

## Improvement on Interface Quality and Reliability Properties of HfAlO<sub>x</sub> MIS Capacitor with Dual Plasma Treatment

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HfO<sub>2</sub> is considered a promising gate dielectric material for sub-45 nm CMOS technology. It has been reported that incorporate Al into HfO<sub>2</sub> forming Hf aluminates in order to increase the crystallization temperature. However, the growth of the low-k interfacial layer at high-k/Si interface during high-k dielectric deposition would result in reliability degradation. Recently, incorporating nitrogen into HfAlO<sub>x</sub> gate dielectrics has beneficial effect on reliability performance. In addition, fluorine incorporation into high-k dielectrics also could have several improvements. In this study, dual plasma (CF<sub>4</sub> pre-treatment and N<sub>2</sub> post-treatment) was performed on HfAlO<sub>x</sub> MIS capacitor in order to improve interface quality and the reliability properties. According to our experimental results, dual plasma treatment could improve interface quality and enhance reliability properties of HfAlO<sub>x</sub> thin films.

### Introduction

Based on the prediction of the International Technology Roadmap for Semiconductors (ITRS), the conventional SiO<sub>2</sub> gate dielectric has met its physical limits (1). Aggressive scaling of the SiO<sub>2</sub> gate dielectric thickness in complementary metal-oxide-semiconductor (CMOS) integrated circuit technology led to excessive gate leakage current (2-4), standby power consumption (2-4), and reliability problems (5). To solve these issues, high dielectric constant (high-k) material became alternative gate dielectrics in order to reduce gate leakage current (6-8). Among all high-k gate materials, HfO<sub>2</sub> is the most promising candidate due to large band gap, high dielectric constant, and large band offset with Si conduction band (9-10). Nevertheless, there are still some issues which need to be considered, including the reliability and thermal stability of the dielectrics (11-12). Al could be added to HfO<sub>2</sub> forming HfAlO<sub>x</sub> to increase the crystallization temperature (13).

Recently, it has been reported that nitrogen incorporated into high-k gate dielectrics could improve thermal stability and increase dielectric constant (14-16).

Nitrogen incorporation can suppress crystallization during high temperature treatment, reduce dopant penetration, increase dielectric constant, and reduce leakage current by about 3-4 orders of magnitude (17-18). Besides, several studies have used fluorine treatment on high-k gate stacks to improve electrical and reliability of dielectric thin films (19-21). Fluorine incorporation could improve interface quality by replacing Si-H bond (3.18eV) to Si-F bond (5.73 eV) (22-23). Pre-CF<sub>4</sub> plasma treatment also could effectively suppress the interfacial layer (IL) formation (24).

In this work, Al/Ti/ HfAlO<sub>x</sub>/Si MIS capacitor structure would be fabricated. We propose to combine CF<sub>4</sub> pre-treatment and N<sub>2</sub> post-treatment (denoted as dual plasma treatment) to examine interface quality and reliability properties of HfAlO<sub>x</sub> MIS capacitor.

## Experimental

In this work, (100) p-type silicon wafers with the resistivity of 1-10 Ω-cm were used. After standard RCA cleaning, the samples were treated in CF<sub>4</sub> plasma (denoted as CF<sub>4</sub> pre-treatment) for various times by using plasma enhanced chemical vapor deposition (PECVD) system. The RF power was set at 20 W and the substrate temperature was 300 °C. The process pressure was 500 mTorr and the gas flow rate of CF<sub>4</sub> was 100 sccm. After CF<sub>4</sub> pre-treatment, metal organic chemical vapor deposition (MOCVD) system was used to deposit HfAlO<sub>x</sub> thin film on the samples. Then, the samples were annealed at 600 °C for 30 sec by rapid temperature annealing (RTA) system. After post deposition annealing (PDA), samples were nitrided in N<sub>2</sub> plasma (denoted as nitrogen post-treatment) by PECVD with RF power 50 W. The post nitridation annealing (PNA) was performed at 600 °C for 30 sec with RTA system so that could reduce plasma damage. Finally, Ti (40 nm) /Al (400 nm) films were deposited by e-beam evaporation system forming top gate electrode, whereas 400 nm Al film was thermal evaporated to form backside contact. The top electrodes were defined as 5000 μm<sup>2</sup>. The current-voltage (I-V) characteristics of MIS structure were measured by Hewlett-Packard 4156C semiconductor parameter analyzer, whereas the capacitance-voltage (C-V) characteristics of MIS structure were measured by using a C-V measurement (Hewlett-Packard 4284).

