Highly Reliable Low Temperature Ultrathin Oxides Grown Using N₂O Plasma

Jam-Wem Lee¹, Yiming Li^{1,2}, and S. M. Sze^{1,3}

¹Department of Nano Device Technology, National Nano Device Laboratories, Hsinchu, 300, Taiwan ²Microelectronics and Information Systems Research Center, National Chiao Tung University, Hsinchu, 300, Taiwan ³Institute of Electronics, National Chiao Tung University, Hsinchu, 300, Taiwan P.O. Box 25-178, Hsinchu city, Hsinchu 300, TAIWAN

Abstract: - In this paper, the N₂O plasma oxides in-situ grown on CF_4 plasma pretreated silicon substrate is proposed and demonstrated having excellent characteristics. Those are precise thickness control, low temperature fabrication, low leakage current, and high reliability. Those good features will enhance the scaling down ability of CMOS devices. The mechanisms that make the process success are also discussed in this paper. Those achievements are caused from the incorporations of nitrogen and fluorine. Owing to the incorporations, the leakage current and the reliability are largely improved. It could be addressed that the low temperature oxides grown by N₂O plasma are very attractive for novel CMOS VLSI circuit manufacturing; especially for the oxides grown on the CF_4 plasma pre-treated substrates.

Key-Words: N₂O plasma, CF₄ plasma pretreatment, VLSI circuit, thin nitrided oxides

1 Introduction

In order to fabricate ultra-high integration device featuring with precise doping profile control, the gate oxides deposited at low temperature were needed. However, the low temperature oxides deposited below 500 °C had poorer characteristics than the thermal grown oxide did [1-2]. Recently, low temperature oxide grown by using high-density microwave-excited Kr/O2 plasma was reported having a sufficient quality to fabricate high-integrity silicon oxide films [3]. However, the high growth rate should cause a scaling down problem. The low temperature nitride-oxide films deposited by using remote plasma or JVD were reported to have relatively low leakage current in comparing with the thermally grown oxides, however, a 800 °C post deposition annealing is needed [4].

The N2O plasma produced at 350 °C by conventional PECVD tool to grown high quality ultra-thin nitrided oxide without post annealed was reported in this paper for the first time. We can find that, the oxides have better quality than the thermal grown oxides do. Additionally, with adding a CF4 plasma pretreatment process, the leakage characteristic was improved largely. The low temperature thin oxides grown by N2O plasma were proved to be a very attractive method, especially with adding CF4 plasma pretreatment.

2 **Experiments**

In this experiment, the n+ polysilicon /thin oxide /n-type silicon MOS (Metal/ oxide/ silicon) structures were fabricated to study thin oxide quality. At first, the n-type silicon wafers were RCA cleaned, and then the N₂O plasma with a power of 50W was treated at 350 °C for 300 seconds to grow a 35Å nitrided oxide. In order to introduce F into native oxide, the CF₄ plasma pretreatment was also processed in the same PECVD chamber with a power of 10W for 30 seconds before the N₂O plasma treatment. In comparison, a 35Å nitrided oxide grown on no CF₄ plasma pretreated wafer was also shown.

After thin nitrided oxide grown, a 3000 Å polysilicon film was then deposited at 620° C in a LPCVD ambient and doped with POCl₃ at 900°C for 20 min to have a sheet resistance of $30\Omega/\Box$. Aluminum film with a thickness of 5000 Å was deposited on the n+ polysilicon film. Aluminum and n+ polysilicon films were then patterned to be the top electrode of the MOS structure. After backside polysilicon and native oxide removed, a 5000 Å Al were deposited. All samples were sintered at 400°C in an N₂ ambient to ensure both electrodes were Ohmic contacts. In studying the characteristics more detail, the MOSFETs with

gate oxides of 1.6nm thick pretreated by CF_4 plasma were also fabricated and characterized in this chapter.

The physical thickness of oxides was measured by using ellipsometer and electrical thickness was by high frequency C-V measurement. In this paper, we use the electrical thickness to be the oxide thickness. The J-E, SILC characteristics were obtained by using HP 4156b.



(b)

Fig. 1. (a) the oxidation rate with respect various plasma power at the fixed chamber temperature (at 350 °C) and (b) the parabolic rate constant B vs. process temperature with various RF power.

3 Results and Discussion

Figure 1 shows (a) the oxidation rate with respect various plasma power at the fixed chamber

temperature (at 350° C) and (b) the parabolic rate constant B vs process temperature with various RF power. We can find that the oxide growth rate of the N₂O plasma is weakly depended on the chamber temperature, however, strongly depend on the RF power of plasma. The result is highly matched with the paper [3]. We can also find that the oxide thickness can be easily controlled within 35Å; in fact, the thickness of the oxide will saturate at 5.0nm. Owing to a weak temperature growth rate, the thickness of oxides could be well controlled between wafer to wafer.



Fig. 2. The J-E characteristics of the oxides grown by N_2O plasma on CF_4 plasma pretreated and un-pretreated wafers. The control sample is the thermally grown oxide with N_2O annealed.

Figure 2 shows the J-E characteristics of the N_2O plasma oxides with a thickness of 3.5nm; for comparison, the thermal grown oxide with the same thickness was also prepared as control sample. The N_2O plasma grown oxides have better J-E characteristics than the thermal grown oxide does, this could be due to the fact that low temperature and low-pressure environment suppresses native oxide growth. The N_2O plasma could also introduce nitrogen into the oxide, therefore, improve oxide quality. We can also find that the CF₄ plasma pretreated sample has the smallest leakage current, this could be due to the fact that F incorporation into the native oxide during plasma pretreated.

