論文 / 著書情報
Article / Book Information

Title	Tantalum Nitride Sputtering Deposition with Xe on Fluorocarbon for Cu Interconnections
Authors	Takenao Nemoto, Hiroshi Imai, Akinobu Teramoto, Takashi Ito, Shigetoshi Sugawa, Tadahiro Ohmi
Citation	Journal of The Electrochemical Society, Vol. 155, No. 5, pp. H323-H328
発行日 / Pub. date	2008, 3
DOI	10.1149/1.2883736
権利情報 / Copyright	(c) The Electrochemical Society, Inc. 2008. All rights reserved. Except as provided under U.S. copyright law, this work may not be reproduced, resold, distributed, or modified without the express permission of The Electrochemical Society (ECS). The archival version of this work was published in Journal of The Electrochemical Society, Vol. 155, No. 5, pp. H323-H328

Journal of The Electrochemical Society, **155** (5) H323-H328 (2008)
0013-4651/2008/155(5)/H323/6/$23.00 © The Electrochemical Society

Tantalum Nitride Sputtering Deposition with Xe on Fluorocarbon for Cu Interconnects

Takenao Nemoto,[a,z] Hiroshi Imai,[b] Akinobu Teramoto,[a,*] Takashi Ito,[b] Shigetoshi Sugawa,[b] and Tadahiro Ohmi[a,*]

[a]*New Industry Creation Hatchery Center and* [b]*Graduate School of Engineering, Tohoku University, Aramaki, Aoba-ku, Sendai, 980-8579, Japan*

TaN was sputter-deposited with radio frequency (rf) bias in Xe gas for a barrier film of Cu interconnects of advanced large-scale integration (LSI). Xe gas has been reported to reduce damage on substrates due to small ion bombardment. While crystalline TaN was formed by sputtering with rf bias, amorphous TaN was formed by sputtering without rf bias. TaN with rf bias shows superior barrier properties against Cu diffusion to that without rf bias. When Cu/TaN/fluorocarbon was annealed in temperatures higher than 200°C, delamination was found at the interface between the Cu and TaN. The SiCN cap layer over fluorocarbon improved adhesion, which increased the critical temperature to an acceptable range for LSI production. Assuming a simple center-of-mass elastic collision of the isolated particle, values of energy-transfer efficiency from an impinging ion to various kinds of substrate atoms were calculated. These result revealed that Xe ions efficiently transfer energy to TaN to build a crystalline structure without energy transferring to fluorocarbon.
 [DOI: 10.1149/1.2883736]

Manuscript submitted November 13, 2007; revised manuscript received January 11, 2008.
Available electronically March 19, 2008.

The demands to save power consumption and to increase clock speed of advanced large scale integration (LSI) have been increasing as generation of LSI products progresses. The developments of a low-resistance wiring material and a low-dielectric-constant (low-k) material have become important toward achieving those requirements.[1,2] A SiCOH film with $k = 3.0$ has been introduced to a 90 nm node LSI product, and a porous SiCOH film aiming for less than $k = 3.0$ has been developed for the 45 nm generation and beyond.[3] The issues of weak mechanical strength due to their porous structure and serious introduction of damage by the plasma process, however, are inhibitions to porous SiCOH film implementation to production.[4] A fluorocarbon film, that is an organic low-k material, is proposed for next-generation intermetal dielectrics.[5] Fluorocarbon has a carbon structure with fluorine and claims an intrinsically lower k-value without a porous structure. The advantageous nonporous fluorocarbon film is expected to improve endurance to etching damage, avoiding plasma damage introduction to the film, and can help to accomplish good film properties and adhesion. It has been demonstrated that plasma damage in etching and ashing processes degrade film properties and adhesion,[6] but few works regarding plasma damage in sputtering have been found.

In this paper, tantalum nitride (TaN) followed by copper (Cu) sputtering deposition with Xe inert gas was performed in order to reduce plasma damage. TaN was reported to show a superior barrier property against Cu diffusion.[7] Regarding the benefits of Xe inert gas over Ar gas, the authors have demonstrated successful formation of TaN on gate oxide by Xe sputtering deposition.[8] They have also reported that polysilicon grown by Xe sputtering showed better crystallinity than that grown in Ar at temperatures as low as 400°C.[9] This study also concluded that lower plasma potential in the Xe plasma than Ar provided less plasma damage to the substrate, and more effective energy transfer by Xe ions than Ar ions improved crystallinity. In this study we applied Xe plasma sputtering to demonstrate the benefits of Cu and TaN on fluorocarbon for next-generation LSI.