## Results and Discussion

Figure 1 shows the C-V characteristics of the HfAlO<sub>x</sub> thin films treated in CF<sub>4</sub> plasma for different process durations and N<sub>2</sub> plasma for 90 sec. The frequency of C-V measurement was set as 50 kHz. It could be observed that the sample treated by single N<sub>2</sub> plasma post-treatment has better capacitance density than fresh sample, which is attributed to the incorporation of nitrogen into HfAlO<sub>x</sub> thin films. Nitrogen atom within gate dielectric resulted in the increase of dielectric constant because of the enhancement of the electronic polarization as well as the ionic polarization (18, 25). Besides, the sample treated by CF<sub>4</sub> pre-treatment for 10 sec and N<sub>2</sub> post-treatment for 90 sec shows the highest capacitance density and the sharpest C-V curve than other samples. Fluorine atoms would pile up at the HfAlO<sub>x</sub>/Si interface by CF<sub>4</sub> pre-treatment, which could strength the quality of interface (23) and suppress the IL formation (24). However, the capacitance density degraded as CF<sub>4</sub> pre-treatment duration is longer than 10 sec because of plasma damage.

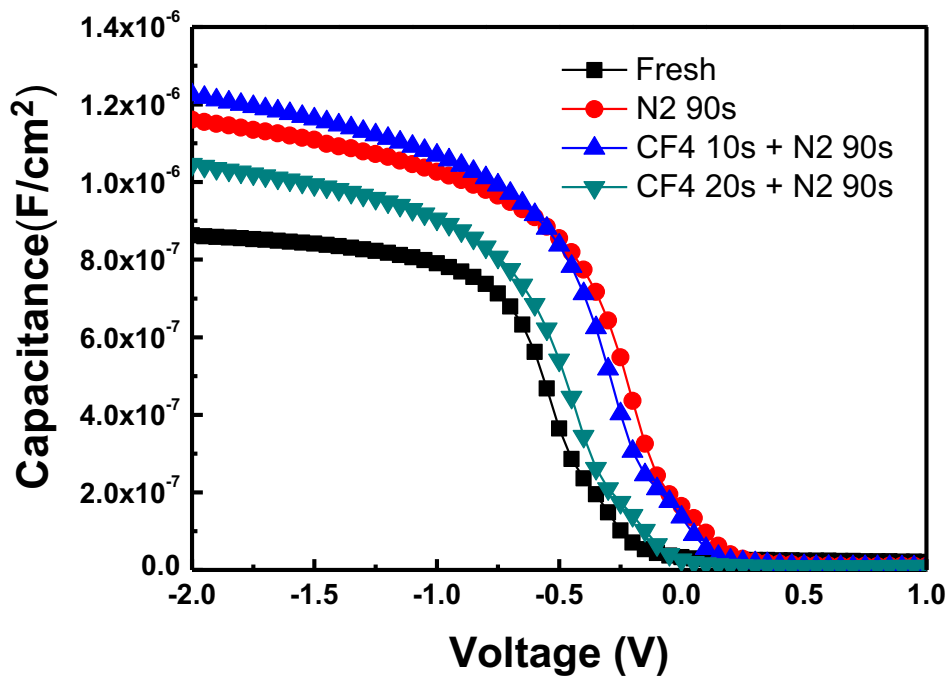


Figure 1. The C-V characteristics of the  $\text{HfAlO}_x$  thin films treated in  $\text{CF}_4$  plasma for different process durations and  $\text{N}_2$  plasma for 90 sec..

