamber. The substrates employed in this study were B-doped *P*-type Si (100) wafers.

The post-plasma treatment of the SiOF films was carried out using O_2 plasma *in situ* at 300 °C with various plasma power values after the deposition. The effect of the post-plasma treatment on the reliability and dielectric properties of the SiOF films was examined in terms of the post-plasma treatment power. The change in surface roughness was measured by an atomic force microscope (AFM). Ellipsometric measurements for determination of film thickness and refractive index were made at five points in each sample using a Rudolph AutoEL MS ellipsometer. The chemical bonding structure of the films was evaluated by Fourier transform infrared spectroscopy (FTIR). The change in SiOF film composition after the post-plasma treatment was investigated using an angle-resolved x-ray photoelectron spectroscope (ARXPS). The *C–V* characteristics of the SiOF films were measured as a function of plasma treatment power. To evaluate the dielectric constant stability of the plasma treated SiOF films, the change in dielectric constant of SiOF films was measured after the boiling treatment in boiling water for 100 min. Specimens for the stability test were prepared in the form of Cu/WN/SiOF/Si system. The WN films were deposited at room temperature by plasma enhanced chemical vapor deposition (PECVD) with WF_6 and NH_3 gases and Cu films were deposited at room temperature by thermal evaporation. The reliability test of Cu/WN/SiOF/Si specimens was carried out as a function of temperature by rapid thermal annealing (RTA) in N_2 ambient for 30 s. After RTA treatment, the degree of diffusion and interface reactions taking place in the Cu/WN/SiOF/Si systems were evaluated by Auger electron spectroscopy (AES) compositional depth profiles, Rutherford backscattering spectrometry (RBS), and secondary ion mass spectrometry (SIMS). In RBS analysis, we utilized the computer simulation program RUMP for simulation and interpretation of RBS spectra. Microstructural analyses of samples were performed by transmission electron microscope (TEM).

III. RESULTS AND DISCUSSION

Figure 1 shows the changes in the surface roughness of the SiOF films as a function of plasma treatment power. The substrate temperature and treatment time were fixed at 300 °C and 3 min, respectively. The surface roughness of the SiOF films increased with increasing plasma treatment power. The surface roughness of a nonplasma treated SiOF film was 19.1 Å. On the other hand, as the plasma treatment power increases to 700 W, the surface roughness of the SiOF film increases to 30.4 Å. These results might be due to the etching effect by the post-plasma treatment.

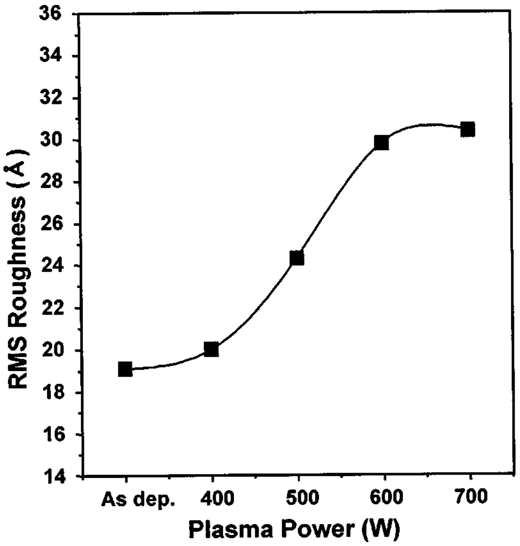

FIG. 1. Surface roughness of SiOF films as a function of plasma treatment power.

Figures 2 and 3 show FTIR spectra and variation of (Si–F)/[(Si–O)+(Si–F)] peak intensity ratio from FTIR spectra of the SiOF films as a function of plasma treatment power. As shown in Fig. 2, the Si–O stretching peak located at around 1080 cm^{-1} and the Si–F stretching peak located at around 930 cm^{-1} were observed. The peak position of Si–O stretching bonds gradually shifted to lower wavenumbers from somewhere around 1080 cm^{-1} with the increasing post plasma treatment power. It is supposed that bonding strength of Si–O was changed with the desorption of Si–F bonds because of ion bombardment during the post-plasma treatment. This result is in agreement with the result of Fig. 3. Figure 3 shows that the (Si–F)/[(Si–O)+(Si–F)] peak intensity ratio of the SiOF films with various plasma treatment powers. The (Si–F)/[(Si–O)+(Si–F)] peak intensity ratio decreased with the plasma treatment power. From the results mentioned above, it is supposed that some of fluorine atoms