Figure 3 shows the (a) C-V characteristics of the N₂O plasma oxides and (b) the Dit calculated from C-V measurement. The Dit of the oxides is less than 10^{11} (cm⁻³ eV⁻¹); this is comparable with the thermal

grown thin oxides and could be used in fabricated novel ULSI circuits. Because of the high leakage current of the control sample, the quasi-static C-V cannot be obtained, the C-V and Dit characteristics of the control sample are not shown in this figure.





Fig. 3. The C-V measurement of the plasma grown oxide samples with, (a) the quasi-static C-V and the high frequency (100KHz) C-V characteristics, (b) the Dit calculated from the C-V measurement.

Figure 4 shows the SILC characteristics of the N_2O plasma samples, we can find that the samples have a good SILC characteristics; especially, the N_2O plasma oxide grown on no CF₄ plasma pretreated sample. The oxide shows nearly no SILC effect even with taking a 300C/cm² stress (with 100A/cm²)

constant current stress for 3000 seconds). The high SILC resistance could be due to the high concentration of N incorporation in oxide. After taking a 300 C/cm² stress, the CF₄ pretreated sample has a J-E characteristic very closely to the non-pretreated one. This could be due to the fact that F incorporation in the native oxide layer during the plasma pretreatment and those Si-F bonds were broken by the high energy electrons while constant current stress. Therefore, the characteristics of the laver are closed to the native oxide. The Si-F bonds suffer severer reliability problem than the Si-N bonds had been reported by Liu et al [6]. This could explain the CF₄ pretreated sample has severer SILC characteristics than the non-pretreated one does; additionally, the phenomenon that the stressed J-E are nearly the same. The control sample was breakdown with taking about 10C/cm² stress, so the SILC characteristic of the sample was not shown in the figure.



Fig. 4. The SILC (stress induced leakage current) characteristics of the N_2O plasma grown oxides. The stress current is 100mA/cm^2 .

Figure shows the drain 5 current and transconductance vs gate voltage of the MOSFETs fabricated by using the 1.6nm gate oxides grown by N₂O plasma. We can find that the device fabricated on the CF₄ pretreatment substrate has better characteristics. That is, the CF₄ pretreated sample has higher drain current and higher transconductance. Additionally, similar results could also found in the drain current vs drain voltage as shown in the Fig 7.6. The improvement could be explained by the gate current shown in the Fig. 7, the figure indicates that the pretreated sample has a gate current 1 order lower than the non-treated sample, thus, the device has higher drain current. The figure also shows that the N_2O grown thin oxides has very good reliability; with stressing for 5000 seconds, the characteristics of the oxides remain unchanged.



Fig. 5. The drain current and transconductance vs. the gate voltage of the MOSFETs with 1.6nm gate oxides grown by N_2O plasma. The F5N sample is the gate oxide grown on the CF_4 pretreated substrate.



Fig. 6. The drain current vs. the drain voltage of the MOSFETs with 1.6nm gate oxides grown by N_2O plasma. The F5N sample is the gate oxide grown on the CF₄ pretreated substrate.

4 Conclusion

We conclude that the high quality thin oxides can be grown at low temperature by using N₂O plasma. The thickness of the oxides can be easily controlled within 35Å, and have a leakage current lower than the thermal grown oxides do. We also find that the CF₄ pretreated method can improve the leakage characteristics of the N₂O plasma grown oxides; it is especially true for the ultra-thin oxides (i. e. 1.6nm thick oxide). The improvement of the CF₄ pretreatment could be due to the fact that the native oxide was fluorinate by the process. The process is very attractive in novel ULSI process.

Acknowledgments

This work is supported in part by the National Science Council of TAIWAN under contract numbers: NSC - 92 - 2112 - M - 429 - 001 and NSC - 92 - 2815 - C - 492 - 001 - E. It is also supported in part by the grant of the Ministry of Economic Affairs, Taiwan under contract No. 91-EC-17-A-07-S1-0011.

References:

- T. Fuyuki, S. Murakawa, and H. Matsunami, "Initial stage of ultra-thin SiO₂ formation at low temperatures using activated oxygen", *Appl. Surf. Sci. Vol.* 117/118, 1997, p.123.
- [2] Y. Kawai, N. Konishi, J. Watanabe, and T. Ohmi, "Ultra-Low-Temperature Growth of High-Integrity Gate Oxide Films by Low-Energy Ion-Assisted Oxidation,", *Appl. Phys. Lett., Vol. 64, 1994, pp.* 2223.
- [3] M. Hirayama, K. Sekine, Y. Saito, and T. Ohmi, "Low-Temperature Growth of High-Integrity Silicon Oxide Films by Oxygen Radical Generated in High-Density Krypton Plasma," *IEDM 99, p.249.*
- [4] Y. Shi, X. Wang, and T. P. Ma, "Electrical Properties of High-Quality Ultrathin Nitride/ Oxide Stack Dielectrics" *IEEE TRANS. ON ELECTRON DEVICES, VOL. 46, NO 2, FEB. 1999.*
- [5] C.G. Parker, G. Lucovsky, and J. R. Hauser, "Ultra-thin Oxide-Nitride Gate Dielectric MOSFET's" *IEEE ELECTRON DEVICE Lett. VOL.* 19. NO. 4 APRIL 1998.



Fig. 7. The gate current vs. the gate voltage of the MOSFETs with 1.6nm gate oxides grown by N₂O plasma. The fresh and stressed samples were the fresh curve and post 5000 seconds stressed samples respectively. The stress condition of the (a) is Vg = 2.0V and (b) is Vg= -2.0V