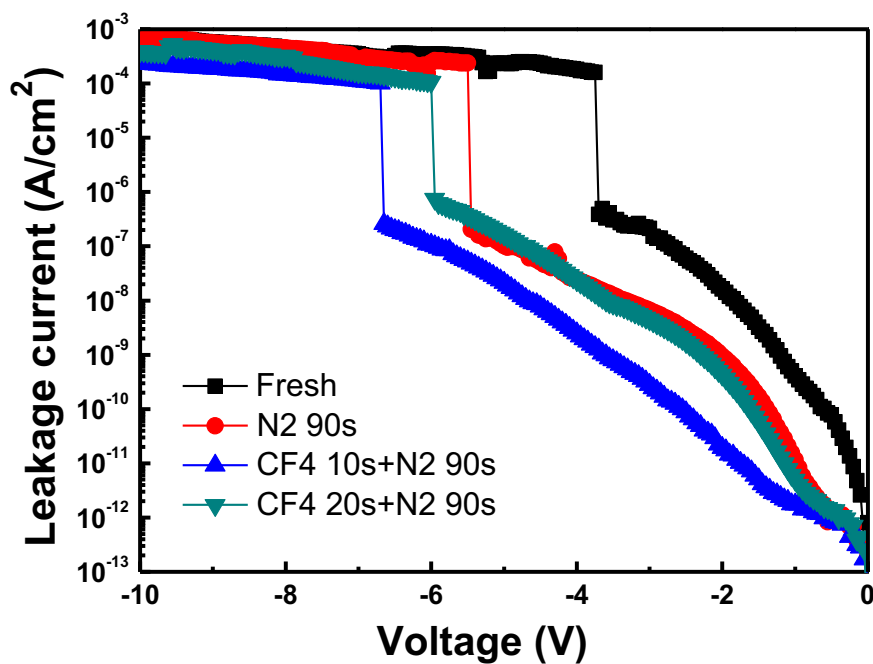


Figure 2. The J-V characteristics of the  $\text{HfAlO}_x$  thin films treated in  $\text{CF}_4$  plasma for different process durations and  $\text{N}_2$  plasma for 90 sec.

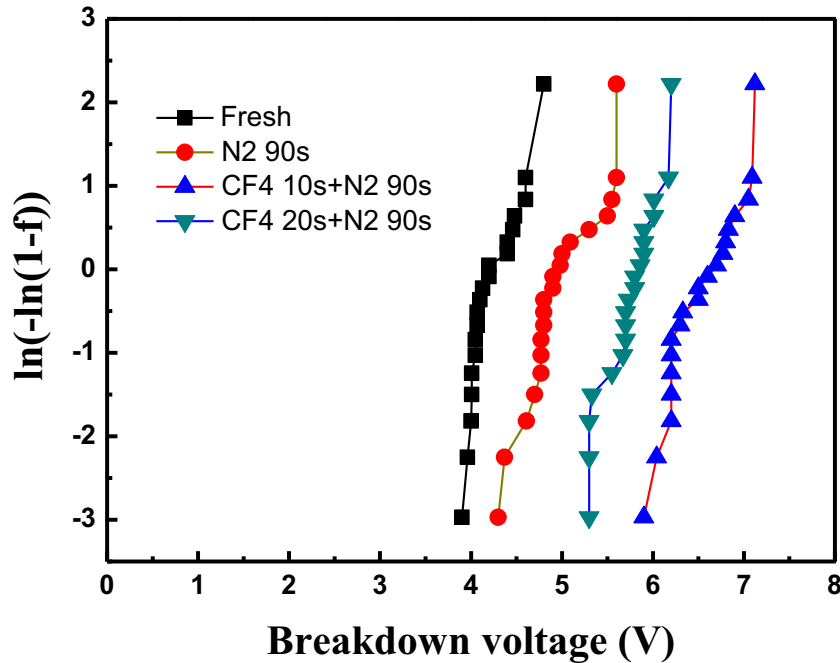


Figure 3. The Weibull plot of the breakdown voltage for HfAlO<sub>x</sub> thin films treated in CF<sub>4</sub> plasma for different process durations and N<sub>2</sub> plasma for 90 sec.

