Available online at www.sciencedirect.com

Thin Solid Films 504 (2006) 243 – 247

www.elsevier.com/locate/tsf

Characterization of spin-on-glass very-low-*k* polymethylsiloxane with copper metallization

K.C. Aw [a,*], N.T. Salim [b], W. Gao [b], Z. Li [b]

[a] *Mechanical engineering, University of Auckland, New Zealand*
[b] *Chemical and materials engineering, University of Auckland, New Zealand*

Abstract

Cu diffusion is one major problem that inhibits low-*k* dielectric to be integrated with existing fabrication technology effectively. This paper demonstrates the effects of surface modification towards polymethylsiloxane low-*k* dielectric (LKD 5109) from JSR Micro using gas mixture of H_2+N_2 plasma in order to improve Cu diffusion barrier. $C-V$ plots indirectly indicated that plasma treatment reduces Cu^+ ions penetration during Cu deposition using magnetron sputtering. XPS confirmed that short duration (10 to 30 s) of H_2+N_2 plasma treatment could cause surface densification of LKD 5109 low-*k* thin film through formation of N–C bonds. However, the negative effect of plasma treatment is the increment of dielectric constant (k) due to possible surface densification.

Keywords: Low-*k* dielectric; Surface modification; Plasma treatment

1. Introduction

Integrated circuits (IC) are the backbone of modern computers and electronic devices. The speed of an electronic circuit is decided by the structure and materials in its IC building blocks. An IC chip contains millions of conducting lines, which need insulating layers to keep them functioning. An example of interlayer dielectric is silicon dioxide (SiO_2), having a dielectric constant (k) of 4 and with the reduction in dimension causes increase in parasitic capacitance. Developments are on going to replace this interlayer dielectric with low-*k* dielectric thin films, which offer low parasitic capacitance [1]. Porous low-*k* thin films can be achieved using a spin-on technique that is applied in the liquid phase with the use of porogen [2–6] to create nano-pores. Spin-On Glass (SOG) low-*k* dielectric polymethylsiloxane resin from JSR Microelectronics (LKD-5109) can achieve a very low dielectric constant ($k \leq 2.2$) and replacing SiO_2 or its associated derivatives with this low-*k* dielectric will reduce the parasitic capacitance. This low-*k* dielectric has porosity and average pore size of approximately 30% and 2.7 nm, respectively. Despite of its potential, SOG low-*k* dielectric film has many problems [7]. One of the problems is Cu diffusion in this low-*k* dielectric thin film. Cu diffusion into the low-*k* dielectric may cause line-to-line leakage and hence lowers the dielectric breakdown voltage.

Plasma treatment using various types of gasses on low-*k* dielectric thin film has been reported [8–11]. The aim of plasma treatment is to create a very thin modified surface layer on the low-*k* dielectric thin film that will improve its Cu diffusion resistance properties. It has been reported that N_2 plasma causes nitriding and H_2 plasma will provide additional hydrogen to passivate the inner structure of the porous film [12]. Therefore, plasma created using H_2+N_2 gas mixture will be used in this work, in an attempt to reap the benefits provided by N_2 and H_2 plasma. The gas mixture ratio used in this work is 7% H_2 and 93%N_2.

2. Experiment

Metal-insulator-semiconductor (MIS) structures were fabricated. P-type silicon <100> substrate was used with 400 nm of LKD-5109 low-*k* thin film deposited using a spin-coater

---

* Corresponding author.
E-mail addresses: k.aw@auckland.ac.nz (K.C. Aw), ntj001@ec.auckland.ac.nz (N.T. Salim), w.gao@auckland.ac.nz (W. Gao), zw.li@auckland.ac.nz (Z. Li).

