Chapter1

Introduction

Oxynitride(SiON) have been reported to show many advantages over thermaloxide. For example, excellent resistance to penetration of dopant and other impurities such as refractory metal, a higher dielectric strength, and enhanced resistance to damage induced by radiation and high-field stress. As the continuing scaling down of MOS devices has made high-field-induced device degradation a major concern, thin oxynitride seem promising for applications as a replacement for a thermally grown oxide in submicrometer-range ULSI devices such as RAM and EEPROM [1]. Oxynitride films also have improved thermal stability, and reduced film stress when compare to silicon nitride. In general, benefit of a oxynitride film is the nitrogen in the film accumulates at the silicon interface to reduce the concentration of strained Si-O bond, potentially reducing the creation of hot electron by as much three order of magnitude. An oxynitride layer at Si/SiO2 interface of thin gate oxides has been found to be beneficial for improving the device electrical performance. This chapter gives the general background of oxynitride and brief review of process technologies. Oxynitride is a promising gate dielectric, which has potential

advantages of ameliorating in the penetration of boron into the channel of the device, and breakdown during device operation. During the past years, the author took a lot of efforts into this study and obtained moderate accomplishment. The result and discussions are collected and summarized in this dissertation.

1.1 Background

The rapid progress of complementary metal-oxide-semiconductor(CMOS) integrated circuit technology since the late 1980's has enabled the Si-base microelectronics industry to simultaneously meet several technological requirements to fuel market expansion. These requirements include performance, for example speed, low static (off-state) power and a wide range of power supply and out voltage [2]. This has been accomplished by developing the ability to perform a calculated reduction of the dimensions of the fundamental active device in the circuit，following the “ Moore' s law ” , doubling about every two or three years since about 1980 [3]-[5]. The result has been a dramatic expansion in technology and communications markets including the market associated with high-performance microprocessors as well as low static-power applications, such as wireless systems. It can be argued that the key element enabling the scaling of the Si-based metal-oxide-semiconductor field effect transistor (MOSFET) is the materials and resultant electrical properties associated with the dielectric employed to isolate the transistor gate from the Si channel for decades: silicon dioxide (SiO2). The use of amorphous, thermally grown SiO2 as a gate dielectric offers several key advantages in CMOS processing including a stable (thermodynamically and electrically), high-quality Si-SiO2 interface as well

as superior electrical isolation properties. In modern CMOS processing, defect charge densities are on the order of $10^{10}\ cm^{-2}$, midgap interface state densities are $\sim 10^{10}\ cm^{-2}\ v^{-1}$ and hard breakdown field of 15 MV/cm are routinely obtained and are therefore expected regardless of the device dimensions. These outstanding electrical properties clearly present a significant challenge for any alternative gate dielectric candidate [6], [7].

Nowadays, advancement of VLSI technologies has resulted in continuous scaling down of metal oxide semiconductor field effect transistor (MOSFET), whose feature size used in IC chips has been reduced to deep-submicron technology node. The continuous shrinkage in MOSFET dimension has engendered a concomitant scaling in gate dielectrics to provide satisfactory circuit performance at low voltage. However, the continuous reduction of the gate-oxide layer thickness in advanced CMOS device leads to excessive gate leakage currents and reliability problem[8],[9]. The p-MOSFET with p+ poly-Si gate, an advanced CMOS structure to achieve low and symmetrical threshold voltages for low voltage operation, suffers from serious boron penetration from p+ poly-Si gate into the underlying Si substrate as devices go into deep submicrometerv regime due to the thin gate dielectrics. It has been shown that boron penetration not only causes a positive shift in threshold voltage but also severely aggravates the time-dependent dielectric breakdown (TDDB) characteristics

[10], [11].

In fact, boron penetration depends on gate dielectric thickness, that is, the thickness variation of gate oxide in wafer will change amount of boron that diffuses into the channel. It has been showed that boron penetration exponentially increase with decreasing oxide thickness [12], [13]. K. S. Krisch et al. [14] have reported the correlation between thickness variation and voltage shifts on wafer with intentional thickness non-uniformity (see Fig. 1-1).

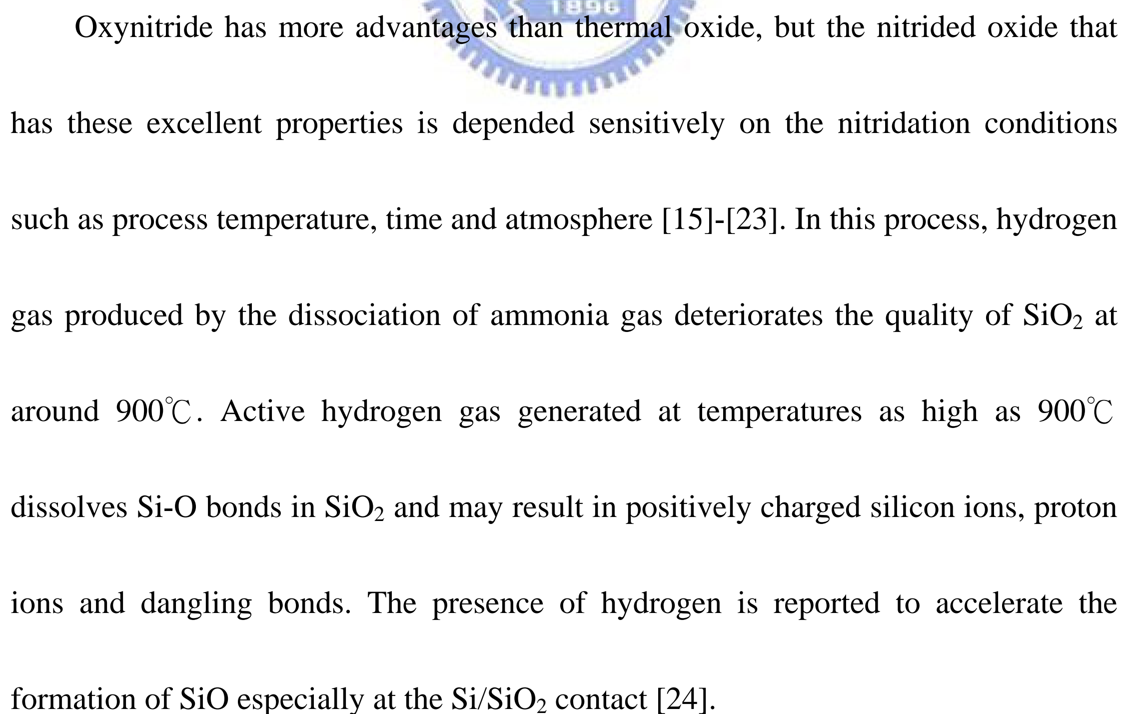
The flat-band voltage (V_{FB}) varies insensitively to the n-type gate device with thickness fluctuations, but p-type gate device is very sensitively, as shown in Fig.1-2, and if gate oxide variation little gives rise to large changes in V_{fb} and V_{th}. While V_T variations degrade many aspects of device performance, increased off-state leakage current has critical importance for systems which must minimize power consumption. In order to maintain high performance with decreased power-supply voltages, low threshold voltage is required, which at the same time increases the off-state leakage current. A large spread in V_T will increases this leakage current. Similarly, tight V_T control is essential to minimize off-state power consumption. Thus precise thickness control is needed for the thin gate dielectrics in submicron CMOS processes.