Figure 2 presents the J-V characteristics of the HfAlO<sub>x</sub> thin films treated in CF<sub>4</sub> plasma for different process durations and N<sub>2</sub> plasma for 90 sec. Although the sample treated by single N<sub>2</sub> plasma shows lower gate leakage current than fresh sample, the leakage is suppressed mostly for the sample with dual plasma treatment (CF<sub>4</sub> pre-treatment for 10 sec and N<sub>2</sub> post-treatment for 90 sec). The reduction of gate leakage current is the result of defect passivation. Nitrogen and fluorine atoms could reduce the oxygen vacancy related states and interface states within HfAlO<sub>x</sub> band gap. Nevertheless, while CF<sub>4</sub> pre-treatment is longer than 10 sec, the non-ideal effect that gate leakage increased. The reason for this phenomenon might be attributed to plasma damage at the interface. These results consisted with the breakdown voltage behaviors and distribution, as shown in Figure 3. It has been reported that the first breakdown happened in the low-k layer because the applied electric field would be largely distributed in the low-k region for high-k/low-k gate stack (26). In other words, interfacial layer (IL) represented the low-k layer and would cause the reliability problems. As shown in Figure 3, the sample treated by dual plasma treatment (CF<sub>4</sub> pre-treatment for 10 sec and N<sub>2</sub> post-treatment for 90 sec) shows the largest breakdown voltage because of the great improvement on interface quality. In short, the best condition of dual plasma treatment is CF<sub>4</sub> pre-treatment in 10 sec with RF power 20W and N<sub>2</sub> post-treatment in 90 sec with RF power 50W.

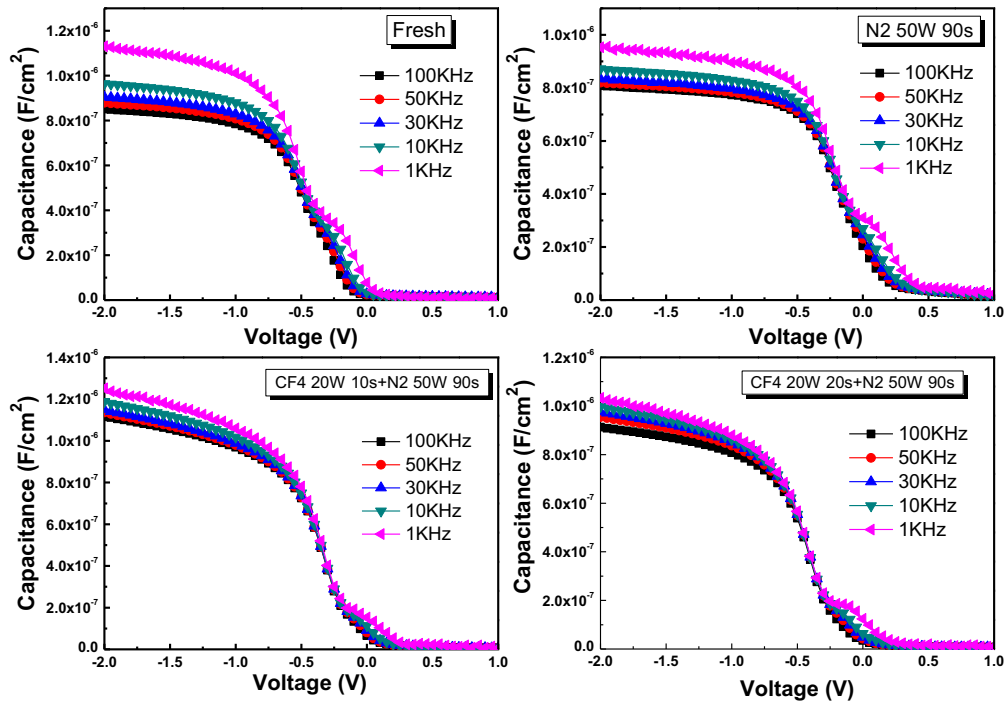


Figure 4 C-V frequency dispersion characteristics of the HfAlO<sub>x</sub> thin films treated in CF<sub>4</sub> plasma for different process durations and N<sub>2</sub> plasma for 90 sec.