0040-6090/$ - see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.tsf.2005.09.163

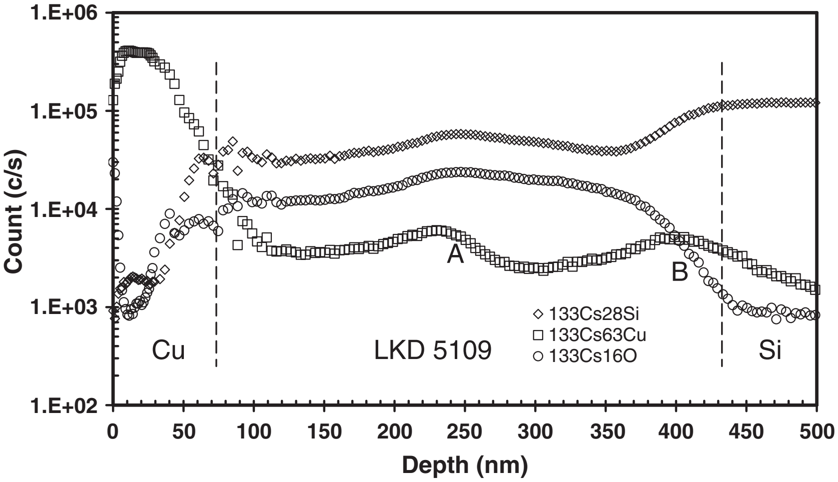

Fig. 1. SIMS plot of MIS with evaporated Cu contacts.

followed by hot plate at 80 and 200 °C for 60 s each to evaporate solvent and initiate cross-linking of polymer, respectively. It is then cured using a furnace at 420 °C in N_2 ambient for 30 min. Cu contacts of 4 mm^2 on top of the low-*k* dielectric thin film were deposited using two different techniques; i.e., magnetron sputtering and thermal evaporation and the technique that yielded higher quality MIS samples will be the choice for subsequent work. The thermal evaporation was performed at a pressure of 5×10^{-5} Torr and the sputtering was performed with an Argon pressure of 2.0 mTorr, substrate bias voltage of -50 V_{DC} and forwarded DC current of 0.5A to the Cu target. The samples were then annealed at 200 °C for 1 h in N_2 ambient. Secondary Ion Mass Spectroscopy (SIMS) was used to determine the Cu depth profile in the low-*k* dielectric thin film. $C-V$ plot at 1 MHz and breakdown voltage were used to determine the charge system and electrical strength of the low-*k* thin film, respectively.

The effect of H_2+N_2 plasma towards the low-*k* dielectric was studied on samples that were subjected to the plasma for 10, 30 and 60 s with a RF power of 500 W before Cu contacts deposition using magnetron sputtering technique. X-ray Photoelectron Spectroscopy (XPS) was used to study the effect of plasma towards the chemistry properties of the low-*k* dielectric. The thickness of the dielectric is confirmed by measuring the cross-sectional thickness using the scanning electron microscope (SEM).

3. Results and discussion

The dielectric breakdown field of thermally evaporated Cu contacts is 0.58 MV/cm while those with sputtered Cu contacts are approximately 1.0 MV/cm. SIMS was used to understand why samples with evaporated Cu have lower breakdown voltage. The Cu, O and Si profile of as-deposited (without plasma treatment) MIS samples which were deposited using evaporated and sputtered technique is shown in Figs. 1 and 2, respectively. The dielectric layer will show traces of Si and O due to Si−O−Si bonds and the silicon substrate will only show traces of Si. The SIMS profiles show traces of Cu in the dielectric on MIS with evaporated and sputtered Cu. However,

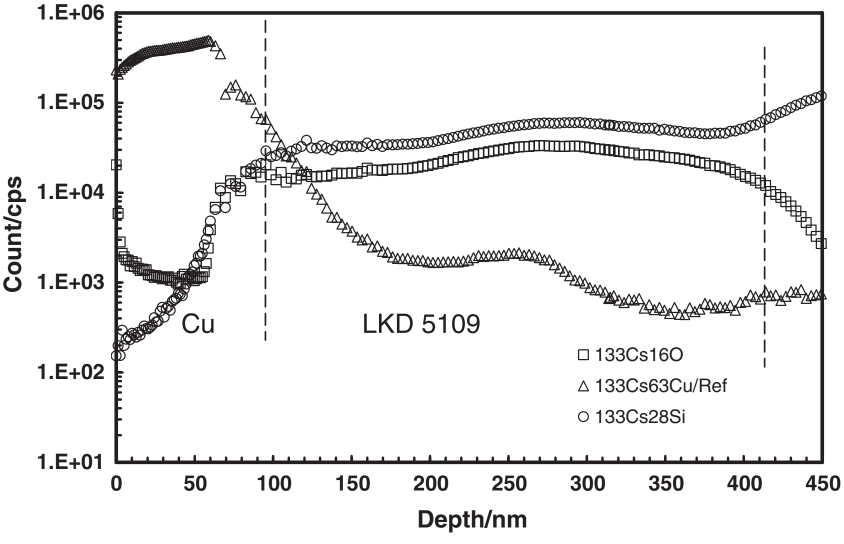

Fig. 2. SIMS plot of MIS with sputtered Cu contacts.