1.2 Processing Techniques for Silicon Oxynitride

Thermally ultrathin oxynitride are important to realize high performance and low-voltage operation CMOS devices than thermal oxide. Nitridation treatment on thin oxide has been used in MOS technology to strengthen the dielectrics robustness to electrical stress and to develop high permittivity gate dielectric stacks. In order to obtain the excellent properties of silicon oxynitride and fulfill the devices, various processing techniques have been developed.

1.2.1 Nitridation of oxide with NH_3 and reoxidation of nitrided-oxide

Oxynitride has more advantages than thermal oxide, but the nitrided oxide that has these excellent properties is depended sensitively on the nitridation conditions such as process temperature, time and atmosphere [15]-[23]. In this process, hydrogen gas produced by the dissociation of ammonia gas deteriorates the quality of SiO_2 at around 900℃. Active hydrogen gas generated at temperatures as high as 900℃ dissolves Si-O bonds in SiO_2 and may result in positively charged silicon ions, proton ions and dangling bonds. The presence of hydrogen is reported to accelerate the formation of SiO especially at the Si/SiO_2 contact [24].



T. Hori et al. [25] reported that the electron trap density is increased in

proportion to the hydrogen concentration in nitrided oxides. In their experiments, Fig. 1-3 shows nitrogen Auger electron spectroscopy (AES) depth profile and Fig. 1-4 shows hydrogen secondary ion mass spectroscopy (SIMS) depth profile for oxide nitrided at 950, 1050, 1150℃ for 60s. In figure 1-3, nitrogen piles up at both the Si-SiO_2 interface and the outer surface. As the temperature is raised, the nitrogen concentration increases monotonically through the film. The increasing rate of nitrogen concentration near the surface with the temperature is larger than that near the Si-SiO_2 interface. In Fig. 1-4, it can be seen that the hydrogen concentrations in nitrided oxide are considerably higher than those in a starting oxide.

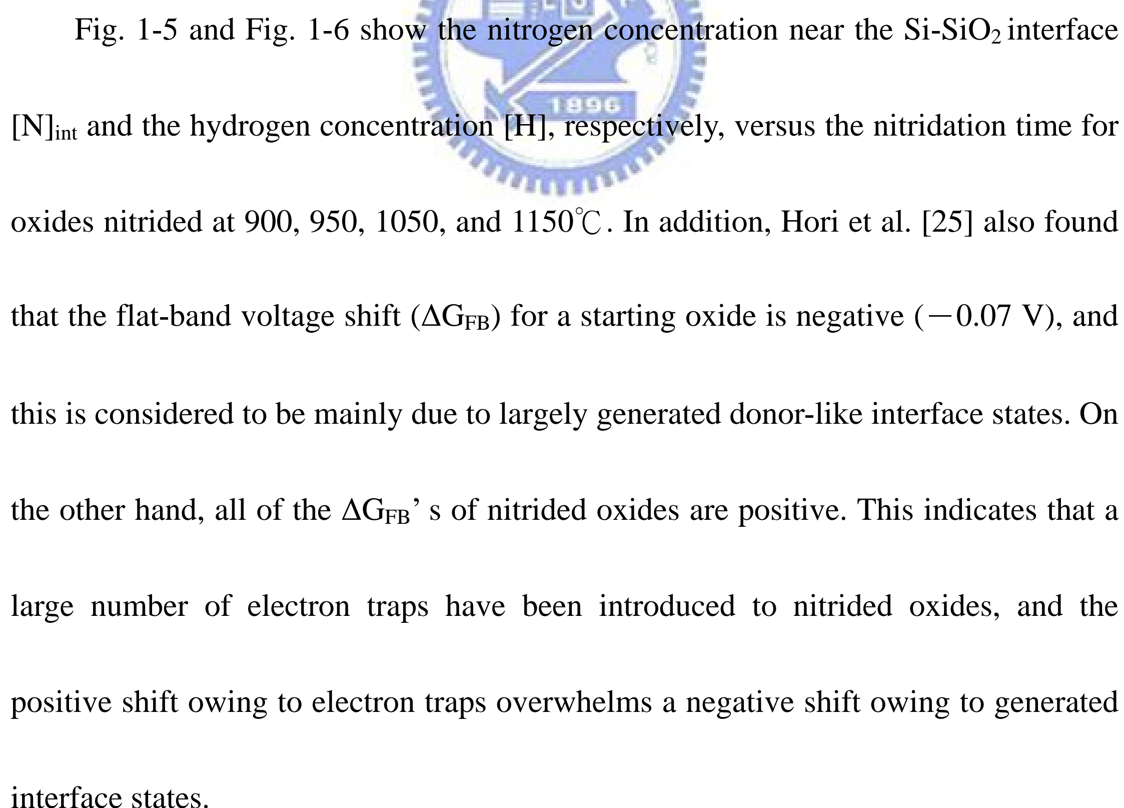


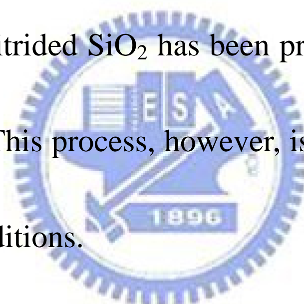
Fig. 1-5 and Fig. 1-6 show the nitrogen concentration near the Si-SiO_2 interface $[N]_{int}$ and the hydrogen concentration [H], respectively, versus the nitridation time for oxides nitrided at 900, 950, 1050, and 1150℃. In addition, Hori et al. [25] also found that the flat-band voltage shift (ΔG_{FB}) for a starting oxide is negative (−0.07 V), and this is considered to be mainly due to largely generated donor-like interface states. On the other hand, all of the ΔG_{FB}' s of nitrided oxides are positive. This indicates that a large number of electron traps have been introduced to nitrided oxides, and the positive shift owing to electron traps overwhelms a negative shift owing to generated interface states.