Experimental

A 300 nm fluorocarbon film was deposited by using the radial line slot antenna (RLSA) plasma-enhanced chemical vapor deposition (PECVD) reactor. The RLSA PECVD reactor utilizing microwave creates very low electron temperature plasma leading to no damage on the substrate.[10] The fluorocarbon film deposited by the RLSA PECVD reactor formed a suitable film for the LSI products.[11] The 300 nm fluorocarbon film and a 30 nm SiCN on fluorocarbon stack film were prepared on the Si substrate. Thermally grown oxide on Si was also prepared as a reference. The 50 nm TaN film and the 100 nm Cu film were sputter-deposited by the self-ionized sputtering chamber.[12] TaN and Cu were formed without exposure to air. TaN was deposited with an 8% flow rate of N_2 in the Xe inert gas. The sputtering pressure of TaN was 3.4 Pa and the temperature was 150°C. Either 350 W radio frequency (rf) bias on the substrate or no bias was applied to investigate the influence of rf bias. DC voltage between plasma and the substrate, V_{dc}, and peak-to-peak voltage, V_{pp}, during rf bias were measured and they were −2 and 11 V, respectively. Cu was deposited in 5.7×10^{-5} Pa at −10°C substrate temperature and with 400 W rf bias on the substrate. These samples were annealed in low oxygen ambient at various temperatures for 1 h. Adhesion was examined by visual inspection, and depth profiles were measured by secondary ion mass spectrometry (SIMS). A TaN film orientation was also detected by X-ray diffraction (XRD). The 0.3 μm width and 0.4 μm depth lines were fabricated in SiO_2/Si substrate to measure step coverage of TaN and Cu/TaN.

Results and Discussion

Adhesion inspection.— Adhesion inspection test results of fluorocarbon films are summarized in Table I. "F" stands for failure and "P" stands for pass, which shows no delamination. Every failure appears as delamination between Cu and TaN. Delamination was found in Cu/TaN with rf bias on the fluorocarbon film after 250°C annealing, while no delamination was found in Cu/TaN without rf bias lower than 300°C annealing. No delamination was also seen in Cu/TaN with rf bias on the SiCN/fluorocarbon stacked film after 350°C annealing. These results show that adhesion at the Cu and TaN interface is weaker than others, and this indicates that the substrate, either fluorocarbon or SiCN/fluorocarbon, should not be dam-

Table I. Result of delamination of Cu and TaN.

Film	Substrate	Temperature 200°C	250°C	300°C	350°C
Cu/with rf bias TaN	Fluorocarbon	P	F	F	F
Cu/without rf bias TaN		P	P	F	F
Cu/with rf bias TaN	SiCN/fluorocarbon				P

* Electrochemical Society Active Member.
z E-mail: tnemoto@fff.niche.tohoku.ac.jp

