

MATERIAL AND PROCESS CONSIDERATIONS FOR ULTRA-THIN SILICON (OXY-) NITRIDE FILMS GROWN OR DEPOSITED ON SILICON AND SiO₂ SURFACES

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Silicon (oxy) nitride films used in the semiconductor fabrication process continue to be grown/deposited thinner and thinner as device dimensions continue to shrink. In this study, we have compared the growth kinetics, nitrogen composition and profile, morphology and electrical characteristics of silicon nitrides and oxy-nitrides prepared by several techniques. These include rapid thermal (RT) processes such as N₂O, NO, NO+O₂, and NH₃ (oxy) nitridations as well as ultra-thin LPCVD and RTCVD nitride and oxy-nitride processes. The measurement techniques used to characterize these films include: ellipsometry, nuclear reaction analysis (NRA), medium energy ion scattering (MEIS), atomic force microscopy (AFM) and C-V and I-V electrical characterization of poly-gate capacitors. With a thorough understanding of the growth behavior, and material properties of ultra-thin silicon (oxy) nitride films grown by different techniques, we can tailor the film thickness, nitrogen concentration and profile to optimize the materials diffusion barrier and electrical properties for desired applications.

INTRODUCTION

Ultra-thin (<5 nm) silicon nitride and oxy-nitride films are becoming increasingly important in the semiconductor industry (1,2). These films find applications for use in gate dielectric stacks, polysilicon sidewall spacers and diffusion barriers for logic and memory devices. The material, diffusion barrier and electrical properties of these films are strongly dependent upon the growth technique that is used. Nitrogen concentration and profile, film thickness and uniformity, and film continuity are all important issues to understand when selecting the appropriate film for a desired application.

The growth kinetics and material properties of thermally grown silicon (oxy) nitrides largely depend on the reactant species used. While the nitrogen concentration in RT-N₂O films is typically 1-2 %, RT-NO films contain up to 10-15% nitrogen. Since the nitrogen content is about ten times higher in RT-NO films than in RT-N₂O, the growth rates are much slower due to the excellent diffusion barrier properties of nitrogen. The growth kinetics of RT-N₂O has been extensively studied by others (3,4,5). The gas chemistry in RT-N₂O processes involves the decomposition of N₂O to O₂, NO and oxygen radicals. These complex reactions yield a nitrogen profile in the film in which nitrogen builds up at the Si/SiO₂ interface and depletes closer to the top surface. RT-NO growth involves only NO as a reactant species, so the nitrogen is uniformly distributed throughout the film. Green, et al. (6) studied RT-NO+O₂ gas mixtures. He found these films to be very smooth from AFM measurements. The nitrogen content of the film as well as the growth

rate could be tailored by changing the dilution of NO in O₂ in the gas stream. Numerous studies have shown that thermally grown oxy-nitride films are effective to stop boron penetration through polysilicon gates. (7) The electrical benefits of incorporating nitrogen into these films have been reported by many. They include improvements in interface quality, immunity to channel hot carrier degradation, and leakage current reduction. (2,8) In this study, we compare the growth kinetics; nitrogen concentrations and profile; morphology and electrical quality for ultra-thin RT (oxy)nitrides. These include RT-O₂, N₂O, NO, NO+O₂ and NH₃ thermal processes.

LPCVD and RTCVD nitrides and oxy-nitride films may be deposited very thin on silicon and SiO₂. However, in some instances, nucleation problems exist. Nucleation inhibition of LPCVD nitrides on oxide surfaces has been previously observed (9). Also, the effects of RTCVD (oxy) nitride processing parameters on incubation time and growth rate has been examined (10). Copel's MEIS study of the early stages of silicon nitride deposition on oxide indicated that films <20 Å show signs of discontinuity (11). Here, we study and compare some aspects of growth kinetics, nitrogen concentration, morphology, and electrical properties of LPCVD nitride and RTCVD nitrides and oxy-nitrides.