Fig. 1-7(a) (Fig. 1-7(b)) shows the ΔG_{FB} (the increase of midgap interface state

density (ΔG_{itm})) induced by electron injection of 0.1 C/cm^2 versus nitridation time for oxides nitrided at 900, 950, 1050 and 1150℃. ΔV_{FB} increases monotonically as nitridation proceeds. In contrast, ΔG_{itm} is found for the first time to show a turnaround with nitridation time: it increases at first, reaches a maximum at a certain nitridation time (t_{max}), and then decreases gradually to a certain value. The value is lower by more than one order of magnitude than that of a thermal oxide for a nitridation at a temperature higher than 1050℃. According to the above, it is difficult to make both ΔG_{FB} and ΔG_{itm} of a nitrided oxide small at the same time. While a heavily nitrided oxide has an advantage of small ΔG_{itm}, it shows a disadvantage of significantly large ΔG_{FB}. In fact, ΔG_{FB} can be reduced corresponding to the reduction of [H] by the reoxidation. Fortunately, reoxidation of nitrided oxides is very effective to eliminate the hydrogen-containing species in nitrided oxides while it keeps $[N]_{int}$ unchange (shown in Fig. 1-5 and Fig 1-6). It is striking that the reoxidation can reduce both ΔG_{FB} and ΔG_{itm} significantly at the same time. Based on the turnaround behavior of ΔG_{itm}, a two-factor model is proposed: one factor is [H], which increases $\triangle D_{itm}$, and the other is $[N]_{int}$, which reduces it. There have been proposed two types of centers as the origins of these weak bonds: one is hydrogen-containing centers [26], [27] and the other is the strained Si-O bond near the Si-SiO_2 [28], [29]. The former corresponds directly to one factor of two-factor model, the hydrogen concentration. The latter may

correspond to the other factor, $[N]_{int}$, by a postulation that nitrogen incorporation to SiO_2 reduces the strained Si-O bonds: it might be possible that tensile stress due to nitrogen incorporation counters the compressive stress that was present prior to nitridation [30].

As the mentioned above, studies on furnace nitridation of thermally grown SiO_2 layers at high temperatures with ammonia followed by reoxidation step have shown very promising trends toward reducing instabilities due to electron trapping, interface-state formation, destructive breakdown, and defect. Furthermore, Rapid thermal reoxidation of NH_3-nitrided SiO_2 has been proven to be effective in reducing the formation electron traps. This process, however, is more complicated and strongly dependent on the process conditions.



1.2.2 Oxynitride growth with nitrous oxide (N_2O) or nitric oxide (NO)

Silicon oxynitride films grown thermally using nitrous oxide (N_2O) and nitric oxide (NO) has been studied [31]-[37]. The first report of oxynitride grown with N_2O by H. Fukuda et al. [38] and H. Hwang et al. [39] is published in 1990. Oxynitride grown with N_2O contained nitrogen had drawn attention as candidate gate dielectrics due to its process simplicity and excellent reliability [40]-[47]. The advantages of N_2O-based oxynitride include (1) excellent boron diffusion barrier characteristics

compared to pure SiO_2, (2) no significant electron trapping atoms compared to NH_3-based oxynitride due to less hydrogen environment during process, and (3) low thermal budget compared to nitridation oxide. It is reported that the nitrided oxide using N_2O has the nitrogen piled up preferentially at the Si-SiO_2 interface [46], [48]-[50].

A study of N_2O nitridation kinetics, P. J. Tobin et al. [45] calculated that N_2O fully decomposed to N_2 (64.3%), O_2 (31.0%) and NO (4.7%) as it heated up to the furnace temperature of 950℃. Tobin et al. found that the peak nitrogen concentration (N_p) in the film depends linearly on the NO gas phase concentration and conjectured that NO is the critical species responsible for nitridation or the interfacial nitrogen concentration. In addition, some researchers study nitridation of oxide directly with NO gas. Two significant findings are observed on oxynitrides, which are treated with NO and N_2O. First, at a process temperature of 950℃, the NO treated oxynitride provides much tighter N distribution and slightly higher N_p than that of N_2O oxynitride. Second, the N_p peak is slightly located inside SiO_2 for the N_2O treated oxynitirde. Contrarily, the NO treated oxynitrde shows its N_p position inside the Si substrate (see Fig. 1-8).

In Y. Okada et al. [44], they show that a much lower thermal budget is required for an NO process than that of N_2O process. Thus it produces an oxynitride with

useful properties. In submicron technology node, MOSFET’ s with NO treated oxynitride showed superior current drive characteristics and comparable hot carrier immunity to those with N_2O treated oxynitride.

1.2.3 Reoxidation of nitride with H_2O

Traditional oxynitride films are formed by nitridation process on an existed oxide film with sequential NH_3, NO or N_2O’ s treatment. However, this approach has its difficulty in fabricating gate dielectric film thinner than 3nm due to gate dielectrics thickness will also keep increasing during oxynitridation. T. Yamamoto et al. [51] proposed that the thin oxynitride can be formed with direct nitirdizing on bare silicon and following sequential oxidation process. In general, the silicon nitride, formed by nitridizing the silicon with NH_3, can block the oxygen (O_2) penetration efficiently even at low temperature range, such as 900℃. T. Yamamoto et al. utilized the H_2O to oxidize the ultra-thin nitride which is formed thermal nitride, not the CVD nitride. No boron penetration, longer hot-carrier lifetime and high drain current are achieved. It also reported that electron trap density can be reduced by introducing hydrogen into nitride film during wet oxidation. Somehow their statements are contrary to the discussion mentioned before. In this report, they did not show any sample’ s SIMS data, which had been annealed at 1050℃, to remove hydrogen concentration

distribution. It is possible that the high temperature annealing process with large thermal budget has driven the hydrogen away leading to low hydrogen concentration in oxynitride film. The arguments proposed by T. Yamamoto that low electron trap is due to existed hydrogen in oxynitride during wet conversion with H_2O is debatable.

It is known that the oxynitride which formed by NO, or N_2O, or NH_3 treatment can effectively suppress boron penetration. However, they also come with several degradation of the oxide reliability due to the nitrogen piles up along the interface between silicon substrate and oxynitride. From D. Wristers et. al. [52], they have demonstrated that BF_2–implanted polysilicon gated p-MOS capacitors using ultra-thin nitrided oxide with NO treatment is highly effective in the alleviation the boron penetration-induced flat-band voltage instability (see Fig. 1-9). Unfortunately, such improvements are observed in conjunction with some degradation of the oxide reliability due to the boron-blocking/accumulation inside the gate dielectric (e.g., charge-to-breakdown and electron trapping, Fig. 1-10). Fig. 1-11 shows the schematic of boron diffusion from the heavily doped p^+ gate into the gate dielectric and substrate interface region. In the conventional SiO_2.device (Fig. 1-11(a)) boron diffuses due to the concentration gradient from the heavily doped p^+ gate into the SiO_2/Si interface and Si substrate. On the contrary, in the NO-nitrided device (Fig. 1-11(b)) the nitrogen-rich layer at the SiO_2/Si interface obtained the excellent

boron-stopping properties at that interface resulting in additional boron accumulation inside the oxide leading the enhanced dielectric reliability degradation. Thus, there is a trade-off between device performance stability and gate oxide time-dependent dielectric breakdown (TDDB) reliability.

