Applied Surface Science 254 (2008) 6116–6118

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

The effects of plasma treatment on the thermal stability of HfO_2 thin films

Kow-Ming Chang*, Bwo-Ning Chen, Shih-Ming Huang

Department of Electronic Engineering and Institute of Electronics, National Chiao-Tung University, 1001 Ta Hsueh Road, Hsinchu 30050, Taiwan, ROC

ARTICLE INFO

Article history:
Accepted 1 February 2008
Available online 18 March 2008

PACS:
77.55.+f (dielectric thin films)
81.65.Lp (surface hardening: nitridation, carburization, carbon nitridation)

Keywords:
Atomic layer deposition (ALD)
Inductively coupled plasma (ICP)
Effective oxide thickness (EOT)
High-κ

ABSTRACT

The thermal stability of pure HfO_2 thin films is not high enough to withstand thermal processes, such as S/D activation or post-metal annealing, in modern industrial CMOS production. In addition, plasma nitridation technology has been employed for increasing the dielectric constant of silicon dioxide and preventing boron penetration. In this experiment, atomic layer deposition (ALD) technology was used to deposit HfO_2 thin films and inductively coupled plasma (ICP) technology was used to perform plasma nitridation process. The C–V and J–V characteristics of the nitrided samples were observed to estimate the effect of the nitridation process. According to this study, plasma nitridation process would be an effective method to improve the thermal stability of HfO_2 thin films.

1. Introduction

To solve the problem of the excessive leakage, Hafnium-based dielectrics have emerged as promising high-κ candidates to replace the SiON dielectric for advanced CMOS technologies [1–3]. Pure HfO_2 is considered as a suitable gate dielectric material because of the acceptable band gap (6 eV) and the large dielectric constant (about 25). In general, the band gap of Hafnium-based dielectrics would not be too small to cause the large gate leakage that may form the large power consumption. Meanwhile, the dielectric constant of Hafnium-based dielectrics is high enough to increase the physical thickness of the gate dielectric and maintain the relatively low effective oxide thickness (EOT). However, there are several challenges having to be considered in order to integrate these high-κ dielectrics into a conventional CMOS process flow such as the interface SiO_2 regrowth and the thermal stability [4]. Furthermore, the nitridation process has been shown to improve the thermal stability of Hafnium-silicate thin films [5]. The purpose of this study was to examine the plasma nitridation effect to pure HfO_2 thin films.

2. Experimental

After initial standard RCA cleaning, wafers were placed into the chamber and a HfO_2 layer was deposited on the every wafer by the atomic layer deposition (ALD) system. Then the samples were annealed (post-deposition annealing) at 600 °C for 30 s in pure N_2 gas and nitrided by an additional ICP plasma treatment at the substrate temperature of 300 °C. The conditions of the plasma treatment were in pure N_2 or N_2O for 30 s, 60 s, and 90 s, respectively. In addition, the process pressure of the plasma nitridation process was 100 mTorr. The RF power of the ICP system was set as 1 W/cm^2 and the DC power of the ICP system was set as 0 W/cm^2. After the plasma nitridation, there was an annealing process (post-nitridation annealing) to reduce the plasma damage caused by the nitridation process. The condition of the annealing process was at 600 °C for 30 s in pure N_2. A pure aluminum film was deposited on the top side of every sample by a PVD process. The top electrodes were defined by the mask process. Finally, backside aluminum electrodes were evaporated by a thermal evaporation.

3. Results and discussions

Different times were tested for the N_2 and N_2O plasma nitridation process to achieve the best nitridation effect for HfO_2 thin films. Fig. 1 shows the capacitance–voltage (C–V) characteristics of the HfO_2 gate dielectrics treated in ICP N_2 plasma for different process times. If the nitridation time was set less than 30 s, the nitridation effect of those samples would be not uniform. On the other hand, if the process time was set more than 90 s, the effect of plasma damage would be serious. So the nitridation time awas set as 30 s, 60 s, or 90 s. The capacitors treated for

---

* Corresponding author. Tel.: +886 3 51712121x54205; fax: +886 3 5731887.
E-mail address: kmchang@faculty.nctu.edu.tw (K.-M. Chang).

