Thermal Nitridation of Si and SiO_2 for VLSI

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Abstract—This paper presents an extensive review of our work on thermal nitridation of Si and SiO_2. High-quality ultrathin films of silicon nitride and nitrided-oxide (nitroxide) have been thermally grown in ammonia atmosphere in a cold-wall RF-heated reactor and in a lamp-heated system. The growth kinetics and their dependence on processing time and temperature have been studied from very short to long nitridation times. The kinetics of thermal nitridation of SiO_2 in ammonia ambient have also been studied. In nitroxide, nitrogen-rich layers are formed at the surface and interface at a very early stage of the nitridation. Then the nitridation reaction mainly goes on in the bulk region with the surface and near interface nitrogen content remaining fairly constant. Our results also indicate the formation of an oxygen-rich layer at the interface underneath the nitrogen-rich layer whose thickness increases slowly with nitridation time. The nitride and nitroxide films were analyzed using Auger electron spectroscopy, grazing angle Rutherford backscattering, and etch rate measurements. MIS devices were fabricated using these films as gate insulators and were electrically characterized using $I-V$, $C-V$, time-dependent breakdown, trapping, and dielectric breakdown techniques. Breakdown, conduction, and $C-V$ measurements on metal-insulator semiconductor (MIS) structures fabricated with these films show that very thin thermal silicon nitride and nitroxide films can be used as gate dielectrics for future highly scaled-down VLSI devices. The electrical characterization results also indicate extremely low trapping in the nitride films. The reliability of ultrathin nitride was observed to be far superior to SiO_2 and nitroxide due to its much less trapping. Studies show that the interface transition from nitride to silicon is almost abrupt and the morphology and roughness of the interface are comparable to the SiO_2–Si interfaces.

I. Introduction

HIGH-QUALITY very thin (⩽100 Å) gate insulators (VTGI) will be required for future scaled VLSI devices. To illustrate the trend of the larger scale of integration and the need for thinner gate insulators, DRAM can be used as an example. Megabit DRAM and high-density FLOTOX E^2PROM devices will need gate or tunnel insulators in the subhundred-angstrom region. The 256-kbit DRAM has a gate insulator thickness of about 200 Å whereas the projected 1-Mbit DRAM using conventional one transistor per bit will require an insulator thickness of less than 100 Å.

VTGI should be grown using an easily controllable process with minimum number of process control parameters. They should be uniform and amorphous with low defect density and conductivity. Furthermore, high breakdown field, sharp breakdown distribution, clean interface, and low trapping efficiency are important requirements. In order to have better control over electrical characteristics of devices, VTGI should be effective masks against impurity diffusion

Thermally grown silicon dioxide films have many obvious applications in silicon devices and technology including gate insulators of IGFET's and the tunnel insulators for nonvolatile memories such as E^2PROM. There are, however, several technological and reliability problems with silicon dioxide in the very thin regime. The fact that very thin layers of thermal SiO_2 are poor masks against impurity diffusion places additional constraints on processing steps following the growth of gate or tunnel oxides. Moreover, the growth of high-quality very thin layers of SiO_2 is rather difficult due to defect density, integrity, and yield problems. It is also known that high-energy radiation can generate a high density of interface states in the oxide, resulting in degradation of device performance. Very thin SiO_2 is not a good mask against impurity diffusion [1], [2] and has high defect density [3]. These poor properties of very thin SiO_2 film and also its tendency to react with electrode material will limit its effective widespread application for gate, tunnel, or DRAM capacitor dielectrics of scaled VLSI devices. As a result of the technological and reliability problems with silicon dioxide in the very thin regime (⩽100 Å), there is a demand for new higher quality ultrathin insulators to replace silicon dioxide in highly scaled down VLSI IGFET's and memory devices such as DRAM and E^2PROM. Thermal nitridation of Si and thin SiO_2 has been investigated in the past few years and appears to be an alternative to the oxidation process to grow good-quality films in the very thin regime. Thermally grown very thin films of silicon nitride have a number of advantages over silicon dioxide. Their growth is self-limited and, therefore, easily controllable. They have less number of process control parameters and high oxidation resistance. Moreover, they are effective barriers against impurity diffusion and their characteristics do not degrade during the VLSI processes [4], [5]. Devices fabricated with these films show a large transconductance and reduced undesired second-order effects [6]–[8].