1.3 The mechanism of oxidation in Reoxidation nitrided-oxide

1.3.1 Nitrogen depletion in reoxidation nitrided-oxide

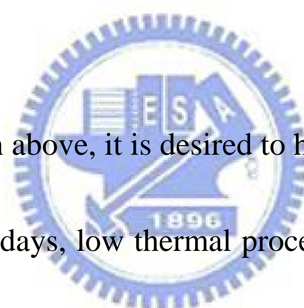
N. S. Saks et al. [53] also propose a nitrogen-related reaction model which occurs in N_2O furnace oxidation. Via this reaction, nitrogen is removed from the bulk of the oxide during oxidation, while at the same time it is incorporated at the growing Si-SiO_2 interface. Thus, the final nitrogen profile relies on the dynamic equilibrium between competing processes which causes both nitrogen incorporation and removal (as shown in Fig. 1-12). The data in Fig 1-12(c) clearly show that a reaction (Si－N－Si+NO→Si－O－Si+N_2) occurs during N_2O reoxidation which removes nitrogen from oxynitride. Summarily, reactions with NO are probably responsible for the nitrogen depletion effect observed for furnace oxidation.

However, given the unknown time required to heat the N_2O gas to decompose (N_2O→N_2+O), Ellis et al. [54] suspect that some N_2O survived to decompose near the wafer, resulting in exposure of the wafers of Saks et al. to atomic oxygen. Under

sufficiently high flow rates, atomic oxygen may survive to reach the wafer. It has been shown previously, with low pressure O_3 annealing, that atomic oxygen is capable of scavenging N from an oxide [55], Ellis suggest that the species responsible for N removal is atomic oxygen.

Finally, Gusev et al. [56], [57] observed that for NO-grown films the nitrogen is distributed relatively evenly in the film. This implies that nitrogen is incorporated but not removed during NO oxynitridation. Thus, it can be concluded that the nitrogen depletion during oxidation in N_2O is caused by atomic oxygen, not the NO.

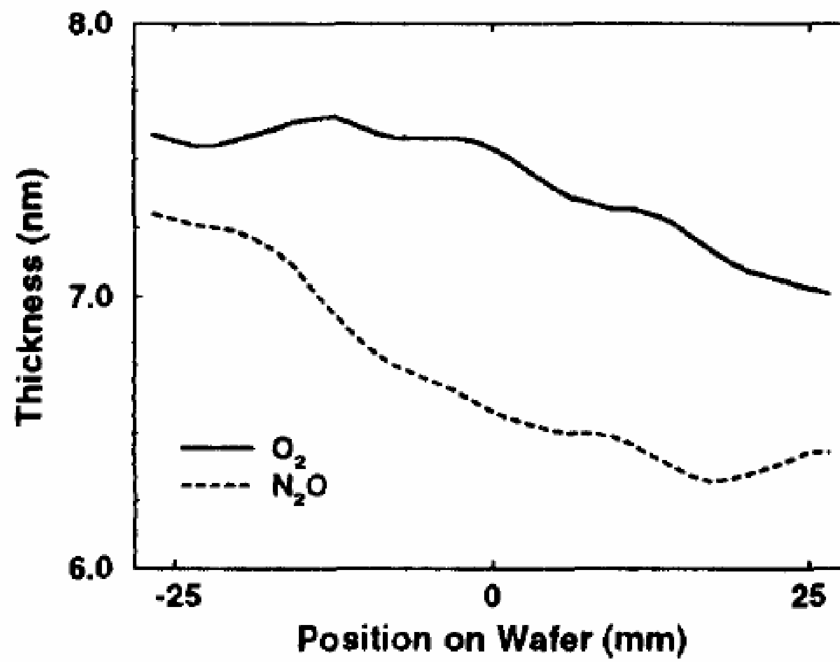
1.4 Thesis Organization



E S A
1896

According to the review given above, it is desired to have a simple way to obtain high quality oxynitride film. Nowadays, low thermal process and thin oxynitride films are preferred in ULSI technology. Chapter 2, we propose a new method to build robust ultrathin oxynitrde with high nitrogen diffusion barrier near its surface which is formed by NH_3 nitridation of chemical oxide and reoxidation with O_2, and then we will describe that the electrical characteristic research of high-nitrogen oxynitride (12 at. %) reoxidation with O_2 which we proposed. Chapter 3 extends the studies in chapter2. We will discuss the reliability of the n-MOSFET with high nitrogen diffusion barrier near its surface which is formed by NH_3 nitridation of chemical oxide and reoxidation with O_2. Chapter 4 concludes with a summary of the results in

the dissertation and Chapter 5 suggests for future work.



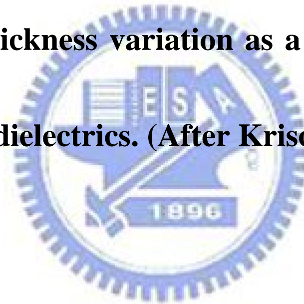
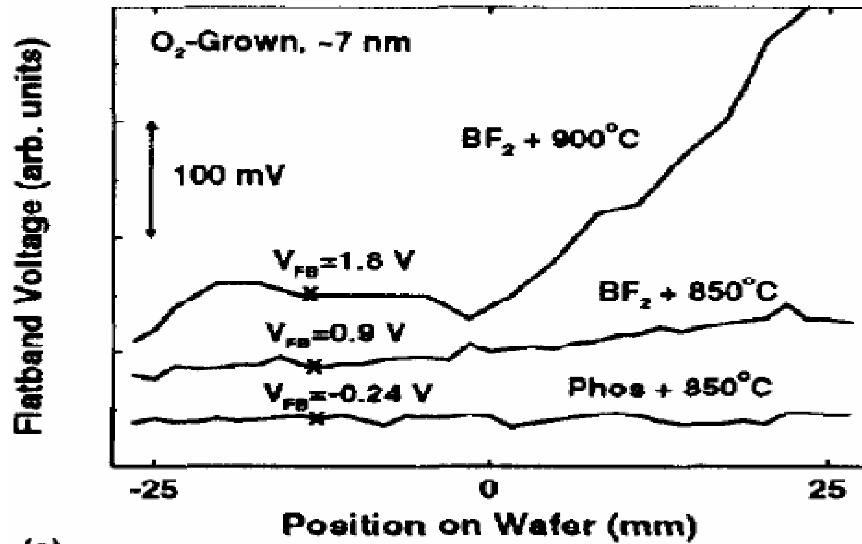