### Frequency Dispersion Characteristics

The C-V characteristics of the HfAlO<sub>x</sub> thin films with CF<sub>4</sub> plasma for different process durations and N<sub>2</sub> plasma for 90 sec measured under different frequencies were compared in Figure 4. The range of measurement frequency was set from 1 kHz to 100 kHz. It could be noticed that the strong frequency dispersion in the accumulation region and the hump in the depletion region in the C-V curve for the fresh sample. The effect of frequency dispersion is attributed to the response of charges to signal frequency (27). Because some of the traps could follow the change of the applied gate voltage, the additional capacitance would be generated (27). Compared to the fresh sample, the sample treated by N<sub>2</sub> plasma showed relatively smaller frequency dispersion and smaller hump. Besides, it could be observed that the sample with dual plasma treatment (CF<sub>4</sub> pre-treatment for 10 sec and N<sub>2</sub> post-treatment for 90 sec) shows nearly no dispersion in the accumulation region and nearly no hump in the depletion region, which is independent of frequency. The reason of the improvement could be ascribed to that dual plasma treatment could effectively improve the interface quality (27-30). However, while CF<sub>4</sub> pre-treatment time is longer than 10 sec, the frequency dispersion and the hump became worst again because of plasma damage at the interface.

### Constant Voltage Stress Characteristics

The C-V curves before and after CVS testing of the HfAlO<sub>x</sub> thin films treated in CF<sub>4</sub> plasma for different process durations and N<sub>2</sub> plasma for 90 sec are shown in Figure

5. The stress voltage was set as -3 V and the stress time was set in a range from 0 to 700 sec. It could be observed that all the C-V curves shift to left when stress time increase indicating that the generation of positive charges are trapped in the dielectric layer, which could be explained by Anode hole injection model (31). The injected electrons traveled from the gate through the dielectric layer and arrived at the interface when constant negative bias stress, resulting in the de-passivation of  $\text{Si}_3 \equiv \text{SiH}$  centers and creating the  $\text{Si}_3 \equiv \text{Si}$ -dangling bonds at the interface (so called  $\text{P}_{b0}$  centers) (32). The released hydrogen transported through the dielectric field by electric field and trapped in the dielectric; as a consequence, it may create the positively charged centers (33). On the other hand, the C-V curve of fresh sample exhibited hump after constant voltage stress, owing to the creation of interface defects. Compared to other samples, it is worth mentioning that the C-V curves had smaller  $V_{fb}$  shift and less distortion for samples with  $\text{CF}_4$  pre-treatment for 10sec and  $\text{N}_2$  post-treatment for 90sec because less interface trap charges generated at the  $\text{HfAlO}_x/\text{Si}$  interface.

