

# A novel process for forming an ultra-thin oxynitride film with high nitrogen topping

Chiung Hui Lai<sup>a,b,\*</sup>, Bo Chun Lin<sup>c</sup>, Kow Ming Chang<sup>a</sup>, Kuang Yeu Hsieh<sup>d</sup>, Yi Lung Lai<sup>e</sup>

<sup>a</sup>Department of Electronics Engineering and Institute of Electronics, National Chiao-Tung University, 1001 Ta-Hsueh Road, Hsin-Chu 30050, Taiwan, ROC

<sup>b</sup>Department of Electrical Engineering, Chung Chou Institute of Technology, Yuanlin, Changhwa 510, Taiwan, ROC

<sup>c</sup>Department of Electronic Engineering, Northern Taiwan Institute of Science and Technology, Taipei 112, Taiwan, ROC

<sup>d</sup>Nano-technology R&D Division/Emerging Central Laboratory, Macronix International Co., Ltd., Hsinchu 300, Taiwan, ROC

<sup>e</sup>Department of Electronic Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan, ROC

## Abstract

We have proposed an approach to grow ultra-thin oxynitride film with high nitrogen concentration ( $\approx 13$  at%) on the top and low interface state density ( $D_{it} = 2 \times 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$ ). In general, a high-nitrogen oxynitride film provides a rather reliable and higher dielectric constant. In this method, oxynitride growth included three process stages—chemical oxide growth, nitridation and subsequent dry oxidation. By this technique, the films demonstrate the desirable nitrogen concentration profile and excellent properties in terms of low  $D_{it}$ , low leakage current, and high endurance in stressing. Better controllability in film thickness may be achieved because the oxidation rate of the nitride-chemical oxide is much smaller than that of the conventional oxide. Most importantly, this process is simple and fully compatible with current process technology.

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## 1. Introduction

In a  $P^+$ -gate device, boron can easily diffuse into the channel region through the ultra-thin gate oxide layer during the dopant activation process [1,2], leading to threshold voltage shift. In principle, a small voltage shift that results from boron penetration will not cause any problem as long as it is predictable. The situation can be improved with modified threshold-adjusted implants. However, boron penetration not only causes the threshold voltage  $V_T$  to be shifted, but also degrades the process margin by increasing the spread of  $V_T$ . Since boron penetration is sensitive to gate dielectric thickness, the thickness variation of the gate oxide plays an important role in controlling the degree of boron penetration. In fact, it has been reported that boron penetration increases exponentially with decreasing in oxide thickness [3,4]. Furthermore, the threshold voltage variation degrades a

device's performance and increases its off-state leakage current.

Nowadays, oxynitride is still the most frequently used gate insulator material in the ultralarge-scale integration (ULSI) semiconductor industry. Various approaches have been employed to produce these dielectric films, such as decoupled plasma nitridation (DPN), remote plasma nitridation (RPN), jet vapor deposition (JVD) and reoxidation of  $\text{NH}_3$  nitridation. Unfortunately, they usually require specific tools or gas. It is desired to have a simple way to obtain the film and retain its quality.

It is well-known that gate dielectric doped with nitrogen can effectively suppress boron diffusion [5–13]. However, the side effect is that the gate oxide suffers from the oxide reliability issue due to nitrogen piled up along the interface between the silicon substrate and oxynitride [14]. Ideally, we would like to have a nitrogen-doped dielectric with high nitrogen content close to the surface, which can effectively block boron diffusion, while low nitrogen content is distributed in the interface, which would not degrade oxide reliability.

In this work, an alternative approach for forming an oxynitride gate dielectric with high nitrogen content

\*Corresponding author. Department of Electronics Engineering and Institute of Electronics, National Chiao-Tung University, 1001 Ta-Hsueh Road, Hsin-Chu 30050, Taiwan, ROC. Tel./fax: +886 3 5712121 31887.

E-mail address: [emily.ee89g@nctu.edu.tw](mailto:emily.ee89g@nctu.edu.tw) (C.H. Lai).

distributed close to the surface is demonstrated. The oxynitride growth includes three process stages—chemical oxide growth, nitridation and subsequent dry oxidation. By this technique, the desirable nitrogen concentration profile can be obtained to meet the requirement of device performance. It is noted that the process proposed here is fully compatible with current ULSI manufacturing platforms.