Fig. 1-1 The exaggerated thickness variation as a function of position on wafer for O_2 and N_2O-grown gate dielectrics. (After Krisch et al, Ref. [14])



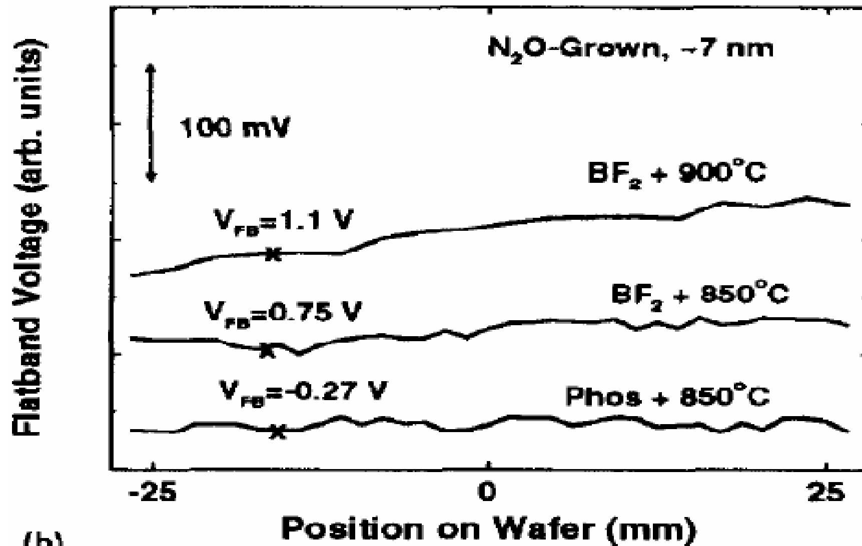


Fig. 1-2 V_{FB} as a function of position on wafer for (a) O_2 and (b) N_2O-grown gate dielectrics with gate electrodes implanted and annealed as indicated. The thickness nonuniformity illustrated in Fig. 1-1 results in a large V_{FB} variation on those samples with substantial boron penetration. (After K.S. Krisch et al, Ref. [14])

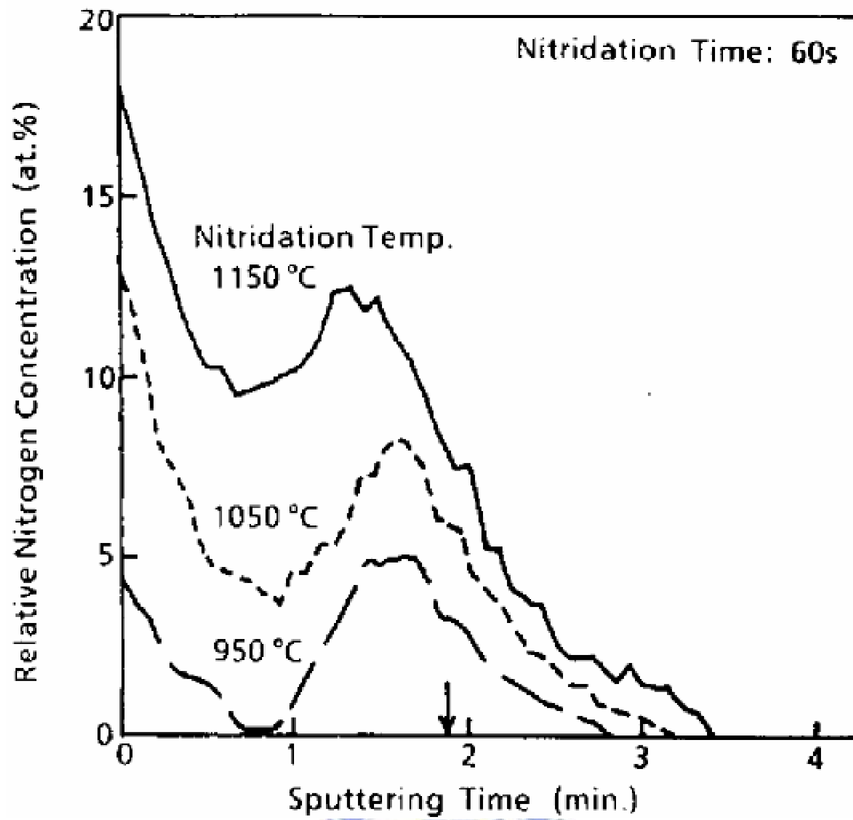


Fig. 1-3 Nitrogen AES depth profiles of 8-nm-thick oxides nitrided at 950, 1050, and 1150℃ for 60 s. The arrow indicates the position of the Si/SiO2 interface. The nitrogen concentration increases monotonically as nitridation proceeds. (After T. Hori et al, Ref. [25])