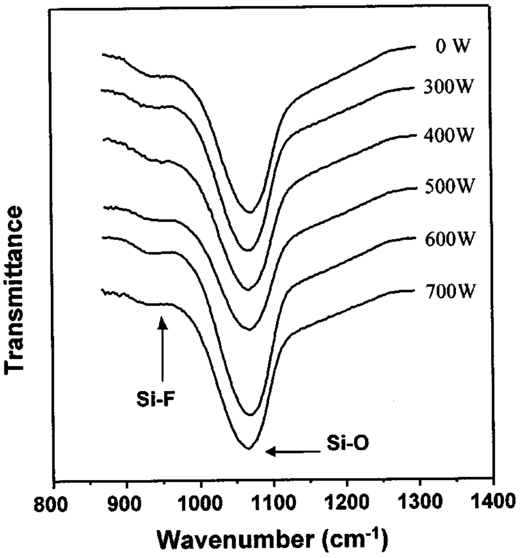

FIG. 2. FTIR spectra of SiOF films as a function of plasma treatment power.

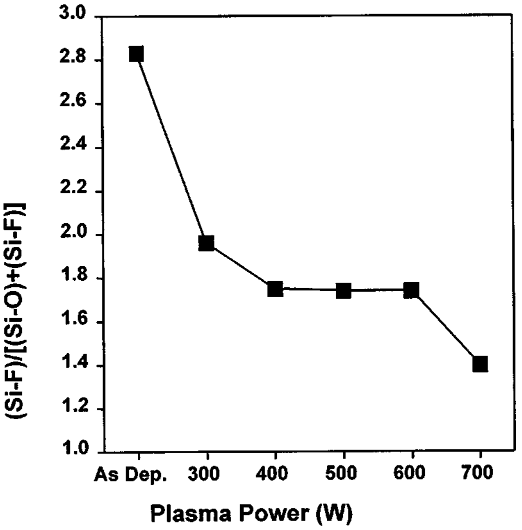

FIG. 3. Variation of (Si–F)/[(Si–O)+(Si–F)] peak intensity ratio in FTIR spectra as a function of plasma treatment power.

in the top layer of the SiOF film were replaced by oxygen atoms by O_2 plasma treatment. This suggestion was verified by ARXPS of the SiOF films.

The atomic concentration values from ARXPS of the SiOF films with various plasma treatment powers are plotted in Fig. 4. In the case of 700 W, fluorine atoms almost disappear in the top layer. The larger the plasma treatment power, the deeper the fluorine desorbed region. Therefore, as the plasma treated power increases, the chemical properties of the plasma treated SiOF films near the top layer tend to resemble those of thermal oxides because of the reduction in the Si–F bonding in the films.

Figure 5 shows relative dielectric constant of the as-plasma treated SiOF films and the boiled SiOF films as a function of microwave power of the post-plasma treatment. The relative dielectric constant of the post-plasma treated SiOF films was increased from 3.16 to about 3.43 with the plasma treatment power. This result suggests that the increment of the relative dielectric constant is due to the change in the surface chemical composition by desorption of fluorine atoms and the densification of the film by oxygen ion bombardment effect. Moreover, the difference of relative dielectric constant of the SiOF films between before and after the boiling treatment decreased with increasing plasma treatment power. In the case of the nonplasma treated SiOF film, the relative dielectric constant after boiling treatment increased from 3.16 to 3.65, while that of the 700 W plasma treated film increased from 3.43 to 3.47, which corresponds to about 15% and 1.2% increments, respectively. This result implies that the resistance to water absorption increased with increasing plasma power because of the densification of the top layer and reduction in the number of Si–F bonds that tend to associate with OH bonds.

RBS spectra taken from the Cu/WN/SiOF/Si stacks that were RTA treated for 30 s at various temperatures are shown in Fig. 6. In the case of the nonplasma treated SiOF films, after 900 °C annealing, apparent movement of all elements involved in the films is shown. However, for the plasma

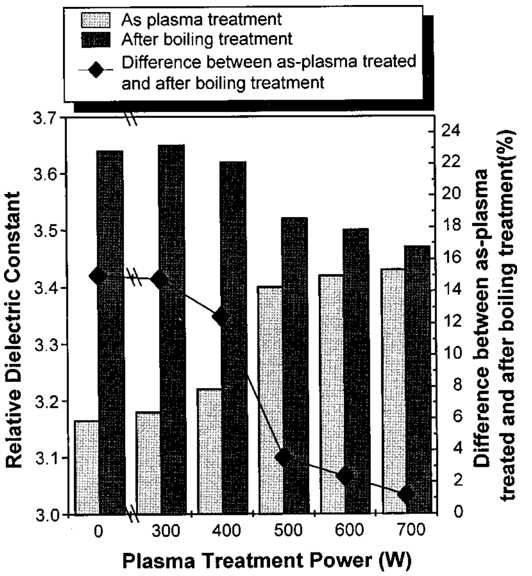

FIG. 5. Relative dielectric constant of SiOF films before and after a boiling treatment as a function of plasma treatment power.