Thermal nitride films can be grown by high-temperature nitridation of silicon in pure ammonia [9], ammonia plasma [10], [11], nitrogen–hydrogen plasma [12], or low-tempera-

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ture laser-enhanced nitridation [13]. Thermal nitridation of Si in resistance-heated hot-wall quartz-tube furnaces can lead to high oxygen contamination of the grown films [5]. Most of the recent work on thermal nitridation has been on technological issues such as composition, growth kinetics, oxidation resistance, and interactions with impurity diffusion [9], [14]–[18]. In a few cases, devices made with nitroxide and nitride have been electrically characterized [6], [8], [19]–[30]. A more detailed electrical characterization of thermal nitride films including trapping, however, had not been reported in the past. In addition to that, most of the work in the past has been on nitroxide. Nitridation of oxide results in the reaction of nitridation species with oxide at the surface and interface regions and to a lesser extent in the bulk region as will be described later. It has been reported that the generation of radiation-induced interface states in MOS devices is eliminated after proper high-temperature nitridation of oxide [31], [32]. This may be attributed to structural changes in the interface region of oxide after nitridation in ammonia. We have observed [19], as Ito *et al.* [33] have also reported, that the breakdown characteristics of MOS structures can be improved by annealing the SiO_2 films in ammonia gas at high temperatures. The effects of nitridation of SiO_2 in ammonia on electron trapping has been investigated [34], [35] and it has been reported that ammonia nitridation results in a significant increase in electron trapping. The data presented so far, however, have not been sufficient to draw firm conclusions regarding trapping in nitroxide insulators. Moreover, effects of annealing of nitroxide insulators in nitrogen, oxygen, or argon ambients on trapping characteristics should be studied in more detail and correlated to the compositional parameters of nitroxide.

It has been observed that thermal nitridation of SiO_2 films results in the formation of a nitrided-oxide or nitroxide layer with composition profile that varies with depth. It has also been reported that both thickness and refractive index of thin oxide films are increased after high-temperature nitridation in ammonia [16], [36]. The changes in composition of the initial oxide film after nitridation in ammonia have been studied using several techniques such as Auger electron spectroscopy (AES), etch rate, Rutherford backscattering spectroscopy, infrared transmittance spectroscopy, and oxidation resistance measurements [9], [16], [17]. Moreover, very thin ($\leqslant$100 Å) nitroxide and reoxidized-nitroxide insulators were used as tunnel insulators of high-endurance E^2PROM (nonvolatile memory) devices [20]–[27].

In the work reported here, thermal nitridation was accomplished in a closed-tube cold-wall RF-heated reactor to minimize the oxygen contamination. Very short time ($\leqslant$5 min) nitridations were performed in a commercial lamp-heated rapid thermal annealing system, again in pure ammonia. The grown films have been characterized using grazing angle Rutherford backscattering (RBS), Auger electron spectroscopy (AES), cross sectional transmission electron microscopy (TEM), ellipsometry, and etch rate measurements. In addition, the electrical properties of the films were determined by doing C–[illegible] time dependent breakdown and trapping measurements on Al-gate capacitors.

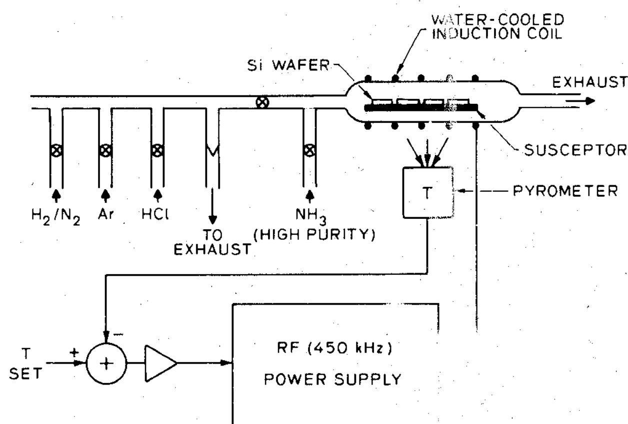

Fig. 1. The RF-heated thermal nit[illegible]tor.

II. Experimental Procedures

All the long time ($\geqslant$5 min) experiments were conducted in a horizontal RF-heated reactor operating at atmospheric pressure, as shown in Fig. 1. Thermal nitridation is performed in pure or diluted ammonia in argon. The oxygen comtamination from outside and from the quartz tube is insignificant because the tube walls [illegible] cold. The short time ($\leqslant$5 min) nitridations [illegible]ormed in a lamp-heated rapid thermal annealing [illegible] in the range of 900–1200°C.