0169-4332/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2008.02.140

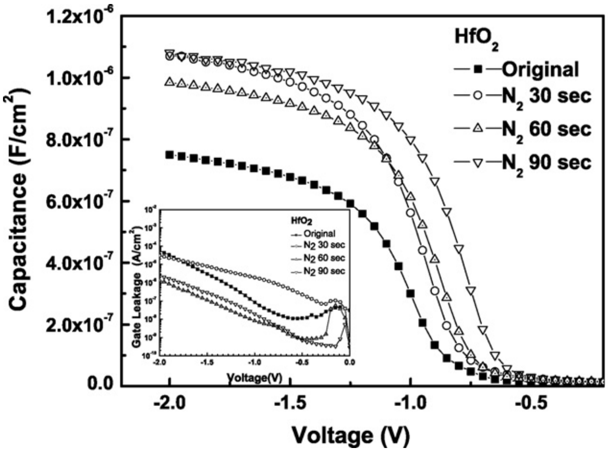

Fig. 1. The *C–V* and *J–V* characteristics of the HfO_2 thin films treated in N_2 plasma for different process times.

90 s performed the maximum capacitance density among those samples with different process times. Furthermore, the capacitors treated for 30 s or 60 s both presented the larger values than the ones without any annealing or nitridation processes. The factor of improvement could be from the post-deposition annealing (PDA) process [6] and the nitrogen incorporation in hafnium oxide, which might enhance the electronic polarization as well as the ionic polarization. As a result, the dielectric constant of the HfO_2 thin films would increase just as nitrided HfSiO thin films [7] and nitrided SiO_2 thin films [8]. The small figure inserted in Fig. 1 describes the leakage–voltage (*J–V*) characteristics of the p-type HfO_2 capacitors treated by ICP N_2 plasma with different process times from 0 V to −2 V. The gate leakage current density was suppressed while the treatment times were 60 s or 90 s. The reduction of the leakage current could be attributed to the PDA process [7]. The gate leakage current density of the samples that were not treated in ICP N_2 plasma at $V_G = -1$ V was about 8.52×10^{-8} A/cm^2 and the gate leakage current density of the capacitors treated in ICP N_2 plasma for 90 s at $V_G = -1$ V was about 1.95×10^{-8} A/cm^2. Specially, the leakage current of the samples treated in N_2 plasma for 30 s was even larger than the one of the as-deposited samples. The reason could be that the nitridation time is too short, thus, the nitridation effect might not be obvious and the crystallization caused by the post-nitridation annealing (PNA) appears.

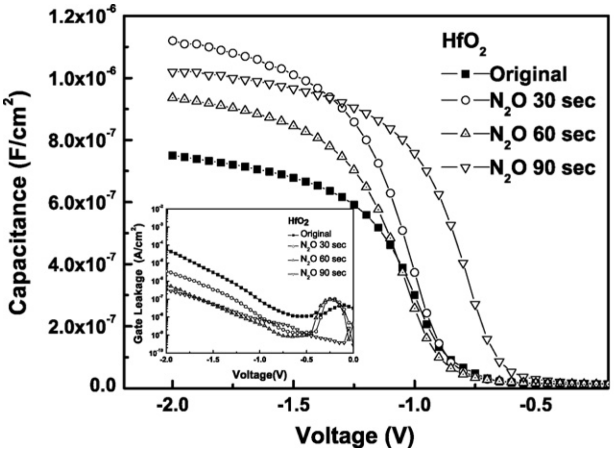

Fig. 2. The *C–V* and *J–V* characteristics of the HfO_2 thin films treated in N_2O plasma for different process times.

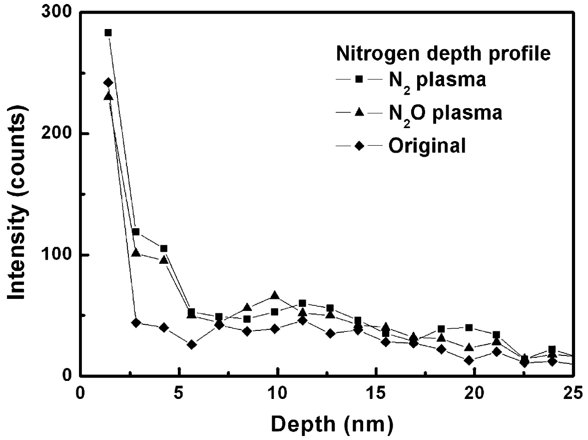

Fig. 3. The nitrogen SIMS depth profiles of the nitrided HfO_2 thin films and the as-deposited HfO_2 thin films.