## 2. Experiment

Experiments were carried out on 4-in p-type (100)-oriented silicon wafers with a resistivity of 15–25  $\Omega$  cm. Wafers were cleaned using standard RCA cleaning. Before growing the oxynitride film, the wafers were dipped in diluted HF solution to remove native oxides. The oxynitride growth was realized by chemical oxide growth, nitridation and subsequent dry oxidation. First, the wafers were immediately immersed into  $\text{H}_2\text{O}_2$  solution at room temperature for 20 min to grow 10-Å-thick chemical oxide. Following that, the chemical oxide was nitrided using a furnace in low-pressure (120 mTorr)  $\text{NH}_3$  ambient at 700 °C for 30 min. The nitrided chemical oxide was then placed in atmospheric  $\text{O}_2$  ambient at 900 °C and annealed in  $\text{N}_2$  at 900 °C for 5 min. The brief process flow is shown in Fig. 1. A 3000-Å-thick polysilicon layer doped with  $\text{POCl}_3$  was deposited by low-pressure chemical vapor deposition (LPCVD) at 900 °C for 30 min. In addition, in order to study boron penetration,  $\text{P}^+$ -polysilicon-gated metal–oxide–semiconductor (MOS) capacitors of oxynitride were fabricated by B implantation (dose,  $5 \times 10^{15}$  atoms  $\text{cm}^{-2}$ ; energy, 30 keV) into the 3000 Å undoped polysilicon layer and subsequent dopant activation annealing at 900 °C for various durations (30 min, 1 and 2 h). Finally, a 5000 Å Al metal film was deposited by sputtering. The MOS capacitor was defined by lithography, and then Al and polysilicon

films were etched by wet etching. After the capacitor was made, another 5000 Å Al film was then deposited on the back surface of the wafer. Samples were sintered in  $\text{N}_2$  ambient at 400 °C for 30 min to ensure good ohmic contact.

Thickness of ultrathin oxynitride was characterized with an ellipsometer. High-frequency (100 kHz) and quasi-static capacitance–voltage ( $C$ – $V$ ) characteristics for 45 Å oxynitride films were measured using a Keithley Model 82  $C$ – $V$  meter and a Hewlett-Packard 4284 LCR meter, respectively. Furthermore, the electrical properties and reliability of MOS capacitors were evaluated by using a Hewlett-Packard 4156C precision semiconductor parameter analyzer.

## 3. Results and discussion

A nitrogen distribution profile across the 70 Å oxynitride gate dielectric revealed by the secondary ion mass spectrometry (SIMS) is shown in Fig. 2. Apparently, high nitrogen concentration with a peak ( $\approx 13$  at%) located at the dielectric surface is observed. Such high nitrogen concentration is more helpful in resisting the boron penetration of the gate dielectric from the  $\text{P}^+$  polysilicon electrode. The low nitrogen concentration at the interface also improves reliability [15,16]. Meanwhile, the oxidation rates for the wafers, which have an existing oxide film grown by the conventional method or our nitrided chemical oxide, are compared in Fig. 3. The results show that the oxidation rate of the nitrided chemical oxide is much smaller than that of the conventional oxide. At this point, it implies that the nitrided chemical oxide provides a wider process window to well control gate oxide thickness if ultrathin oxide is needed.

The measured gate current–voltage ( $I$ – $V$ ) and  $C$ – $V$  curves of the  $\text{N}^+$ -gated MOS capacitor with 45 Å oxynitride films are shown in Figs. 4 and 5, respectively. An  $I$ – $V$  curve with a very low leakage current of  $2 \times 10^{-13}$  A ( $= 2 \times 10^{-9}$  A  $\text{cm}^{-2}$ ) is obtained. This is attributed to the clean chemical oxide. When the process of chemical oxide formation proceeds, the clean oxide

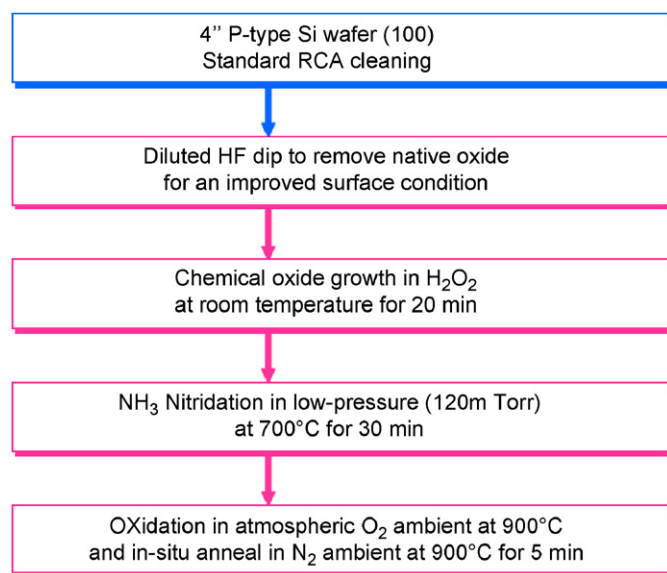


Fig. 1. Brief process flow to form high-nitrogen oxynitride.