For kinetics studies, both n- and p-type (111) and (100) silicon wafers with resistivities ranging from 0.002 to 3 $\Omega \cdot$cm, and oxidized silicon wafers were used. The samples were first cleaned chemically, loaded on a silicon carbide-coated graphite susceptor, and then inserted in the quartz tube. After an initial purging of the system with pure nitrogen, the flow of pure ammonia ($\leqslant$1 ppm contaminants) was established. After flushing N_2 out of the tube with ammonia, temperature was ramped up to the growth temperature and stabilized. Nitridations were performed at temperatures ranging from 950 to 1230°C for periods of 30 min to 4 h. For compositional studies of nitroxide, the oxide films were grown in dry O_2 at [illegible]°C to a thickness of 95 Å and at 1000°C to thicknesses of [illegible], 405, and 1021 Å, on 5–10 $\Omega \cdot$cm (100) silicon wafers. The nitridations were performed for times from 15 s to 4 h at 900 to 1200°C in pure ammonia at atmospheric pressure. To investigate the effect of heavy doping an experiment was performed where heavily phosphorus-doped silicon wafers with (100) and (111) orientations were nitrided at 1190°C for 2 h. Phosphorus doping had been done at 1050°C from $POCl_3$ resulting in a sheet resistance of 1.6 Ω/sq.

The thicknesses of the grown nitride films were measured using a microcomputer-controlled ellipsometer with a 6328-Å laser source and substrate index of refraction fixed at 3.85–0.02i. In the measurements the refractive

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index of the silicon nitride films was fixed at 2.0. This method is adopted because it is not possible to measure both thickness and refractive index of very thin films ($\leqslant 100$ Å) accurately by ellipsometry. The variation of the film refractive index in the range between 1.6 and 2.0 exhibits little effect on the nitride thickness measurement results. The measured thickness values are almost independent of the film refractive index N_f for its value in between 1.8 and 2.0. All kinetics data presented in this paper, however, are for $N_f = 2.0$ which is the established value for thick CVD nitride. The nitride and nitroxide films were investigated using AES, RBS, TEM, etch rate, and electrical characterization techniques. In the etch rate measurements the thickness of remaining film was measured after step by step etching in 50:1 DI H_2O:HF using ellipsometry.

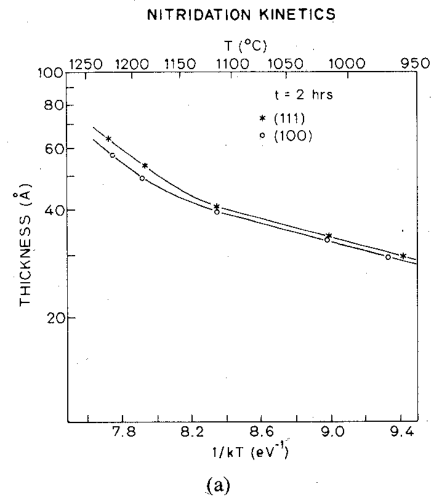
MIS devices with thin oxide, nitroxide, and nitride gate insulators were fabricated with aluminum-gate electrodes on n- and p-type Si substrates. The SiO_2 used in devices with oxide and nitroxide was grown to a thickness of about 100 Å in a furnace in oxygen at 900°C. The wafers were annealed in forming gas at 450°C for 20 min before patterning and after deposition of metal. Finally aluminum was patterned into dots. The gate areas were 2.01×10^{-2}, 5.03×10^{-3}, 1.26×10^{-3}, 3.14×10^{-4}, and 7.85×10^{-5} cm^2. The gate electrode was Al-(1 percent) Si deposited in a flash evaporator.

III. Composition and Growth Kinetics Studies

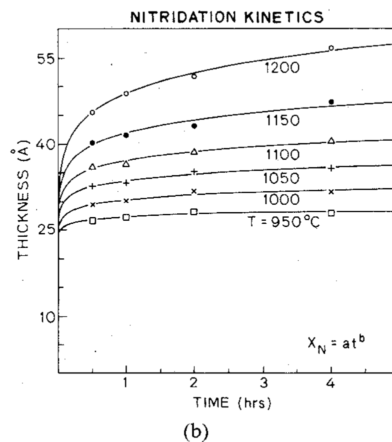
A. Growth Kinetics

Fig. 2(a) shows the thickness of thermal silicon nitride films as a function of nitridation temperature for nitridation period of 2 h on (100) and (111) silicon wafers. Under identical processing conditions the films grown on (100) silicon are thinner than those on (111) silicon, and the orientation effect is more pronounced at higher temperatures. Below 1000°C, however, the effect of substrate orientation on nitridation kinetics is negligible. Murarka *et al.* [5] did not observe any orientation dependence of nitridation kinetics. We believe that their observation could be due to large scatter in their thickness measurements and also very high oxygen contamination of their nitride films. It is evident that in contrast to the silicon thermal oxidation process, the nitridation kinetics has a rather weak dependence on the substrate orientation. This could be due to the fact that the latter process is diffusion-limited during most of the growth time except for the fast initial growth.