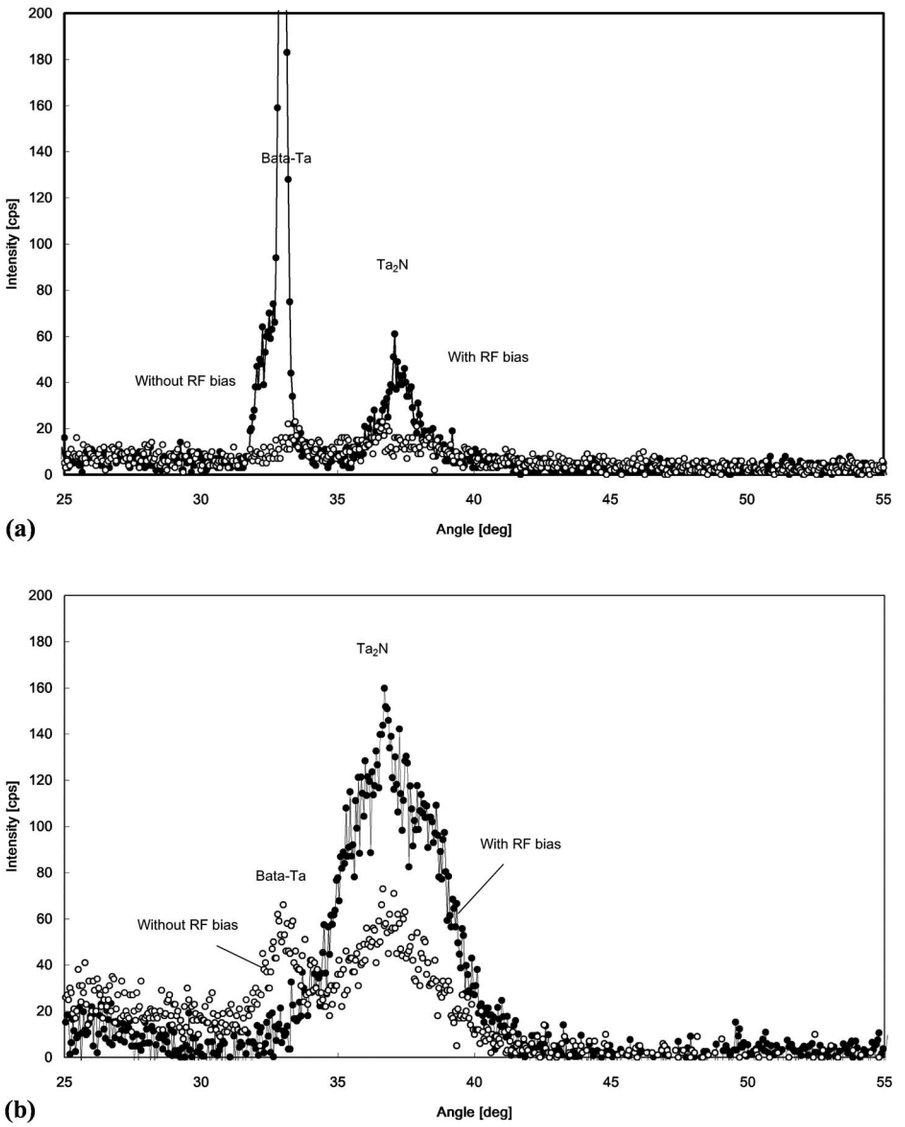

Figure 1. Crystalline orientation of TaN with and without rf bias: (a) as-deposited TaN and (b) after 500°C annealing.

aged by Xe plasma sputtering during TaN deposition. Moreover, rf bias degrades adhesion when TaN deposits on the fluorocarbon film, and the SiCN capping layer improves adhesion properties. No delamination was observed in Cu/TaN on thermal oxide after 500°C annealing.

Film properties of TaN with and without rf bias on thermal silicon oxide.— Crystal orientations of TaN, with and without rf bias, measured by XRD, are shown in Fig. 1. Figures 1a and b show the result of TaN and that after 500°C and 1 h annealing. In Fig. 1a, significant body-centered cubic (bcc)-Ta and Ta_2N peaks appeared in TaN with rf bias, but smaller peaks were found in TaN without rf bias. In Fig. 1b, for TaN with rf bias, the bcc-Ta was diminished and the Ta_2N peak was evolved by annealing. However, crystallinity was not significantly improved by annealing for the TaN without rf bias. These results reveal that TaN with rf bias shows good crystallinity and Ta grains change to those of Ta_2N after annealing. TaN without rf bias constructs an amorphouslike structure even after annealing. The authors reported that Cu(111) orientation formed by sputtering deposition with rf bias was increased by ion bombardments.[13] Even though Xe plasma reduces plasma potential, TaN crystallinity is improved by ion bombardment produced by rf bias. Figures 2a and b show the Ta and N binding energies of TaN, with and without rf bias, measured by X-ray photoelectron spectroscopy (XPS), respectively. In Fig. 2b, more N 1s intensity is found in TaN without rf bias than that in TaN with rf bias; thus, more N atoms incorporate in TaN without rf bias than in TaN with rf bias. This result is supported by the results of Fig. 2a, because more N atom incorporation makes Ta $4f_{7/2}$, which is a Ta main peak, in TaN without rf bias chemical-shift toward higher energy.[14] Consequently, a crystalline TaN film with fewer N atoms was grown by sputtering in Xe with rf bias to substrate, compared to the amorphous TaN film with more N atoms without rf bias.

Cu/TaN on thermal silicon oxide.— Figures 3a and b show the results of TaN as-deposited and that after 500°C and 1 h annealing. Few Cu atoms diffuse in TaN after annealing, thus, TaN with rf bias inhibits Cu diffusion. Figures 4a and b show SIMS depth profiles of Cu/TaN without rf bias on thermal silicon oxide before and after 500°C annealing. Cu atoms diffuse to thermal silicon oxide through the TaN layer, as shown in Fig. 4b. These results reveal that TaN with rf bias has superior barrier properties to TaN without rf bias. Cu diffusion barrier properties of TaN were studied in some reports, and they concluded that TaN with an amorphous structure or a few N atoms incorporation shows inferior barrier properties.[15,16] In this examination, sputtering-deposited TaN with rf bias, which incorpo-

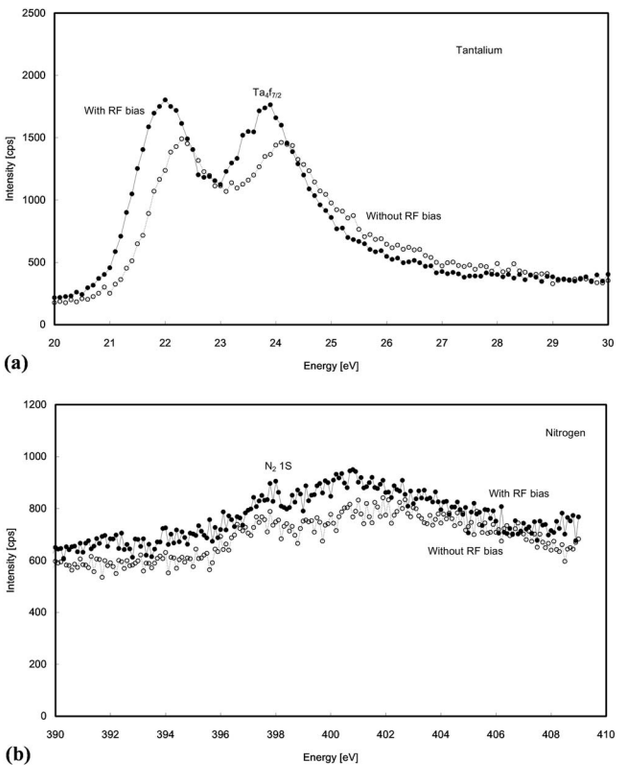

Figure 2. Binding energy of (a) Ta $4f_{7/2}$ and (b) N 1s profiles measured by XPS.