Fig. 2 describes the *C–V* characteristics of the HfO_2 gate dielectrics treated in N_2O plasma for different process times. The capacitance of the samples nitrided by N_2O plasma was larger than the one of the samples just deposited by the ALD system. In fact, the HfO_2 thin films treated in N_2O plasma for 90 s displayed the largest capacitance density. It indicates that the N_2O plasma treatment is also a practicable method to improve the *C–V* characteristics of HfO_2 thin films. The inserted figure in Fig. 2 presents the *J–V* characteristics of the p-type HfO_2 capacitors treated in N_2O plasma for different process times from 0 V to −2 V. After the N_2O plasma nitridation, the reduction of the leakage current could be observed. The gate leakage current density of the capacitors treated in ICP N_2O plasma at $V_G = -1$ V for 90 s was about 7.20×10^{-9} A/cm^2. The reason of the improvement in the N_2O plasma nitridation process could be the same as the one in the N_2 plasma nitridation process. As mentioned above, the best process time of the plasma nitridation in N_2 and N_2O plasma are both set as 90 s. It appears that the samples treated in N_2 plasma for 90 s displayed the most excellent value (the EOT of the samples was about 2.7 nm).

The nitrogen depth profiles of the nitrided samples are shown in Fig. 3 and the incorporation of nitrogen caused by the nitridation process could be proved. The nitrogen that is incorporated into the dielectric could maintain the amorphous homogeneous film without the phase separation at high temperature [5].

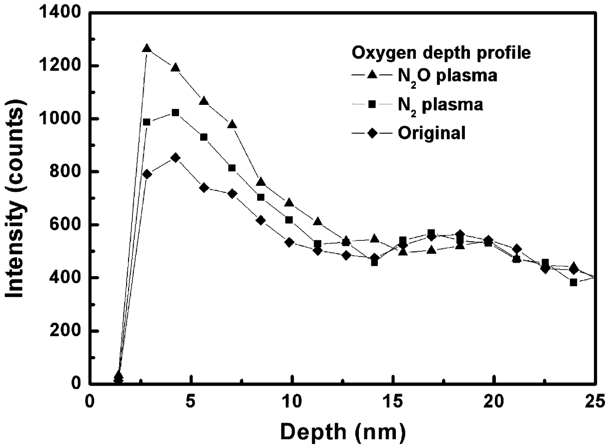

Fig. 4. The oxygen SIMS depth profiles of the nitrided HfO_2 thin films and the as-deposited HfO_2 thin films.

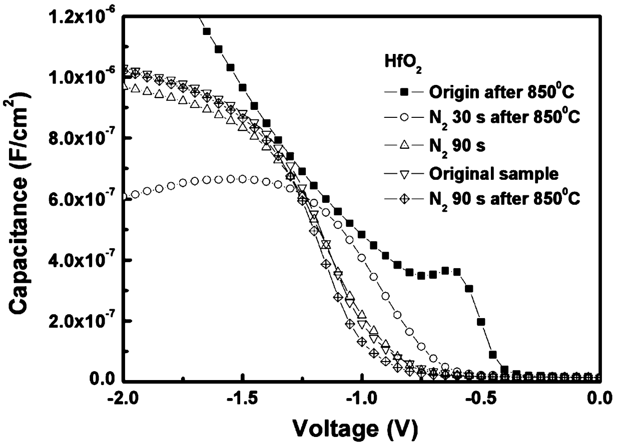

Fig. 5. The *C–V* characteristics of the HfO_2 thin films treated by the various plasma nitridation and the annealing processes.

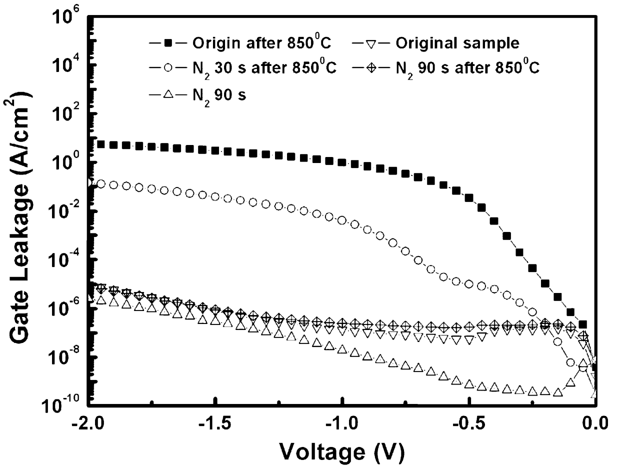

Fig. 6. The *J–V* characteristics of the HfO_2 thin films treated by the various plasma nitridation and the annealing processes.