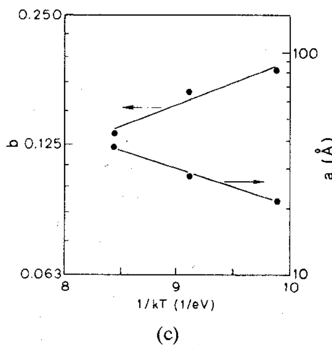
For shorter times (like 30 min), nitridation of silicon shows an approximately Arrhenius behavior with temperature whereas for longer times ($t \geqslant 1$ h) the behavior is not quite Arrhenius because more than one activation energy is observed in the temperature range of growth. Applying exponential least-squares curve fits of the form $X_N = X_\infty \exp(-E_a/kT)$ to the experimental kinetics data, the values of the activation energy E_a and the coefficient X_∞ (The thickness as $T \to \infty$) were evaluated as a functions of



(a)



(b)



(c)

Fig. 2. Silicon nitridation kinetics. (a) Arrhenius plot of nitride thickness versus nitridation temperature for 2-h nitridation and (100) and (111) substrate orientations. (b) Thickness of nitride grown on (100) Si versus nitridation time and temperature. (c) Temperature dependences of a and b in the power law expression.

tion of (111) silicon shows a higher activation energy than that of (100) silicon. The activation energies as given in Table I, are fairly small but larger than that reported by Murarka *et al.* [5] who observed an activation energy of 0.23 eV for 40 min nitridation in 5 percent NH_3 and 16 h nitridation in 100 percent NH_3. Hayafuji and Kajiwara [16] obtained an activation energy of 0.35 eV for 5 hour nitridation in ammonia partial pressures of 10^{-3} kg/cm^2 and 1 kg/cm^2.

Fig. 2(b) illustrates the thickness of thermal nitride films

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TABLE I

NITRIDATION TIME	(100)		(111)	
	X_∞ (Å)	E_a (eV)	X_∞ (Å)	E_a (eV)
30 MIN.	667.4	0.342	869.5	0.369
1 HOUR	1052.9	0.390	1525.2	0.429
2 HOURS	1183.9	0.398	1706.0	0.434
4 HOURS	3295.1	0.513	7455.2	0.602

The constants X_∞ and E_a ($X_N = X_\infty \mathrm{EXP}(-E_a/kT)$) for various nitridation times of (100) and (111) silicon.

to 4 h with temperature as a parameter. The thicknesses were measured with the refractive index fixed at 2.0. The experimental data indicate a very fast initial growth in a short time ($\leqslant 5$ min) followed by a self limiting growth. To express the longer time ($\geqslant 5$ min) experimental kinetics results in a functional form, we have found several simple empirical relationships useful [9]. One relationship which fits the experimental data best is $X_N = a \times t^b$ as shown by the solid curves in Fig. 2(b), where a and b are temperature dependent constants, and X_N and t are the silicon nitride thickness and nitridation time, respectively. The constants a and b are found by fitting the experimental data using the method of least squares. In the temperature range of interest they show nearly Arrhenius behavior with nitridation temperature with single activation energies. We can obtain the activation energies of 0.381 and 0.238 eV for temperature dependence of a and b, respectively. Fig. 2(c) illustrates the temperature dependences of a and b for the power law expression. Their functional dependences on nitridation temperature can be expressed as $a = 920.2\ e^{(-0.381/kT)}$ Å and $b = 0.0183\ e^{(0.238/kT)}$. In the power law expression, a and X_N are in angstroms, t is normalized to 1 min, and b is unitless. Reisman *et al.* [37] have also observed power law dependence of nitride thickness grown in Ar–NH_3 plasma on nitridation time ($t^{0.2}$ dependence). The power law relationship is only an empirical relationship which fits the experimental data fairly well. We have not investigated the physics of a growth that follows the $X_N = a \times t^b$ kinetics. As will be described, at present we have a good physical understanding of the mechanism of nitridation of oxide; however, this knowledge is not yet available for nitridation of silicon. The major remaining question in the case of silicon nitridation is regarding the species (Si ions and/or nitrogen species) that diffuse through the film and react with silicon or nitrogen at the opposite interface (nitride/ambient or nitride/silicon). This question has not yet been answered.