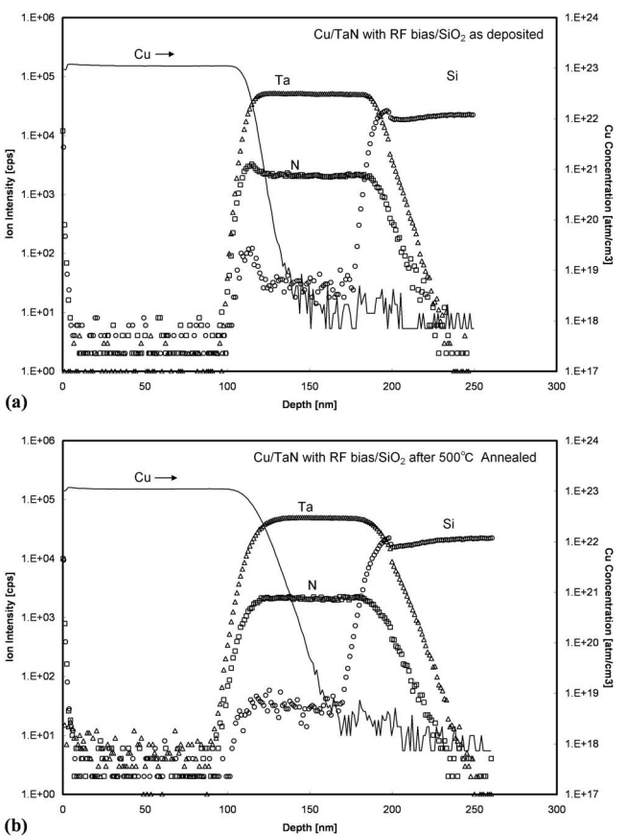

Figure 3. SIMS depth profiles of Cu/TaN with rf bias/SiO_2: (a) as-deposited Cu/TaN/SiO_2 and (b) Cu/TaN/SiO_2 after 500°C annealing.

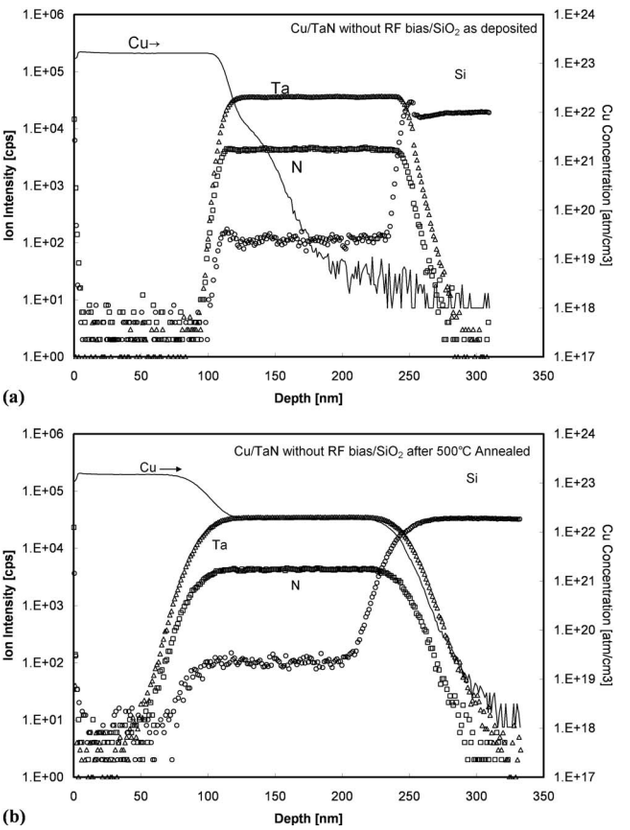

Figure 4. SIMS depth profiles of Cu/TaN without rf bias/SiO_2: (a) as-deposited Cu/TaN/SiO and (b) Cu/TaN/SiO_2 after 500°C annealing.

rates fewer N atoms and more crystallinity than that without rf bias, exhibits better Cu diffusion barrier properties; thus, crystallinity is considered to improve Cu barrier property compared to N atom concentration.