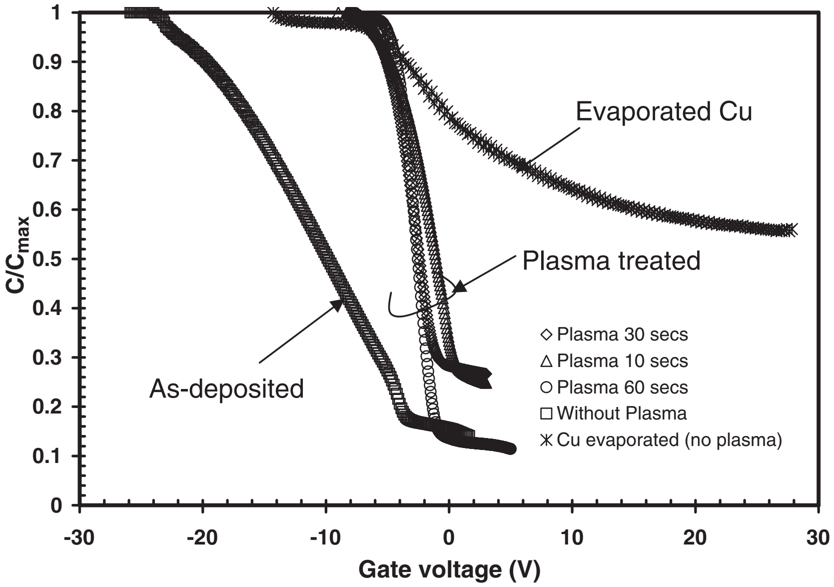

Fig. 3. $C-V$ plot of MIS samples.

samples with evaporated Cu showed distinctive profile with two humps (A and B in Fig. 1) and this shows sign of greater Cu concentration in the dielectric and could be the cause of lower breakdown field. The higher concentration of Cu traces in evaporated samples as shown by the two humps is believed to be due to induced thermal Cu diffusion during the deposition process since Cu need to be heated to approximately 950 °C to evaporate. Based on this information, sputtering technique will be used to deposit Cu to form MIS structure in subsequent work.

The $C-V$ plot of MIS samples with sputtered Cu with and without plasma treatment is shown in Fig. 3. From the $C-V$ plot it is obvious that the as-deposited MIS samples consistently have larger negative shift and were "stretched-out" than those with plasma treatment and could indicate greater penetration Cu^+ ions and interface states [13] into the low-k dielectric, respectively. This indicates that plasma treatment could have increased the Cu^+ penetration resistance.

The value of dielectric constant can be calculated using the capacitance at accumulation (1 MHz) and thickness of the dielectric. The dielectric constant (k) at 1 MHz of as-deposited samples averaged at 2.26. The k value increases as the exposure to $H_{2+}N_2$ plasma increases and was graphed in Fig. 4. Plasma treatment for duration between 10 to 30 s causes slight increase in the dielectric constant however; the k value increases significantly after 60 s of treatment.