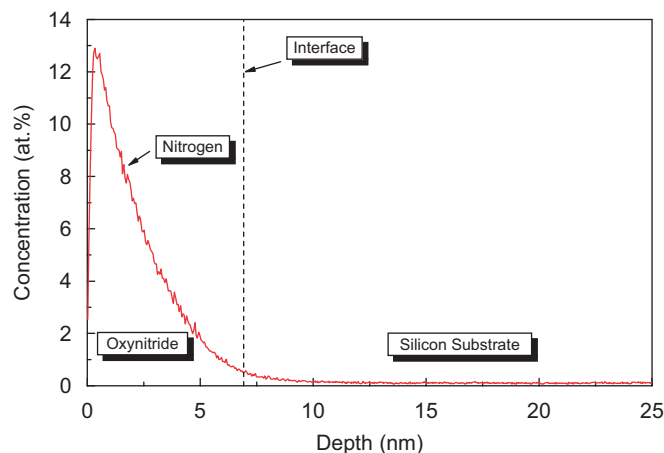


Fig. 2. SIMS profile of nitrogen distribution of the 70 Å oxynitride.

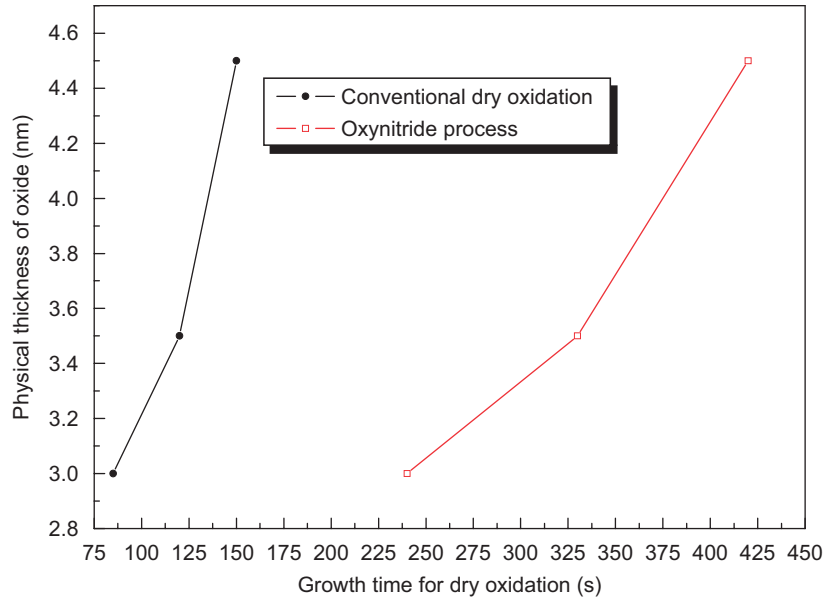


Fig. 3. Growth time for dry oxidation versus physical thickness of oxide for conventional dry oxidation and oxynitride processes.

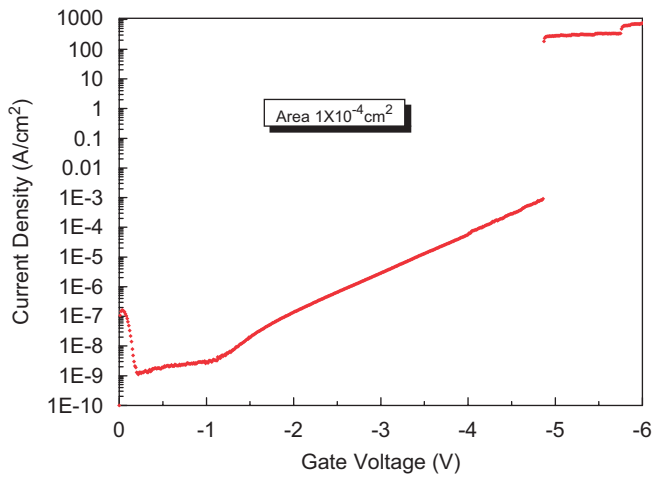


Fig. 4.  $I$ - $V$  characteristics for MOS capacitor. The measured area is  $1 \times 10^{-4} \text{ cm}^2$ .