Cu/TaN on fluorocarbon.— Figures 5a and b show SIMS depth profiles of Cu/TaN with rf bias on the fluorocarbon film before and after 200°C annealing. In these results, fluorine (F), carbon (C), and tantalum (Ta) atoms diffused into Cu, but no Cu atoms diffused into TaN. Since Ta_2N is more stable than Ta, because the Gibbs energies of Ta and Ta_2N are reported to be 0.7 eV and 4.5 eV,[17] Ta atoms in bcc-Ta grains are considered to diffuse into Cu layer. Figure 6 shows SIMS depth profiles of TaN without rf bias before and after annealing. F and C atoms existed in TaN and they stayed after annealing. Cu atoms diffused to the thermal silicon oxide through the fluorocarbon layer. These results are consistent with the results of Fig. 4, which reveal that Cu atoms are in TaN after annealing. The result that delamination appeared in TaN with rf bias at 250°C annealing and no delamination in TaN without rf bias at 300°C annealing is evidence that adhesion between TaN with rf bias and Cu should be less than that between TaN without rf bias and Cu. Carbon is reported to degrade adhesion to form an amorphous layer on metal,[18] and fluorine is also known to raise adhesion issues.[19] The occurrence of intermixing of Ta and Cu is considered to improve adhesion at the TaN and Cu interface in a TaN without rf bias sample. Therefore, while F and C were found in both TaN and without rf bias at the TaN and Cu interface, intermixing of Cu and TaN without rf bias improved adhesion at the interface between Cu and TaN. However, Cu atoms in dielectric can degrade LSI reliability. Thus, TaN without rf bias should not be implemented on an actual LSI product.

Ion bombardment in plasma is considered to result in accommodation of substrate materials in a deposited film, and this more likely

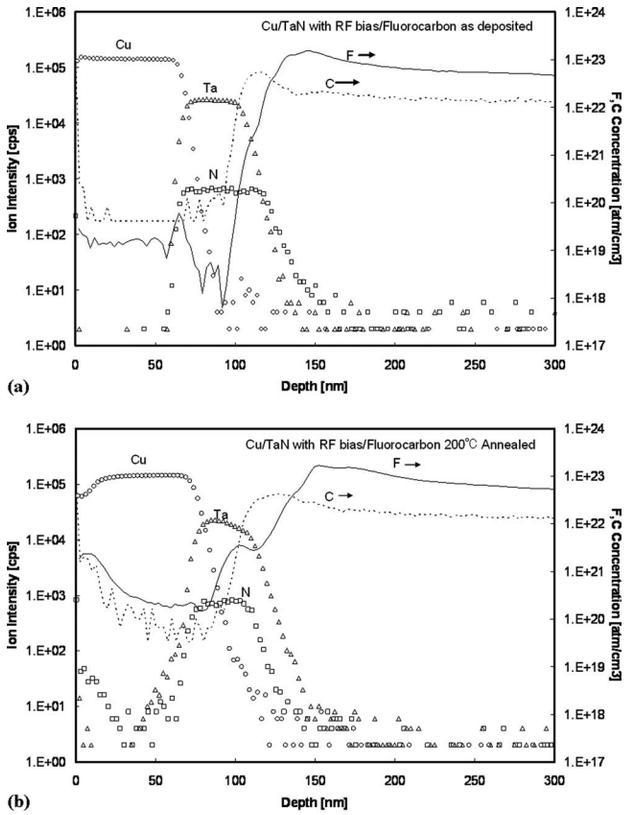

Figure 5. SIMS depth profiles of Cu/TaN with rf bias on fluorocarbon: (a) as-deposited Cu/TaN/fluorocarbon and (b) after 200°C annealing.

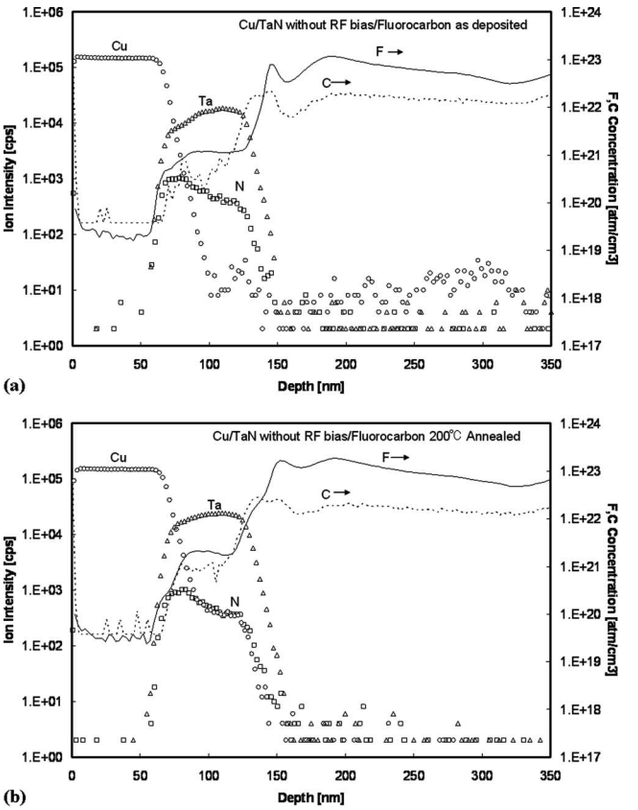

Figure 6. SIMS depth profiles of Cu/TaN without rf bias on fluorocarbon: (a) as-deposited Cu/TaN/fluorocarbon and (b) after 200°C annealing.