XPS proved that there is no Nitrogen (N 1 s) peak in as-deposited samples but is presence in samples treated with plasma as shown in Fig. 5. This has confirmed that nitrogen bonding has occurred when the low-k dielectric was treated with N_2+H_2 plasma. The N 1 s binding energy of 399.5 eV could suggest the presence of N–C bond since the mixture of N_2+H_2 plasma could form volatile species with carbon such as $C_xN_yH_z$ [14]. This N–C bond was believed to cause surface densification [15] and this could act as a Cu diffusion

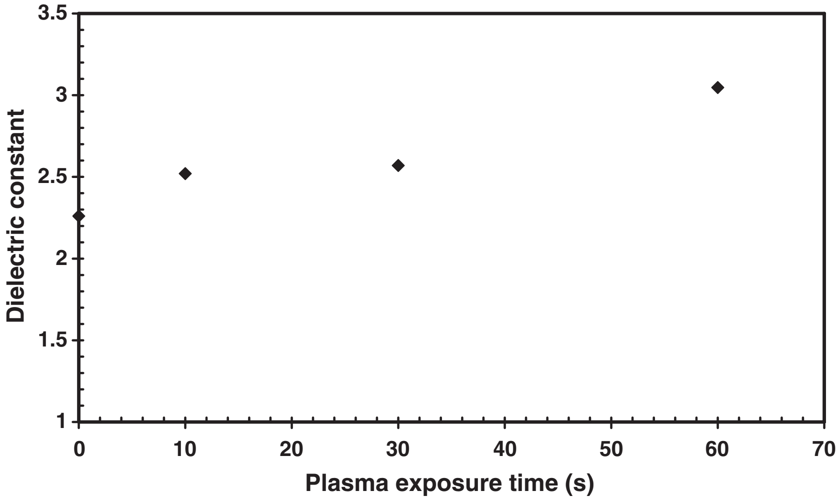

Fig. 4. Dielectric constant versus plasma treatment time.

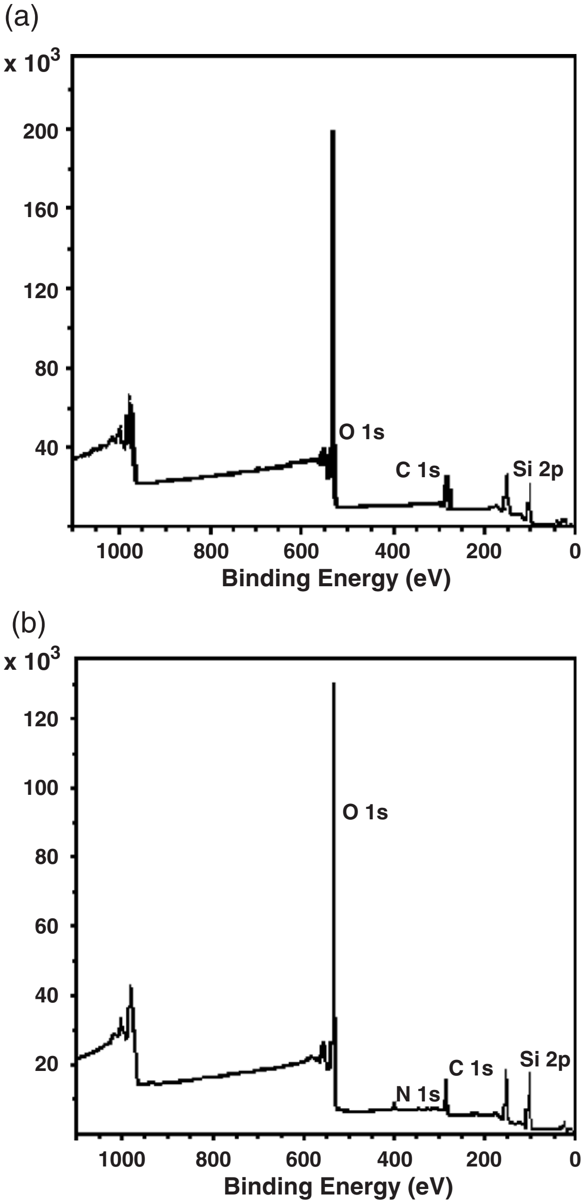

Fig. 5. XPS spectra of LKD 5109 (a) as-deposited and (b) after 10 s plasma treatment.

barrier. The carbon peak (C 1 s) detected by XPS can be decomposed into two peaks (Fig. 6). The main peak which was due to hydrocarbon with a binding energy of 285 eV and would be used as a reference. However, the secondary peak is of interest as it shifts to higher energy with reference to the main peak with plasma treatment. The secondary peaks are 287.5 and 288 eV, respectively for 10 and 60 s plasma treatment, respectively and translated to a shift of 2.5 and 3 eV from the reference hydrocarbon main peak. This C 1 s secondary peak further confirmed the presence of N–C bond [16–19]. However, with 60 s plasma, the secondary C 1 s peak shift from the reference main peak is 3.0 eV and could suggest the presence of carboxyl-like species. The carboxyl-like species could cause further densification and was believed to increase the *k* value to 3.00. In addition, 60 s of plasma treatment reduces the dielectric thickness to 387 nm whereas the dielectric thickness with plasma treatment up to 30 s remains constant.