Fig. 3 illustrates the growth kinetics data for silicon wafers nitrided at 1100°C for times from 30 to 120 s in a lamp-heated rapid thermal annealing system in pure ammonia. The data indicate that for very short nitridation times, the growth is linear with nitridation time.

The kinetics of nitridation have also been studied by some other investigators. Hayafuji and Kajiwara [16] studied nitridation of bare Si and 100 Å SiO_2 at

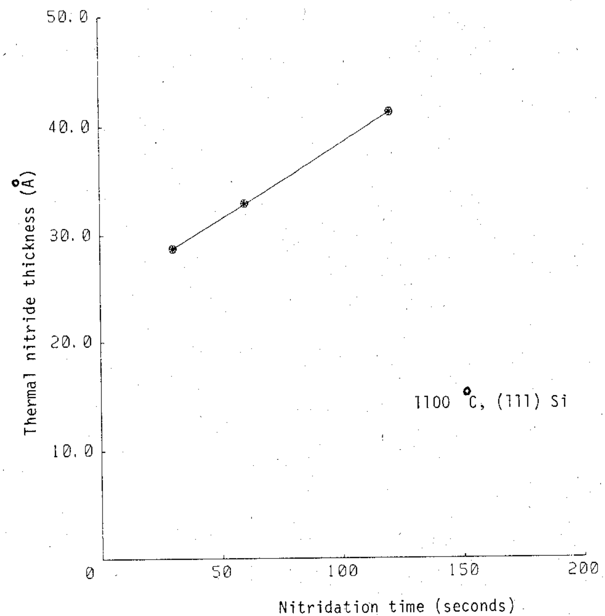

Fig. 3. The short time Si nitridation kinetics data for 1100°C nitridation.

kg/cm² in high-purity ammonia and ammonia–nitrogen mixture. They performed all the nitridation experiments in a resistively heated high-pressure system. For 5-h nitridation at 900°, 1000°, and 1100°C, they studied the dependence of self-limited nitride thickness on NH_3 pressure from 10^{-3} to 5 kg/cm². For less than atmospheric pressures nitrogen was used to dilute the NH_3. The pressure dependence of the nitridation growth kinetics was found to be rather small. The film thickness increased only by 20 percent when the NH_3 partial pressure was increased from 10^{-3} to 5 kg/cm². The oxidation resistance data of Murarka *et al.* [5], however, show more ammonia partial pressure dependence than those of Hayafuji and Kajiwara [16]. We believe that in the presence of oxidant impurities in the ambient the pressure dependence is more significant and lower partial pressure of NH_3 results in higher oxygen contamination of the films. The nitride films of Hayafuji and Kajiwara were much more oxygen free compared to those of Murarka *et al.* Chen *et al.* [38] also studied the high-pressure nitridation process and found that for high-pressure nitridation of silicon in the range of 1–10 atm, the nitride thickness for a given nitridation time and temperature increases slightly with increasing the ammonia pressure.

The growth kinetics of nitride in pure nitrogen at 1200–1300°C has been investigated [39]. The results indicated that for a given temperature, smooth and amorphous nitride films could be grown for short reaction times but they start to become rough and crystalline for long reaction times. The maximum reaction time for growth of amorphous uniform nitride is reduced by increasing the nitridation temperature. Contrary to ammonia nitridation, no self-limiting of growth could be observed for high-temperature nitridation in nitrogen.