happens in the higher energy ion bombardment. The fact that there are no F and C atoms in TaN with rf bias before annealing is attributed to the fact that there is no significant ion bombardment by Xe plasma. The existence of F and C atoms in TaN without rf bias before annealing is, however, caused by the poor Cu barrier properties of the TaN film without rf bias. The benefits of Xe plasma are discussed in a later section.

Cu/TaN on SiCN/fluorocarbon.— Figures 7a and b show SIMS depth profiles of Cu and TaN with rf bias on the SiCN/fluorocarbon stacked film before and after 350°C annealing. No F and C atoms in TaN after annealing represents that the SiCN cap layer on fluorocarbon stopped their diffusion. No delamination higher than 350°C annealing, which is much improved from results of fluorocarbon, should be contributed by the SiCN cap layer. While SiCN has been investigated for implementation as a cap layer on porous SiCOH to avoid moisture diffusion,[20] SiCN is considered to be a suitable material to stop F and C atoms from diffusing into the fluorocarbon layer. This result indicates that when Cu and TaN formed on the low-*k* fluorocarbon material, the TaN film prepared with rf bias sputtering deposition and the SiCN cap layer improves the thermal budget so that it can be applied to an actual LSI product process.

Step coverage.— A picture of step coverage for TaN with rf bias followed by Cu sputtering is shown in Fig. 8. Step coverage for TaN with rf bias achieved 70%; however, that for TaN without rf bias showed less than 50%. The small gap between Cu and TaN in Fig. 8 is considered to be a shadow for the cleaved sample. Therefore, no critical void was found in the Cu wiring, indicating TaN with rf bias in Xe sputtering is practically applicable to actual damascene structures.

Benefits of Xe plasma.— Assuming a simple center-of-mass elastic collision of the isolated particle, the energy transfer efficiency, η, from an impinging ion to substrate atoms is given by Eq. 1 [21]

$$\eta = \frac{4M_{\text{ion}}/M_{\text{sub}}}{(1 + M_{\text{ion}}/M_{\text{sub}})^2} \qquad [1]$$

where M_{ion} is the atomic mass of Ar or Xe ion, and M_{sub} is that of Ta, C, and F atoms. According to Eq. 1, the maximum energy transfer efficiency, η, becomes 100% when the atomic mass number of ion, M_{ion}, equals the atomic mass number of ion, M_{sub}.

By using Eq. 1 and the atomic mass values listed in Table II, various combinations of the energy transfer efficiency can be calculated and they are shown in Table II. In Table II, the energy transfer efficiency of the Xe ion to the Ta, C, and F atom are calculated as 97, 37, and 44%, respectively. Thus, most of the energy transferred from the Xe ion to the Ta atom compared with the Ar ion to the Ta atom was (η = 59%), but some energy transferred from the Xe ion to the C and F atom compared with the Ar ion to the C atom (η = 71%) and F atom (η = 81%). The energy of ion bombardments is reported to be necessary to improve film crystallinity, but this also generates damage on the substrate. Thus, more energy transfer to TaN and less energy transfer to the substrate, which consists of C and F atoms, from the Xe ion should be suitable to form metal films on a delicate substrate.

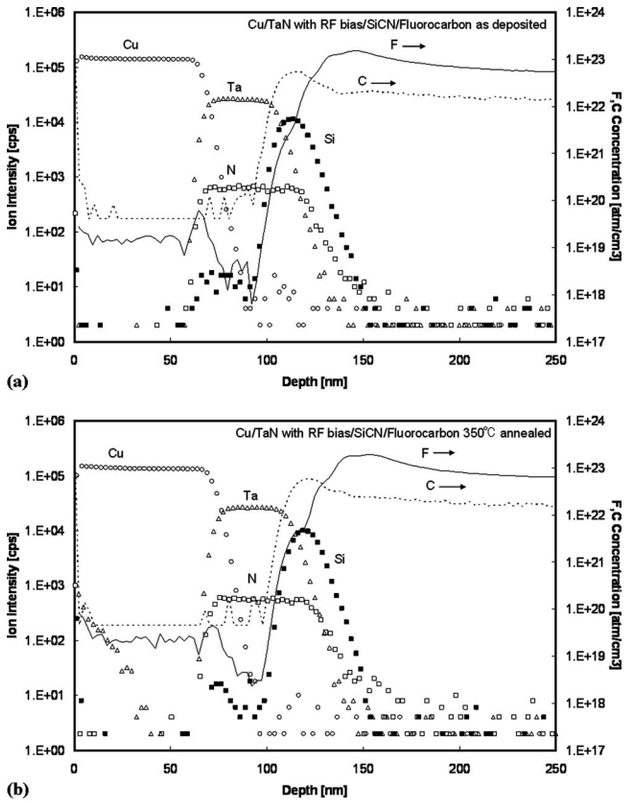

Figure 7. SIMS depth profile of Cu and TaN with rf bias on the SiCN/fluorocarbon stacked film: (a) as-deposited Cu/TaN/SiCN/fluorocarbon and (b) after 350°C annealing.