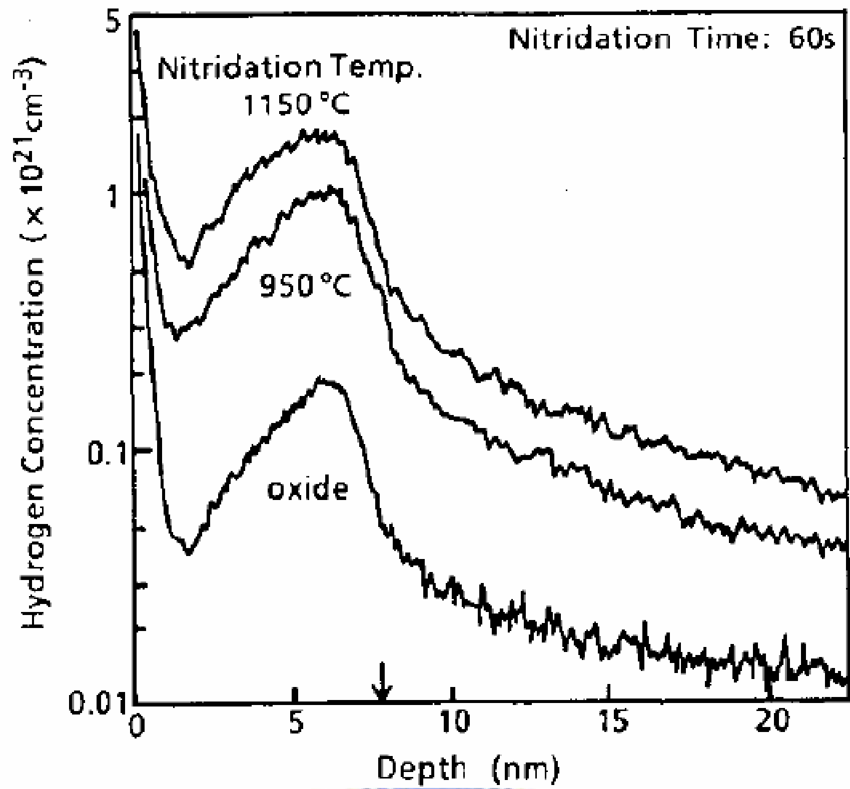


Fig. 1-4 Hydrogen SIMS depth profiles of 8-nm-thick oxide nitrided at 950 and 1150℃ for 60 s. The arrow indicates the position of the Si/SiO2 interface. The hydrogen concentration increases monotonically as nitridation proceeds. (After T. Hori et al, Ref. [25])

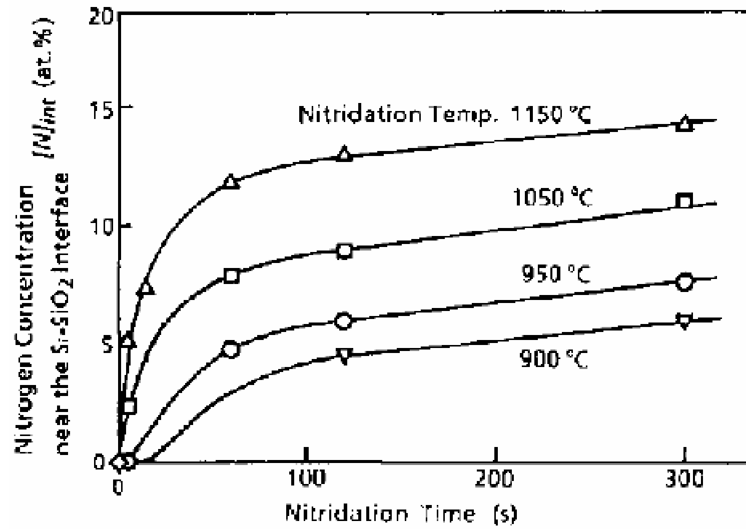


Fig. 1-5 Nitrogen concentration near the Si-SiO_2 interface $[N]_{int}$ versus nitridation time for oxides nitrided at 900, 950, 1050, and 1150℃. $[N]_{int}$ increases monotonically as nitridation proceeds. (After T. Hori et al, Ref. [25])

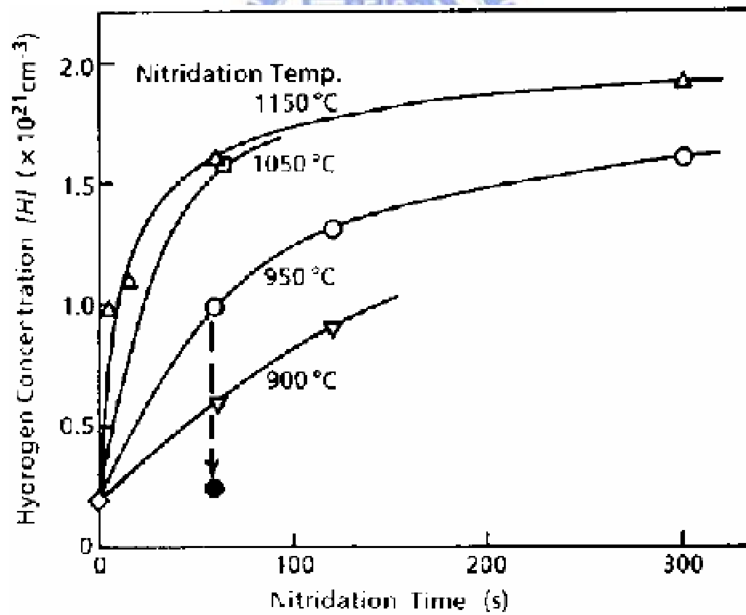


Fig. 1-6 Hydrogen concentration [H] versus nitridation time for oxides nitrided at 900, 950, 1050, and 1150℃. The dashed arrow and • in the figure indicate the effect of re-oxidation at 1150℃ for 60 s following a nitridation at 950℃ for 60 s. (After T. Hori et al, Ref. [25])

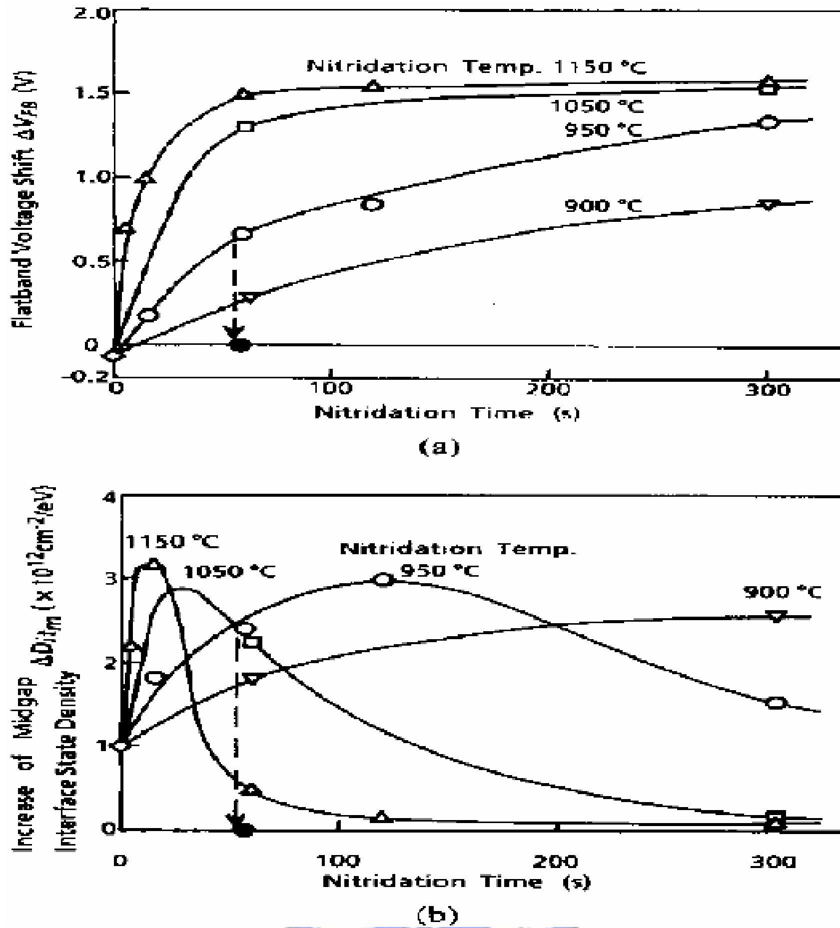


Fig. 1-7 (a) The flat-band voltage shift ΔG_{FB} and (b) the increase of midgap interface state densityΔG_{itm} by 0.1C/cm^2 electron injection versus nitridation time for oxides nitrided at 900, 950, 1050, and 1150℃. The dash arrow and • in each figure indicate the effect of re-oxidation at 1150℃ for 60 s following a nitridation at 950℃ for 60 s. While ΔV_{FB} increase monotonically as nitridation proceeds, ΔG_{itm} shows a turnaround. (After T. Hori et al, Ref. [25])