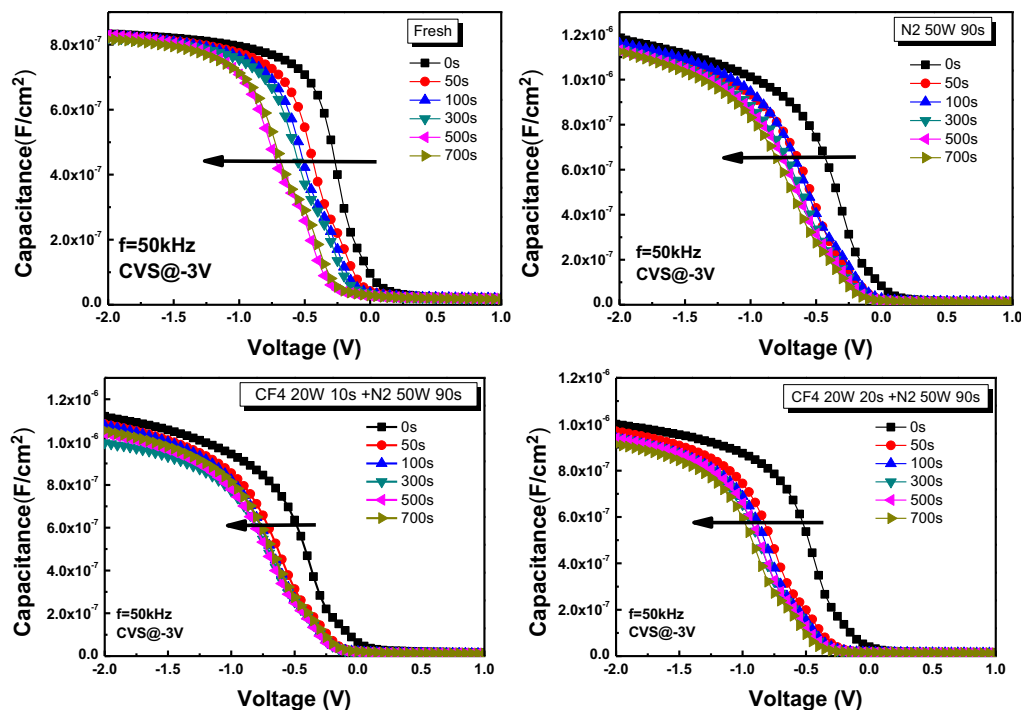


Figure 5 The C-V curves before and after CVS characteristics of the  $\text{HfAlO}_x$  thin films treated in  $\text{CF}_4$  plasma for different process durations and  $\text{N}_2$  plasma for 90 sec.

## Conclusion

The interface quality and reliability properties of  $\text{HfAlO}_x$  gate dielectric with dual plasma have been verified. According to our study, the best condition is  $\text{CF}_4$  pre-treatment for 10 sec and  $\text{N}_2$  post-treatment for 90 sec time. In conclusion, dual plasma treatment could improve interface quality and enhance reliability properties of  $\text{HfAlO}_x$  thin films.

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## References

1. International Technology Roadmap for Semiconductors, presented at public.itrs.net (2009).
2. N. Yang, W. K. Henson, and J. J. Wortman, *Tech. Dig. - Int. Electron Devices Meet.*, **1999**, 453 (1999).
3. S.-H. Lo, D. A. Buchanan, Y. Taur, and W. Wang, *IEEE Electron Device Lett.*, **18**, 209 (1997).
4. G. Timp et al., *Tech. Dig. - Int. Electron Devices Meet.* **1997**, 930 (1997).
5. J. H. Stathis and D. J. DiMaria, *Tech. Dig. - Int. Electron Devices Meet.*, **1998**, 167, (1998).
6. S. W. Huang and J. G. Hwu, *IEEE Trans. Electron Devices*, **53**, 1608 (2006).
7. L. A. Ragnarsson, V. S. Chang, H. Y. Yu, H. J. Cho, T. Conard, K. M. Yin, A. Delabie, J. Swerts, T. Schram, S. D. Gendt, and S. Biesemans, *IEEE Electron Device Lett.*, **28**, 486(2007).
8. Z. Ren, M. V. Fischetti, E. P. Gusev, E. A. Cartier, and M. Chudzik, *IEDM Tech. Dig.*, 2003, pp. 33.2.1–33.2.4.
9. G. D. Wilk, R. M. Wallace, and J. M. Anthony, *J. Appl. Phys.*, **89**, 5243 (2001)
10. J. Robertson, *J. Vac. Sci. Technol. B*, **18**, 1785 (2000).
11. 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, and S. Kadomura, *Symposium on VLSI Technology Digest of Technical Papers*, IEEE, p. 192, (2006).
12. J.-P. Han, E. M. Vogel, E. P. Gusev, C. D'Emic, C. A. Richter, D. W. Heh, and J. S. Suehle, *IEEE Electron Device Lett.*, **25**, 126 (2004).
13. W. J. Zhu, T. Tamagawa, M. Gibson, T. Furukawa, and T. P. Ma, *IEEE Electron Dev. Lett.* **23**, 649 (2002).
14. J. Molina, K. Tachi, K. Kakushima, P. Ahmet, K. Tsutsui, N. Sugii, T. Hattori, and H. Iwai, *J. Electrochem. Soc.*, **154**, 110 (2007).
15. K.-M. Chang, B.-N. Chen, and S.-M. Huang, *Applied Surface Science*, **254**, 6116 (2008).
16. S. Lee, S. Bang, S. Jeon, S. Kwon, W. Jeong, S. Kim, and H. Jeon, *J. Electrochem. Soc.*, **155**, 516 (2008)
17. C. H. Choi, S. J. Rhee, T. S. Jeon, N. Lu, J. H. Sim, R. Clark, M. Niwa, and D. L. Kwong, *Tech. Dig. - Int. Electron Devices Meet.*, **2002**, 857 (2002).
18. M. Koyama, A. Kaneko, T. Ino, M. Koike, Y. Kamata, R. Iijima, Y. Kamimuta, A. Takashima, M. Suzuki, C. Hongo, S. Inumiya, M. Takayanagi, and A. Nishiyama, *Tech. Dig. Int. Electron. Device Meet.*, p. 849, (2002).
19. C.S. Lai, W.C. Wu, J.C. Wang, and T.S. Chao, *Appl. Phys. Lett.* **86**, 222905 (2005).