The floating potential, V_f, is estimated by Eq. 2

$$V_f = V_{pp} - V_{dc} \quad [2]$$

where V_f is floating potential. The transferred energy of the ion, E_{ion}, can be calculated by Eq. 3

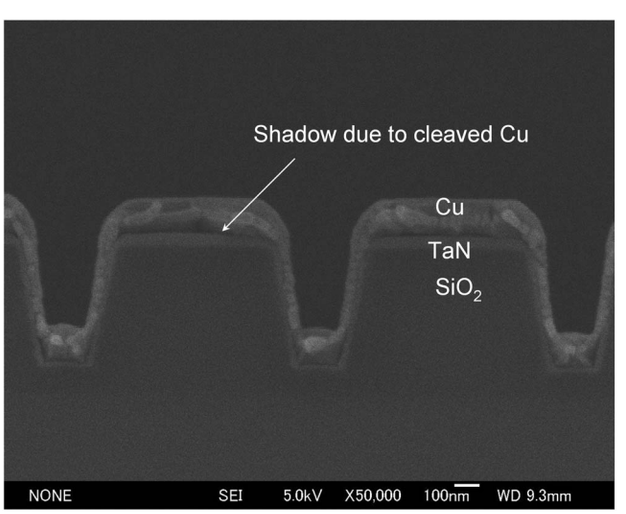

Figure 8. Step coverage of Cu/TaN with rf bias on damascene structure.

Table II. Efficiency of energy transfer.

	M_{ion}	M_{sub}	Transfer efficiency
Xe/Ta	131.3	180.9	0.97
Xe/C	131.3	12.0	0.31
Xe/F	131.3	19.0	0.44
Ar/Ta	40.0	180.9	0.59
Ar/C	40.0	12.0	0.71
Ar/F	40.0	19.0	0.87

$$E_{ion} = \eta \times V_{ion} \quad [3]$$

where V_{ion} is the energy of ion on the substrate through plasma, and this was given by Eq. 2. Binding energies of various substrates are shown in Table III.[22]

All binding energies relating with C and F atoms were less than both E_{ion} values; thus, no damage is considered to the substrate in Xe plasma. This estimation is in good agreement with the result in Fig. 6 that there were no C and F atoms in TaN, even after rf bias plasma was applied. Larger energy transferred to Ta and TaN films is expected to improve the crystallinity. While the difference of E_{ion} values with rf bias and without rf bias is almost 1.0 eV, this amount should be effective, because Ta–Ta or Ta_2N binding energies are as small as 0.7 and 4.5 eV, respectively.[17] Ar plasma has been reported to show about 10 eV higher energy than Xe in high-density plasma, and higher energy transfer efficiency in Table II influences the generation of damage on fluorocarbon substrates.

Conclusions

Cu and TaN were sputter-deposited in Xe inert gas on fluorocarbon or SiCN/fluorocarbon prepared by an RLSA PECVD reactor. Adhesion was examined after annealing at various temperatures, and depth profiles were detected by SIMS. The following conclusions were obtained:

1. A crystalline TaN film with fewer N atoms was grown by sputtering in Xe with rf bias to substrate, while the amorphous TaN film with more N atoms was grown without rf bias. After 500°C annealing, a Ta_2N peak evolved in the TaN film with rf bias, but an amorphous structure was kept in the TaN film without rf bias.
2. The adhesion between Cu and TaN film deposited with rf bias on the fluorocarbon layer was worse than that between Cu and TaN film without rf bias. While no Cu atoms were detected in the TaN with rf bias, Cu atom diffusion occurred in the TaN without rf bias. Intermixing of Cu and TaN contributes to improved adhesion of Cu and TaN. However, the existence of Cu in TaN raises LSI reliability issues; thus, TaN without rf bias is inadaptable to the Cu interconnect process.
3. The SiCN cap layer on fluorocarbon prevents F and C atom diffusion and improves the adhesion of Cu and TaN. The multilayer structure composed of Cu on TaN with rf bias on SiCN/fluorocarbon demonstrated to result in no delamination for as low as 350°C annealing.
4. Step coverage of TaN with rf bias achieved 70% for 0.3 μm width and 0.4 μm depth line. Cu integration was complete on damascene structures.

Table III. Comparison of the binding energy and energy of ion bombardment.