4. Conclusion

SIMS has been successful in identifying Cu diffusion or penetration into LKD-5109 low-*k* dielectric film although caution has to be taken due to "knock-in effect". Nevertheless, SIMS has showed that the Cu profiles in thermally evaporated Cu MIS samples are consistently different to those that were sputtered and could account for the lower breakdown voltage. Gas mixture of N_2+H_2 plasma could have caused surface densification and is believed to act as Cu diffusion barrier with slight increment in the dielectric constant. $C–V$ measurements have indirectly showed the effects of increase in Cu penetration resistance after N_2+H_2 plasma treatment. XPS have been successfully employed to confirm surface modification effect using H_2+N_2 plasma through the creation of N–C bonds. A brief plasma treatment of 10 to 30 s should be sufficient to improve the Cu diffusion barrier properties but with an increase of dielectric constant to 2.55. However, 60-s of plasma treatment could cause further densification due to possible carboxyl-like species and resulted in increase of dielectric constant to 3.00, which defeat the purpose of using low-*k* dielectric material. Carboxyl-like species could be the result of H_2 gas in the plasma at extended duration (e.g., 60 s). In addition, extended exposure to plasma reduces the thickness of the dielectric due to its etching properties.

Acknowledgement

This work was performed with the support of The University of Auckland new staff research fund no. 3605323/9274 and Australian Institute of Nuclear Science and Engineering (AINSE) award no. AINGRA05005. The authors would like to thank Dr. K. Prince and Mr Armand Atanacio of ANSTO, NSW, Australia for their technical support in SIMS; Dr. B. James and C. Hobbis of Chemical and Materials Engineering, University of Auckland for SEM and XPS support; and finally Prof Kamarulazizi of University Science Malaysia for Cu evaporation.

References

[1] Materials Research Society, Materials Research Symposium Proceeding, 1997, p. 381.
[2] J. Maxwell-Garnett, Phil. Trans. Roy. Soc. (London) 203 (1904) 385.
[3] U. Russow, Phy. Stat. Sol. (a) 184 (1) (2001) 51.
[4] J. Golden, C.J. Hawker, P.S. Ho, Semicond. Int. (2001) 224.
[5] M. Morgan, E. Todd Ryan, Jie-Hua Zhao, Chuan Hu, Taiheui Cho, Paul S. Ho, Annu. Rev. Mater. Sci. 30 (2000) 645.
[6] J. Golden, E. Carrubba, J. Jung, DCMIC Conference, 2001.
[7] C.M. Garner, G. Kloster, G. Atwood, L. Mosley, A.C. Palanduz, J. Microelectron. Rel. 45 (2005) 919.
[8] C.H. Chen, F.S. Huang, Thin Solid Films 441 (2003) 248.
[9] Martin Hoyas, J. Schuhmacher, C.M. Whelan, J.P. Celis, K. Maex, Microelectron. Eng. 76 (2004) 32.