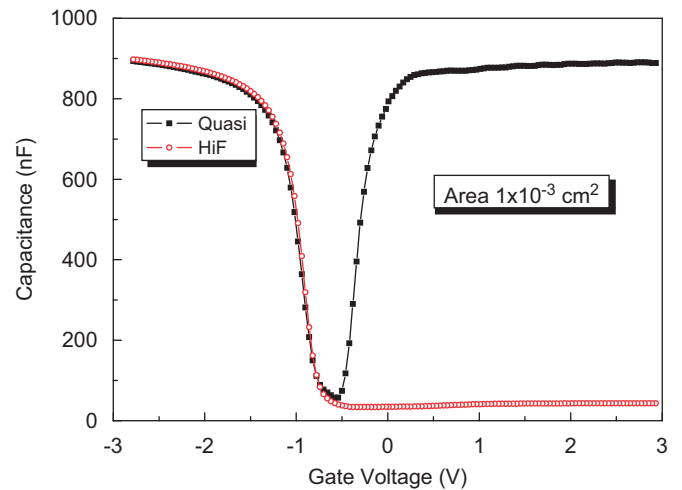


Fig. 5.  $C$ - $V$  characteristics for MOS capacitor. The measured area is  $1 \times 10^{-3} \text{ cm}^2$  and the CET = 38 Å.

inhibits defect formation because it does not require a high-temperature process. Moreover, the  $I$ - $V$  curve in the low-voltage ( $\leq 0.2 \text{ V}$ ) region shows a negative differential resistance, which is attributed to the slow interface states [17,18]. The interface trap density ( $D_{it}$ ), which is an important indicator for interface properties, can be extracted from low-/high-frequency  $C$ - $V$  curves (Fig. 5) using the quasi-static measurement technique. Fig. 6 shows that the 45 Å oxynitride film possesses a relatively low density of interface state  $D_{it} = 2 \times 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$ . By operating the capacitor under accumulation conditions, the capacitance equivalent thickness (CET) of oxynitride is extracted as 38 Å. As a result, it is confirmed that we have an oxynitride film that possesses a high- $k$  property. Finally, we doped the polycrystalline silicon (poly-Si) with implanted boron, and annealed at 900 C for various annealing times (30 min, 1

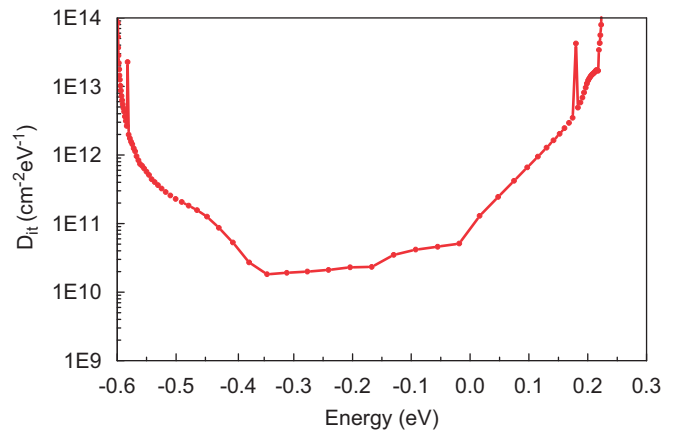


Fig. 6. Distribution of  $D_{it}$  versus energy for MOS capacitor.

and 2 h). High-frequency (100 kHz)  $C$ - $V$  measurements are applied and the results are shown in Fig. 7. It is clear that the  $C$ - $V$  curves do not shift in parallel in spite of the longer annealing time. This indicates that boron penetration is significantly suppressed with this desirable nitrogen profile.

For further study, the hysteresis in the  $C$ - $V$  characteristics of the  $N^+$ -gated sample with 23 Å oxynitride film was also evaluated. The data are shown in Fig. 8. The figure shows that there is no hysteresis found in the high-frequency  $C$ - $V$  curve, indicating that the film has a very low bulk or interface trap density. The  $C$ - $V$  curve profile will be affected by quantum-mechanical effect when the oxide is very thin [19]. Therefore, equivalent oxide thickness (EOT) was determined from the  $C$ - $V$  curve in a strong accumulation region at  $-3$  V. The result takes the quantum-mechanical effects [20] into account and the EOT of oxynitride is estimated as 18 Å. Fig. 9 shows the results after constant-current stressing at 4 and 10 mA  $\text{cm}^{-2}$ . No significant stress-induced leakage current