Ion	Sub	Binding energy[21] (eV)	$E_{ion}(\eta \times V_p)$ with rf (eV)	E_{ion} $(\eta \times V_f)$ without rf (eV)
Xe	C–C	3	3.1	2.8
	C–F	5	4.4	3.9
	C=C	6	3.1	2.8
	C ≡ C	8	3.1	2.8

5. Xe ions give most of their energy to Ta atoms leading to improved TaN crystallinity, while Xe ions give a small amount of energy to F and C atoms, and this saves fluorocarbon.

In this paper a crystalline TaN was successfully prepared on ultralow-*k* material without introducing damage, demonstrating good Cu barrier properties and good adhesion.

Tohoku University assisted in meeting the publication costs of this article.

References

1. International Technology Roadmap for Semiconductors, Semiconductor Industry Association, San Jose, CA (2006).
2. T. Nitta, T. Ohmi, T. Hoshi, T. Takwaki, and T. Shibata, *IEEE Trans. Electron Devices*, **E76**, 626 (1993).
3. S. Sankaran, et al., *Tech. Dig. - Int. Electron Devices Meet.*, **2006**, 13.2.1.
4. V. Arnal, A. Farcy, M. Aimadeddine, V. Jousseaume, L. G. Gosset, J. Guillan, M. Assous, L. Favennec, A. Zenasni, T. David, K. Hamioud, et al., in *Proceedings of the 10th International Interconnect Technology Conference*, IEEE, p. 1 (2007).
5. K. Miyatania, Y. Kobayashi, K. Kawamura, S. Hosaka, T. Nozawa, T. Matsuoka, M. Hirayama, A. Teramoto, N. Sugawa, and T. Ohmi, in *Proceedings of the 68th Symposium on Semiconductors and Integrated Circuits Technology*, The Electrochemical Society of Japan, p. 53 (2005), In Japanese.
6. L. G. Jacobsohn, D. F. Franceschini, M. E. H. Maia de Costa, and F. L. Freire, Jr., *J. Vac. Sci. Technol. A*, **18**, 2230 (2000).
7. M. Stavrev, D. Fischer, C. Wenzel, K. Drescher, and N. Mattern, *Thin Solid Films*, **307**, 79 (1997).
8. T. Ushiki, K. Kawai, M.-C. Yu, T. Shinohara, K. Ino, M. Morita, and T. Ohmi, *IEEE Trans. Electron Devices*, **45**, 2349 (1998).
9. W. Shindo, S. Sakai, H. Tanaka, C. J. Zhong, and T. Ohmi, *J. Vac. Sci. Technol. A*, **17**, 3134 (1999).
10. T. Ohmi, M. Hirayama, and T. Teramoto, *J. Phys. D*, **39**, 43 (2006).
11. T. Nozawa, T. Nishizuka, Y. Kobayashi, M. Hirayama, and T. Ohmi, in *Abstracts of the 18th Symposium on Plasma Science for Materials*, Japan Society for the Promotion of Science, p. 2 (2005).
12. J. Wada, A. Sakata, H. Matsuyama, K. Watanabe, and T. Katata, in *Proceedings of the 3rd International Interconnect Technology Conference*, IEEE, p. 108 (2000).
13. T. Ohmi, K. Hashimoto, M. Morita, and T. Shibata, *J. Appl. Phys.*, **69**, 2062 (1991).
14. A. Arranz and C. Palacio, *Surf. Interface Anal.*, **29**, 653 (2000).
15. C.-C. Chang, J. S. Chen, and W.-S. Hsub, *J. Electrochem. Soc.*, **151**, G746 (2004).
16. S. Nakao, M. Numata, and T. Ohmi, *Jpn. J. Appl. Phys., Part 1*, **38**, 2401 (1999).
17. Z. Chen, V. Misara, R. Ph. Haggerty, and S. Stemmer, *Phys. Status Solidi B*, **241**, 2253 (2004).
18. G. S. Chang, K. H. Chae, C. N. Whang, E. Z. Kurmaev, D. A. Zatsepin, R. P. Winarski, D. L. Edere, A. Moewes, and Y. P. Lee, *Appl. Phys. Lett.*, **74**, 522 (1999).
19. H. Igarashi, H. Oyamatsu, M. Kodera, N. Kaji, T. Matsuno, H. Shibata, M. Kinugawa, and M. Kakumu, *1996 Symposium on VLSI Technology, Digest of Technical Papers*, IEEE, p. 84.
20. S. Gandikota, S. Voss, R. Tao, A. Duboust, D. Cong, L. Y. Chen, S. Ramaswami, and D. Carl, *Microelectron. Eng.*, **50**, 547 (2000).
21. W. Shindo and T. Ohmi, *J. Appl. Phys.*, **79**, 2347 (1996).
22. K. W. Lee, S. L. Lee, S. H. Yang, Y. I. Kim, and J. W. Park, *Jpn. J. Appl. Phys., Part 2*, **38**, L1457 (1999).