Recently two models have been proposed for thermal

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a model which is based on the solution of the continuity equation. Except for the definition of an unrealistic diffusion length, their assumptions are similar to the Deal–Grove oxidation model [41]. Their assumptions that the grown film has a uniform composition and the reaction only takes place at the nitride/silicon interface are inconsistent with their result showing a variable nitridant flux through the film. Furthermore, the introduction of the characteristic diffusion length implies the annihilation of the nitridant species inside the grown film which they assume to be stoichiometric and uniform. We believe this model partially neglects the physics of the process. Our experiments show the existence of nonuniform (in depth) and nonstoichiometric films which should be considered in developing a physical kinetics model. A second model proposed by Hayafuji and Kajiwara [16] assumes that nitridation occurs due to the reaction of ammonia with silicon which is diffused out to the surface of the film by a strong internally induced electric field. They suggest this model in order to explain the pressure independence of silicon nitridation kinetics. At present, the exact mechanism of thermal nitridation of silicon is unclear and there is no strong experimental evidence to show if nitridant species or silicon ions are the dominant diffusers through the film during nitridation. Tan and Gosele [42] found the model proposed by Hayafuji and Kajiwara [16] acceptable. They suggested that the Si cations leaving the nitride–silicon interface are formed by interstitials diffused from the silicon interior to the interface. If true, this would imply that thermal nitridation does not consume any silicon atoms taken from the nitride–silicon interface region and the interface is not a moving boundary. More experimental evidence is needed to conclude that the silicon consumed during thermal nitridation of silicon is either provided by breaking the Si–Si bonds at the nitride–silicon interface or by the flow of silicon interstitials from the substrate into the film. Whether the actual nitridation mechanism might be Si cation diffusion or nitridant diffusion (or a combination), we believe that the depletion of interstitials during nitridation of silicon can not be used as a very strong evidence to come up with the actual nitridation mechanism.

In the experiments conducted to study the effects of heavy doping on nitridation kinetics, we observed that the nitride films grown on heavily phosphorous-doped silicon had the same thickness as those grown on lightly doped silicon wafers. Therefore, no significant effect of heavy doping on nitridation growth kinetics was detected.

Thermal nitridation of ≈ 100 Å SiO_2 resulted in an increase in the film thickness. Oxide films 95 Å thick were thermally nitrided at various temperatures for periods of 30 min, 1 h, 2 h, and 4 h. The thickness increase as a function of processing temperature and time is shown in Fig. 4. The thickness change does not show an Arrhenius behavior with temperature because the film thickness increases more rapidly at higher temperatures. The thickness of all nitroxide films were measured using ellipsometer with the film optical refractive index fixed at 1.46. The oxide samples nitrided at very high temperatures for long

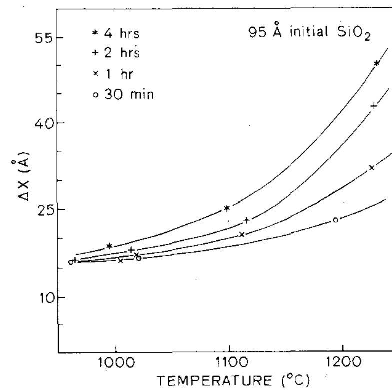

Fig. 4. The increase in the thickness of 95-Å SiO_2 due to nitridation versus nitridation time and temperature. The actual thickness may be slightly lower because the index of refraction was fixed at 1.46.

periods (e.g., 1200°C, 4 h), however, exhibited enhanced refractive indices up to more than 1.7. Our experience shows that in the thickness measurement of very thin films by ellipsometry, fixing the refractive index at a value lower than the true index value results in a measured value slightly higher than the real thickness. Therefore, in the foregoing high-temperature experiments for long processing times the measured thickness might be somewhat higher than the actual value.

There is some disagreement in the literature on whether the thickness of oxide is increased or decreased after exposure to ammonia. Aucoin *et al.* suggest that the nitridation of oxide causes a shrinkage in the film thickness [14]. Hayafuji and Kajiwara [16] reported that nitridation of oxidized silicon resulted in a small increase in the thickness of the films. According to their data, nitridation of 100-Å oxide at 1100°C for 5 h increased the thickness of the original oxide by about 20 Å. The change of thickness, however, can depend on nitridation conditions and the original oxide thickness. As we will explain, the growth of interfacial oxide layer during nitridation of oxide tends to increase the thickness of the film and the exchange bulk reaction may result in a slight shrinkage of the bulk. In general the change in the film thickness due to nitridation of oxide is fairly small. Most of the thickness measurements are the data obtained with ellipsometry which can have some error due to the nonhomogeneous structure of nitroxide. Based on the results of our work on kinetics studies of nitridation of oxide, we have come up with a simple theoretical model which relates the final thickness of the nitroxide to the thickness of the initial oxide, and the bulk composition of nitroxide which is a function of the nitridation conditions [43]. According to this simple model, depending on the thickness of original SiO_2 and the nitridation conditions, the nitridation of oxide may result in increase or decrease in the film thickness. The ellipsometer data agree fairly well with this model.

B. Auger Electron Spectroscopy and Grazing Angle RBS

The nitride and nitroxide samples were analyzed using AES and some of the Auger depth profiles for them are

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