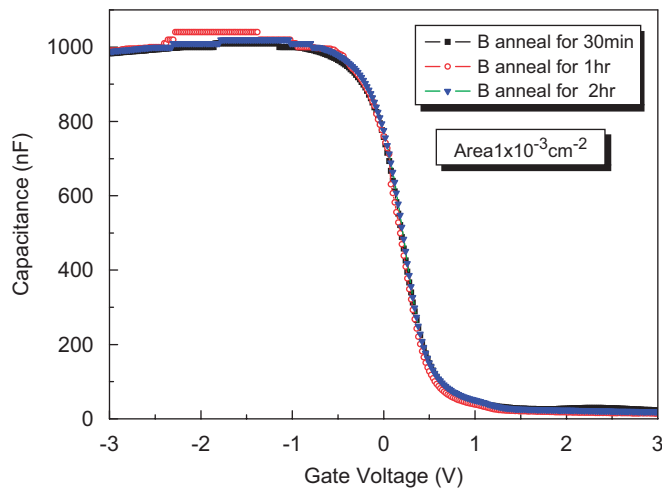


Fig. 7. High-frequency  $C$ - $V$  characteristics for MOS capacitor. Boron is annealed for 30 min, 1 and 2 h.

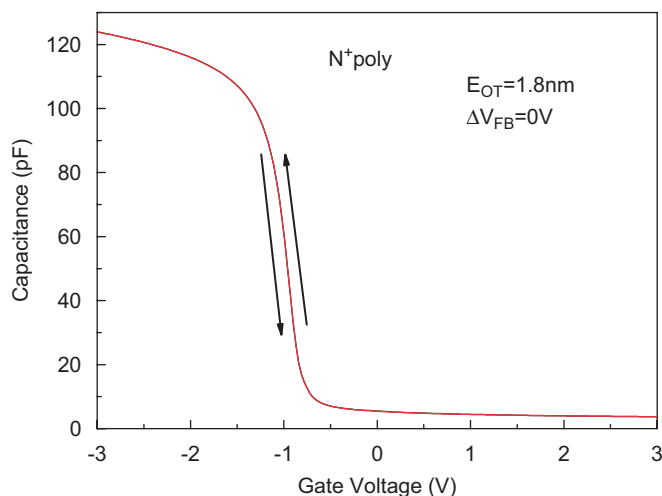


Fig. 8. Hysteresis characteristics for sample with EOT = 18 Å oxynitride.

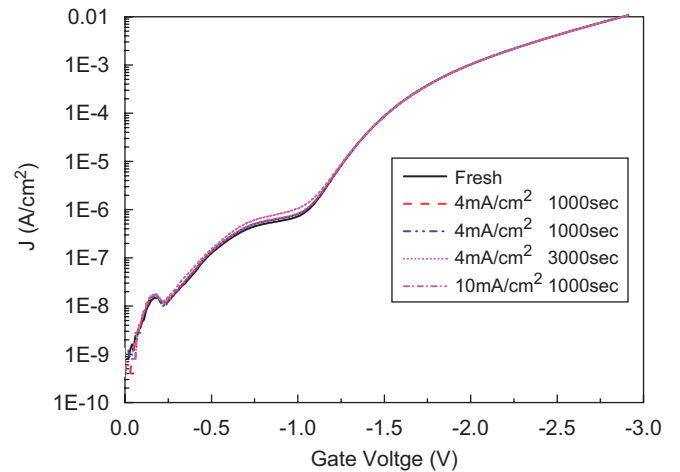


Fig. 9. SILC under constant-current stressing for sample with EOT = 18 Å oxynitride.

(SILC) was observed after stressing. Again, this implies that this new process can provide a high-quality gate dielectric film.

#### 4. Conclusions

We have proposed an approach for forming ultrathin oxynitride films with a non-uniform nitrogen content distribution, which has high content at the surface (13 at%) and low content (1 at%) at the interface between the oxynitride and the silicon substrate, without using extra equipment or gas and method is totally compatible with current semiconductor fabrication technology. The EOT of the oxynitride is less than 18 Å and the leakage current is as low as  $2 \times 10^{-9}$  A  $\text{cm}^{-2}$ . With appropriate process adjustment,  $D_{it}$  can be reduced within the  $2 \times 10^{10}$   $\text{cm}^{-2}$   $\text{eV}^{-1}$  range and the film demonstrates excellent suppression of boron diffusion and there is no significant SILC effect.

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