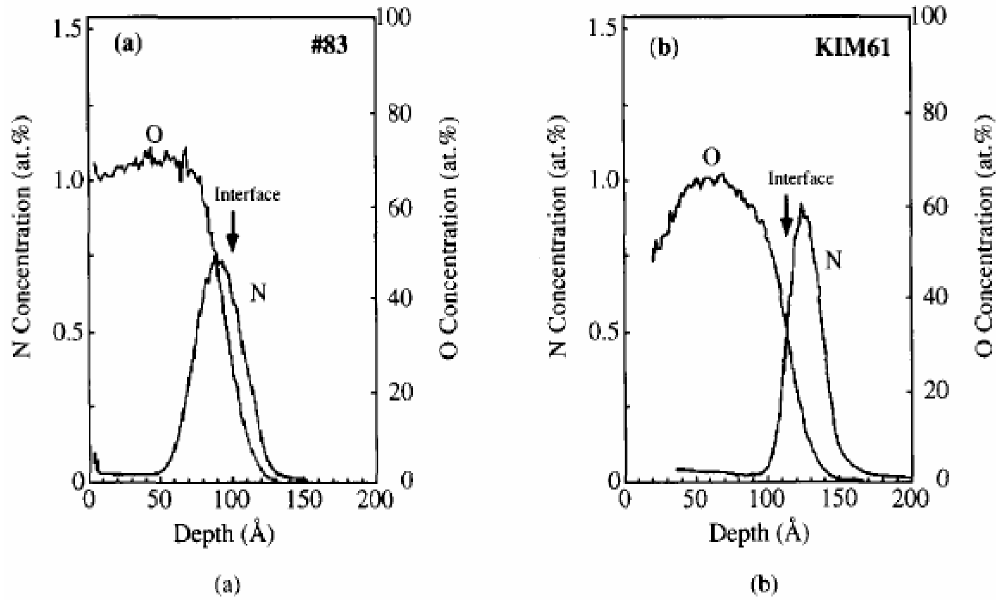


Fig. 1-8 SIMS profiles of (a) N_2O oxynitride grown at 950℃, (b) NO oxynitride processed at 950℃. (After Okada et al, Ref. [44])

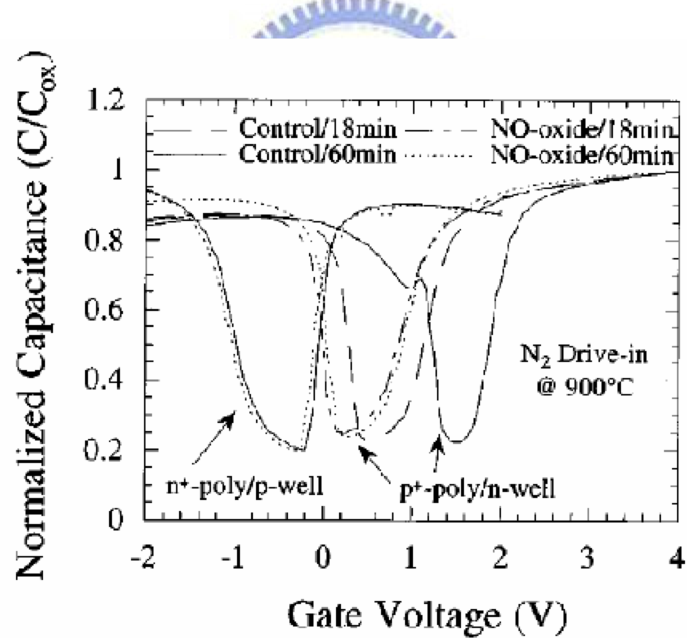


Fig. 1-9 Normalized quasistatic C-V curves for both p^+-poly and n^+-poly MOS capacitors with different gate dielectrics. The drive-in anneal was performed at 900℃in N_2 for 18 or 60 min (After Wristers et. al, Ref. [51]).

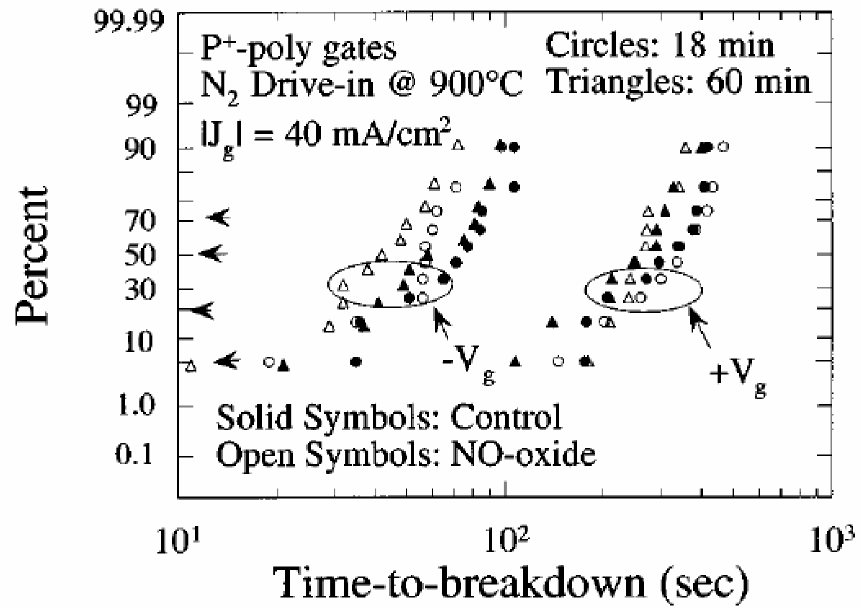
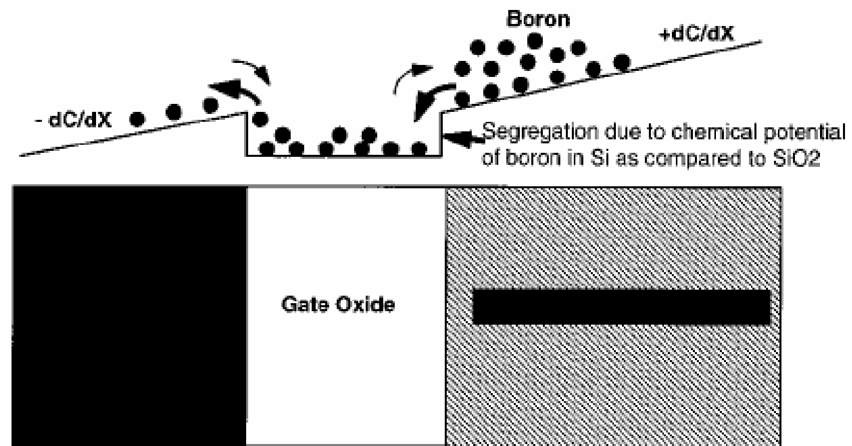