20. W.C. Wu, C.S. Lai, J.C. Wang, J.H. Chen, M.W. Ma, and T.S. Chao, *J. Electrochem. Soc.*, **154** H561 (2007).
21. K. Tse and J. Robertson, *Appl. Phys. Lett.* **89**, 142914 (2006).
22. K.I. Seo, R. Sreenivasan, P.C. McIntyre, and K.C. Saraswat, *Tech. Dig. - Int. Electron Devices Meet*, pp. 17.2.1–17.2.4., (2005).
23. C.S. Lai, W.C. Wu, K.M. Fan, J.C. Wang, and S.J. Lin, *Jpn. J. Appl. Phys.*, **44**, pp. 2307-2310, (2005)
24. C.S. Lai, W.C. Wu, T.S. Chao, J.H. Chen, J.C. Wang, L.L. Tay, and N. Rowell, *Appl. Phys. Lett.* **89**, 072904 (2006).
25. M. R. Visokay, J. J. Chambers, A. L. P. Rotondaro, A. Shanware, and L. Colombo, *Appl. Phys. Lett.*, **80**, 3183 (2002).
26. H. Wong, B. Sen, V. Filip, and M. C. Poon, *Thin Solid Films*, **504**, 192 (2006).
27. H. X. Xu, J. P. Xu, C. X. Li, and P. T. Lai, *Appl. Phys. Lett.*, **97**, 022903 (2010).
28. T.M. Pan, C.S. Liao, H.H. Hsu, C.L. Chen, J.D. Lee, K.T. Wang, and J.C. Wang, *Appl. Phys. Lett.*, **87**, 262908 (2005).
29. H. Kim, C. O. Chui, K. C. Saraswat, and P. C. McIntyre, *Appl. Phys. Lett.*, **83**, 2647 (2003).
30. H. Harris, K. Choi, N. Mehta, A. Chandolu, N. Biswas, G. Kipshidze, and S. Nikishin, *Appl. Phys. Lett.*, **81**, 1065 (2002).
31. D. J. DiMaria, E. Cartier, and D. A. Buchanan, *J. Appl. Phys.*, **80**, 304 (1996).
32. M. Houssa, J. L. Autran, A. Stesmans, and M. M. Heyns, *Appl. Phys. Lett.*, **81**, 709 (2002).
33. E. Efthymiou, S. Bernardini, J.F. Zhang, S.N. Volkos, B. Hamilton, and A.R. Peaker, *Thin Solid Film*, **517**, 207 (2008).