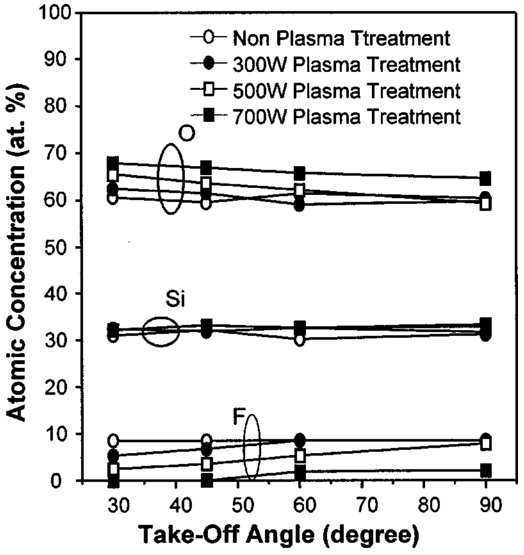

FIG. 4. ARXPS atomic concentration of SiOF films with various plasma treatment power.

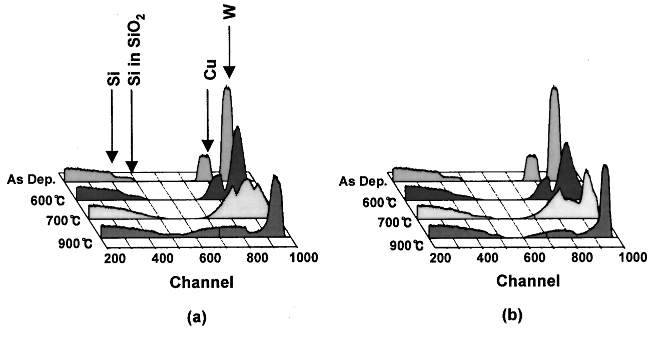

FIG. 6. RBS spectra of Cu/WN/SiOF/Si multilayers with various RTA treatment temperatures; (a) nonplasma treated SiOF films and (b) plasma treated SiOF films at 700 W.

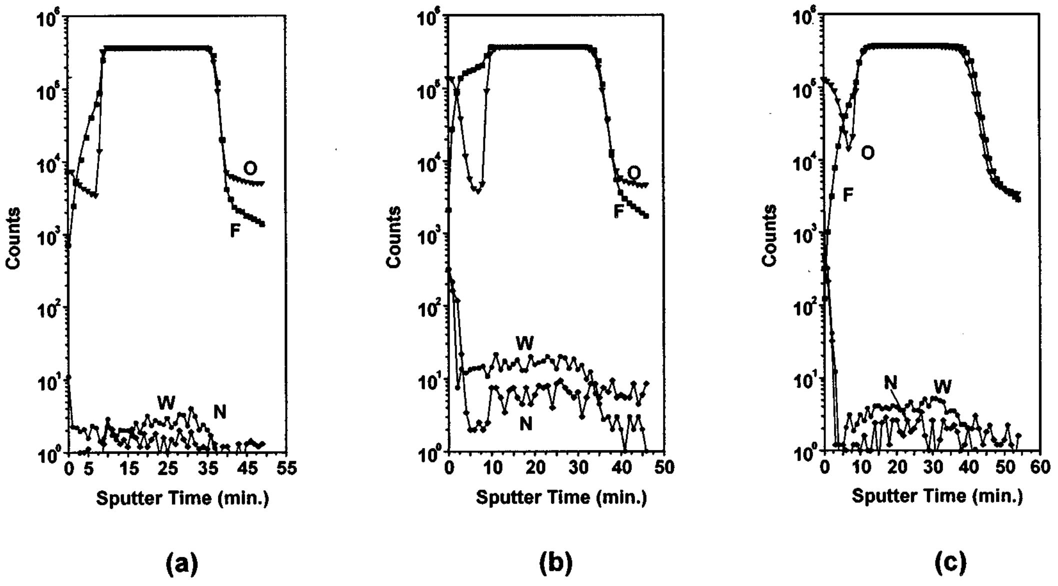

FIG. 7. SIMS depth profiles of Cu/WN/SiOF/Si multilayer before and after RTA treatment. The top Cu/WN films were removed before SIMS profiling; (a) 700 W plasma treatment and no RTA treatment, (b) nonplasma treatment and 800 °C RTA treatment, and (c) 700 W plasma treatment and 800 °C RTA treatment.

treated SiOF case, even though some intermixing between Cu and WN layers was occurred, Cu and/or WN were not observed to diffuse into the SiOF layer. It is thought that surface oxidation and densification due to the plasma treatment seemed to play a role in obstructing the interdiffusion between SiOF and metal interconnects.