Fig. 1-10 Time-dependent dielectric breakdown (TDDB) distribution for p^+-poly gated PMOS capacitors under ±Vg gate bias stress. (After Wristers et. al, Ref. [51]).



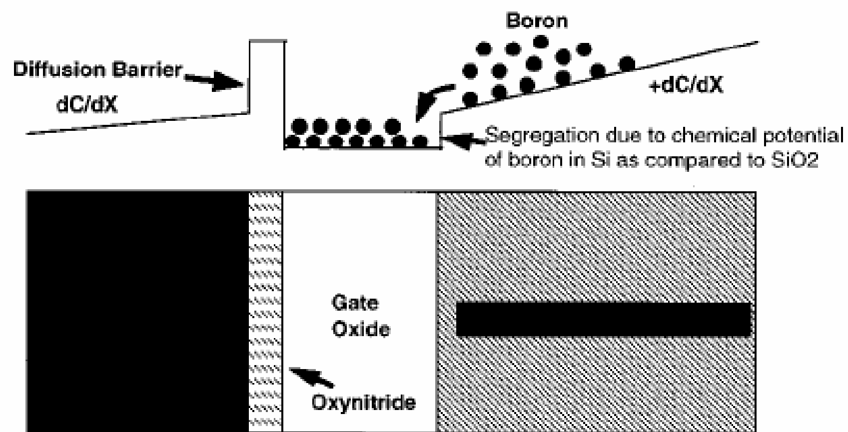


Fig. 1-11 The schematic of boron diffusion from the heavily doped p^{+}-gate into the gate dielectric and substrate interface region for conventional SiO_2 gate dielectrics (a) and interaction of the boron with the nitrogen at the interface for the NO nitrided gate (b) (After Wristers et. al, Ref. [51]).

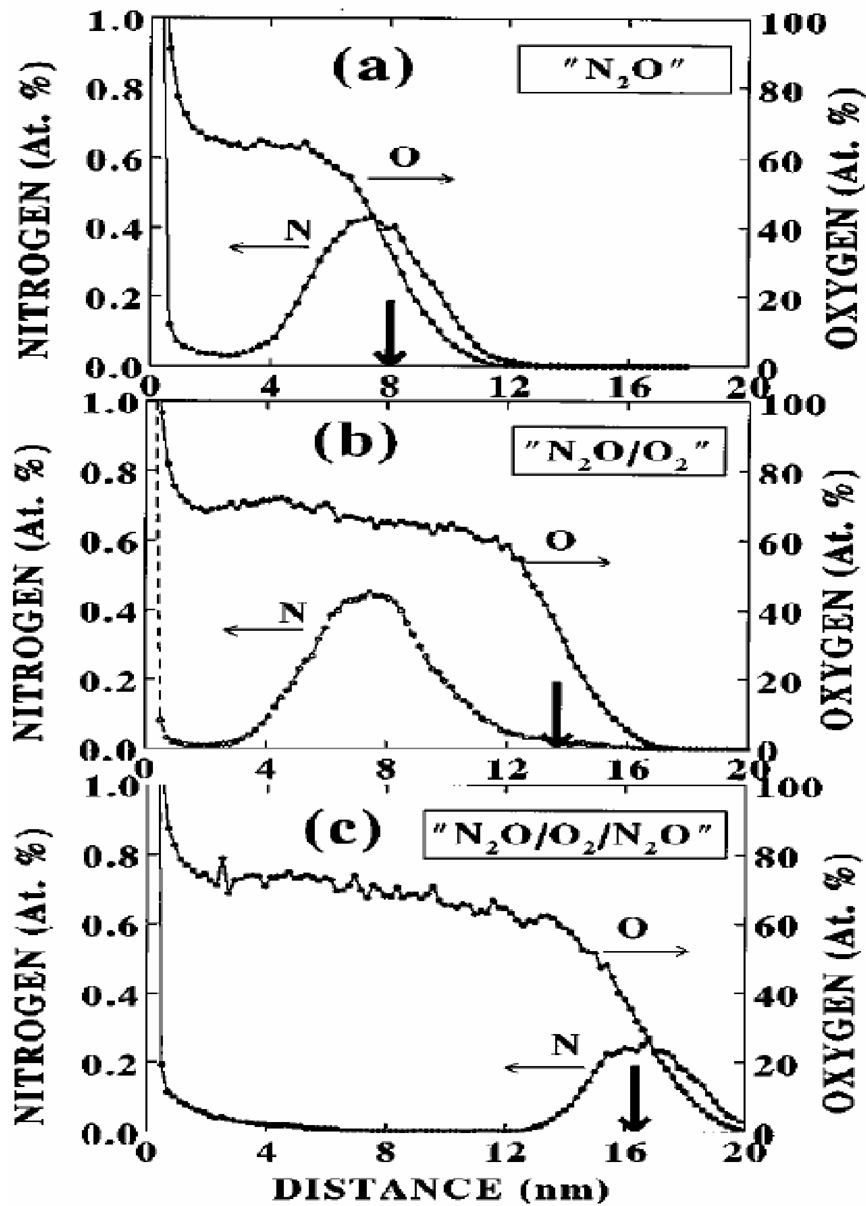


Fig. 1-12 SIMS profiles of nitrogen (N) and oxygen (O): (a) Nitrogen peak is located at Si–SiO_2 interface. (b) Despite the substantial increase in oxide thickness, the nitrogen profile is essentially unchanged. (c) New nitrogen peak has formed at the new Si–SiO_2 interface position. (After Saks et al., Ref. [53])