Fig. 4 demonstrates the oxygen depth profiles of the nitrided samples. The reason why that the capacitance of the sample treated in N_2O plasma is lower than the one of the samples treated in N_2 plasma could be the growth of the dielectric layer due to the oxygen in N_2O plasma. According to Figs. 1 and 2, it also presents that there is smaller gate leakage current that might be caused by the thicker dielectric layer in the N_2O nitridation process than the one in the N_2 nitridation process. In addition, the nitridation effect to thinner HfO_2 thin films (the EOT of the samples was about 1.5 nm) was also corroborated in other experimental result.

In Figs. 5 and 6, the *C–V* and the *J–V* characteristics of the HfO_2 gate dielectrics treated by different plasma nitridation processes and thermal treatments are shown. As demonstrated in Fig. 5, for the samples just deposited by the ALD system and not nitrided, there is an obvious difference between the *C–V* characteristic of the samples with and without the high temperature annealing (in N_2 gas at 850 °C for 30 s). Therefore, from the electrical characteristic, the original samples could not withstand the high temperature annealing. On the other hand, for the samples nitrided in N_2 plasma for 90 s, the *C–V* characteristic of the samples without the high temperature annealing was very similar to the one with the annealing. Thus, it seems to prove that the nitridation process could improve the thermal stability of HfO_2 thin films. Furthermore, if the nitridation time was not enough, the thermal stability of the high-κ thin films would be not enough, either. Just like the samples treated in N_2 plasma for 30 s could not withstand the high temperature annealing. In Fig. 6, after suffering the high temperature annealing, the leakage of the samples with nitridation could maintain a relatively lower value than the one without nitridation. In summary, the above electrical characteristics could also confirm the improved effect of the plasma nitridation to the thermally stability of HfO_2 thin films.

4. Conclusions

In conclusion, the suitable process time for ICP N_2 and N_2O plasma nitridation processes were discussed. Moreover, the nitridation effect and the plasma damage might need to be traded off to achieve the optimum result. According to our study, the whole plasma nitridation process, that also includes the PDA process and the PNA process, could be used to strengthen HfO_2 thin films in order to enhance the *C–V* characteristic and suppress the gate leakage from as-deposited thin films. Furthermore, the plasma nitridation could be also used to improve the thermal stability of HfO_2 thin films to bear a high temperature process at 850 °C for at least 30 s.

Acknowledgement

The authors would like to thank Technology Development Program for Academia DOIT MOEA 95EC-17-A-01-S1-047.

References

[1] International technology roadmap for semiconductors (ITRS), 2006 update.
[2] Y. Shimamoto, J. Yugami, M. Inoue, M. Mizutani, T. Hayashi, K. Shiga, F. Fujita, M. Yoneda, H. Matsuoka, VLSI Symp. Tech. Dig. 132 (2005).
[3] C. Hobbs, L. Fonseca, V. Dhandapani, S. Samavedam, B. Taylor, J. Grant, L. Dip, D. Triyoso, R. Hegde, D. Gilmer, R. Garcia, D. Roan, L. Lovejoy, R. Rai, L. Hebert, H. Tseng, B. White, P. Tobin, VLSI Symp. Tech. Dig. 9 (2003).
[4] S. Yamaguchi, K. Tai, T. Hirano, T. Ando, S. Hiyama, J. Wang, Y. Hagimoto, Y. Nagahama, T. Kato, K. Nagano, M. Yamanaka, S. Terauchi, S. Kanda, R. Yamamoto, Y. Tateshita, Y. Tagawa, H. Iwamoto, M. Saito, N. Nagashima, S. Kadomura, VLSI Symp. Tech. Dig. 192 (2006).
[5] M.A. Quevedo-Lopez, J.J. Cambers, M.R. Visokay, A. Shanware, L. Colombo, Appl. Phys. Lett. 87 (2005) 12902.
[6] G.D. Wilk, M.L. Green, M.-Y. Ho, B.W. Busch, T.W. Sorsch, F.P. Klemens, B. Brijs, R.B. van Dover, A. Kornblit, T. Gustafsson, E. Garfunkel, S. Hillenius, D. Monroe, P. Kalavade, J.M. Hergenrother, VLSI Symp. Tech. Dig. 88 (2002).
[7] M. Koyama, A. Kaneko, T. Ino, M. Koike, Y. Kamata, R. Iijima, Y. Kamimuta, A. Takashima, M. Suzuki, C. Hongo, S. Inumiya, M. Takayanagi, A. Nishiyama, Tech. Dig. Int. Electron Devices Meet. 849 (2002).
[8] H. Takashi, I. Hiroshi, N. Yasushi, E. Hideya, IEEE Trans. Electron Devices 34 (1987) 2238.