In order to confirm the RBS data and investigate the interdiffusion between metal interconnects and SiOF ILD, SIMS depth profiles of the Cu/WN/SiOF/Si multilayers are shown in Fig. 7 after the top Cu/WN layers were removed for the cases of (a) no RTA treatment with 700 W plasma treatment, (b) 800 °C RTA treatment without plasma treatment and, (c) 800 °C RTA treatment with 700 W plasma treatment. After 800 °C RTA treatment, in the case of the nonplasma treated SiOF films, the fluorine atoms were observed to out-diffuse into the WN layer and W and N atoms diffuse into the SiOF layers. However, in the case of the 700 W plasma treated SiOF films, no significant change in the depth profile was observed after the 800 °C annealing as compared to that of the specimen with 700 W plasma treatment but without RTA treatment. This result implies that the interdiffusion of W, N, and F atoms at the WN/SiOF interface was suppressed by forming dense silicon oxide layer caused by post oxygen plasma treatment.

Figure 8 shows cross-sectional TEM (XTEM) images of Cu/WN/SiOF/Si multilayers. XTEM specimens were prepared after removing Cu layer by a Cu etchant (H_3PO_4:HNO_3:$HC_2H_3O_2$:H_2O=80:5:5:10) in order to circumvent poor adhesion problem between Cu and WN layers during preparation of the attached specimen. The XTEM image of the Cu/WN interface which was rapid thermal annealed at 800 °C shows that a large amount of WN diffused into the SiOF layer and reacted with the SiOF during annealing in good agreement with the RBS spectra.

IV. CONCLUSIONS

The effect of the post-plasma treatment on the dielectric property and reliability of SiOF films as well as the thermal stability of Cu/WN interconnect system with SiOF intermetal dielectrics were investigated. The surface roughness of SiOF films increased from 19.1 to 30.4 Å with the increasing plasma treatment power. As the plasma treatment power increased, the dielectric constant increased from 3.16 to 3.43, nevertheless, the change in the relative dielectric constant of the plasma treated films by the boiling treatment was decreased in magnitude. Furthermore, as the plasma treated power increased, the chemical properties of the plasma treated SiOF films near the top surface tend to resemble those of thermal oxides because of the reduction in the Si–F bonding in the films. In the case of the Cu/WN/SiOF/Si multilayer structure, the plasma treatment seemed to play a big role in suppressing the interdiffusion between SiOF and metal interconnects.

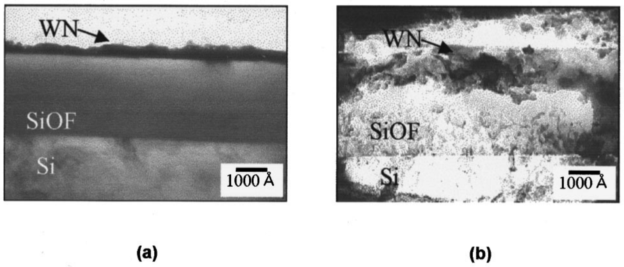

FIG. 8. Cross-sectional TEM images of Cu/WN/SiOF/Si films after Cu etched; (a) as-deposited and (b) 800 °C RTA treatment for 30 s.

ACKNOWLEDGMENTS

This work was financially supported by Korea Science and Engineering Foundation (95-0300-15-01-3) and Korean Ministry of Education through Inter-University Semiconductor Research Center (ISRC 97-E-1053) in Seoul National University.

[1] R. K. Laxman, Semicond. Int. **18**, 71 (1995).
[2] *The National Technology Roadmap for Semiconductors* (Semiconductor Industry Association, San Jose, CA, 1997).
[3] T. Homma, Y. Murao, and R. Yamagushi, J. Electrochem. Soc. **140**, 3599 (1993).
[4] S. Lee and J.-W. Park, J. Appl. Phys. **80**(9), 5260 (1996).
[5] S. Lee and J.-W. Park, Mater. Chem. Phys. **53**, 150 (1998).
[6] T. Tamura, Y. Inoue, M. Satoh, H. Yoshitaka, and J. Sakai, Jpn. J. Appl. Phys., Part 1 **35**, 2526 (1996).
[7] Y. J. Mei, T. C. Chang, S. J. Chang, F. M. Pan, M. S. K. Chen, A. Tuan, S. Chou, and C. Y. Chang, Thin Solid Films **308/309**, 501 (1997).
[8] M. J. Shapiro, S. V. Nguyen, T. Matsuda, and D. Dobuzinsky, Thin Solid Films **270**, 503 (1995).
[9] T. Homma, Thin Solid Films **278**, 28 (1996).
[10] S. Mizuno, A. Verma, P. Lee, and B. Nguyen, Thin Solid Films **279**, 82 (1996).
[11] R. J. Gutmann, T. P. Chow, A. E. Kaloyeros, W. A. Lanford, and S. P. Muraka, Thin Solid Films **262**, 177 (1995).