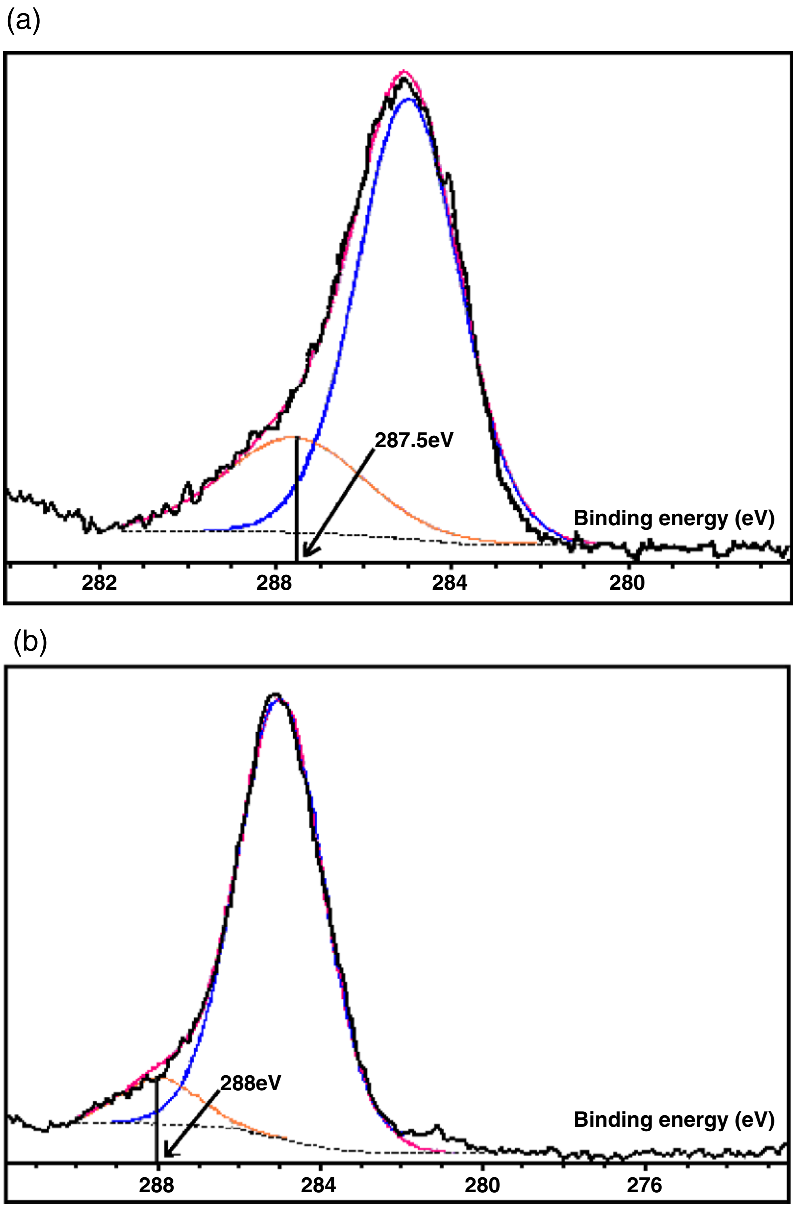

Fig. 6. (a) Secondary C 1 s peak binding energy of 287.5 eV with 10 s plasma treatment. (b) Secondary C 1 s peak binding energy of 288 eV with 60 s plasma treatment.

[10] T.K. Goh, T.K.S. Wong, Microelectron. Eng. 75 (2004) 330.

[11] Y.H. Wang, R. Kumar, X. Zhou, J.S. Pan, J.W. Chai, Thin Solid Films 473 (2005) 132.

[12] T.C. Chang, P.T. Liu, Y.J. Mei, Y.S. Mor, T.H. Perng, Y.L. Yang, S.M. Sze, J. Vac. Sci. Technol., B 17 (1999) 2325.

[13] E.H. Nicollian, J.R. Brews, MOS Physics and Technology, John Wiley and Sons, 1982, p. 252.

[14] D. Fuard, O. Joubert, L. Vallier, M. Bonvalot, J. Vac. Sci. Technol., B 19 (2001) 447.

[15] H.J. Lee, E.K. Lim, W.L. Wu, B.M. Fanconi, J.K. Lan, Y.L. Cheng, H.C. Liou, Y.L. Wang, M.S. Feng, C.G. Chao, J. Electrochem. Soc. 148 (2001) F195.

[16] Hongbing Liu, R.J. Hamers, Surf. Sci. 416 (1998) 354.

[17] Xiaoping Cao, R.J. Hamers, J. Vac. Sci. Technol., B 20 (2002) 1614.

[18] G. Beamson, D. Briggs, The Scientific ESCA3000 Database, Wiley and Sons, 1992.

[19] D. Briggs, J.T. Grant, Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy, IM Publications, 2003, p. 465.