EXPERIMENTAL

For the growth kinetics experiments, 200 mm diameter, p-type monitor wafers (9-18 ohm-cm) were first cleaned using a concentrated dissolved ozone water rinse followed by a diluted RCA clean (12) in an automated wet deck with megasonics. Oxy-nitride growth and depositions were performed in a commercial single wafer cluster tool. It is equipped with 2 load locks, a transfer chamber and 3 process chambers. The thermal oxy-nitrides were grown in an RTO chamber in N₂O, NO, or O₂ gases and the RTCVD silicon nitride or oxy-nitride was deposited in a second chamber using NH₃, SiH₄ or SiH₂Cl₂ and N₂O chemistries. Wafer transfer between chambers and loadlock was performed under 5 torr pressure and each chamber uses lamp heating and wafer rotation to improve thickness uniformity of the deposited films. LPCVD was performed in a commercial horizontal furnace using dichlorosilane and ammonia.

Single wavelength ellipsometry was used to determine the optical thickness of the (oxy) nitrides. For O₂, N₂O and NO films, a fixed index of 1.46 was used. The film's refractive index will vary from 1.46 to 2.0 depending on the nitrogen content in the film. Thus, for the more heavily nitrated RT-NO films, a fixed index of 1.46 results in a slight overestimation of the oxy-nitride's physical thickness. An index of 2.0 was used for the RT-NH₃ thermally grown silicon nitride films. The refractive indices of the RTCVD (oxy) nitride films were measured by ellipsometry on thick films (>500 Å). To measure the optical thickness of the top (oxy) nitride in a oxide/(oxy) nitride stack, the refractive index of the stack was fixed to the (oxy) nitride's previously measured value and the oxide contribution (measured separately at the (oxy) nitride's refractive index) was subtracted away. Electrical measurements of the films were performed by high-frequency capacitance techniques on poly-gate capacitors with locos isolation. The electrical thicknesses were corrected for polysilicon and substrate depletion effects as well as quantum mechanical effects. (13)

Nitrogen analysis of the films was performed by nuclear reaction analysis (NRA). Total nitrogen content was determined with the $^{14}\text{N}(d, \alpha)^{12}\text{C}$ nuclear reaction using an annular silicon surface-barrier detector in back scattering geometry covered by a 12.7 micron Mylar R absorber foil. Samples were irradiated with 20-200 nanoampere beams of 1.05 MeV deuterons from the Yorktown NEC 9SDH-2 tandem accelerator. At this low energy, the elastically scattered beam particles are stopped by the mylar foil and do not cause problems due to high count rates in the detector. The large amount of energy released from the reaction resulted in alpha particles corresponding to the first excited state in ^{12}C with sufficient energy to pass through the absorber foil and still have over 5 MeV of energy to deposit in the detector. The detector bias was lowered to reduce the depletion depth to the point that protons from (d,p) reactions could not deposit more than 4 MeV of energy in the detector, eliminating interference with the signal of interest. Interference from Si (d, α) reactions were reduced by using a target tilt of 0 degrees, a channeling geometry. The background typically was equivalent to a nitrogen area density of about $1\text{E}14$ $^{14}\text{N}/\text{cm}^2$, and was not subtracted from the data. It was assumed that any nitrogen present was in the layers of interest, since this particular technique has poor depth resolution.

Medium energy ion scattering (MEIS) is a technique that can give high resolution depth profiles of oxynitrides. Based on the same principles as Rutherford backscattering, MEIS makes use of electrostatic analysis of ions, resulting in sub-nanometer depth sensitivity. For an extensive review of the application to oxynitrides, see ref. (4,14). The data shown below was obtained using an incident beam of 200 keV He+, channeling in the (111bar) direction. The backscattered ions were detected at a scattering angle of 60 degrees.

Atomic force microscopy (AFM) was used to determine the roughness/morphology of the surface. The measurements were completed using a D-5000 AFM manufactured by Digital Instruments of Santa Barbara, CA. Imaging was done using an etched silicon tip with a radius of 5-10 nm. The surface roughness calculations were derived from two 5 μm x 5 μm areas per wafer approximately 25 mm apart located near the wafer center. Imaging for surface morphology was done using 1000 \AA x 1000 \AA area scans.

RESULTS AND DISCUSSION

Thermal Processes

Growth Kinetics. The growth kinetics of rapid thermal oxy-nitridation processes usually involves two stages of growth. As shown in Figure 1, oxy-nitridation in RT-N₂O occurs quickly at the initial stage and then slows for longer times. This is indicative, in general, of thermal oxidation processes, where mechanisms for this rapid initial growth have been proposed by many (15,16).

The growth rates of these processes depends largely on the type of reactant used. Reactant gases which incorporate substantial amounts of nitrogen in the film tend to slow

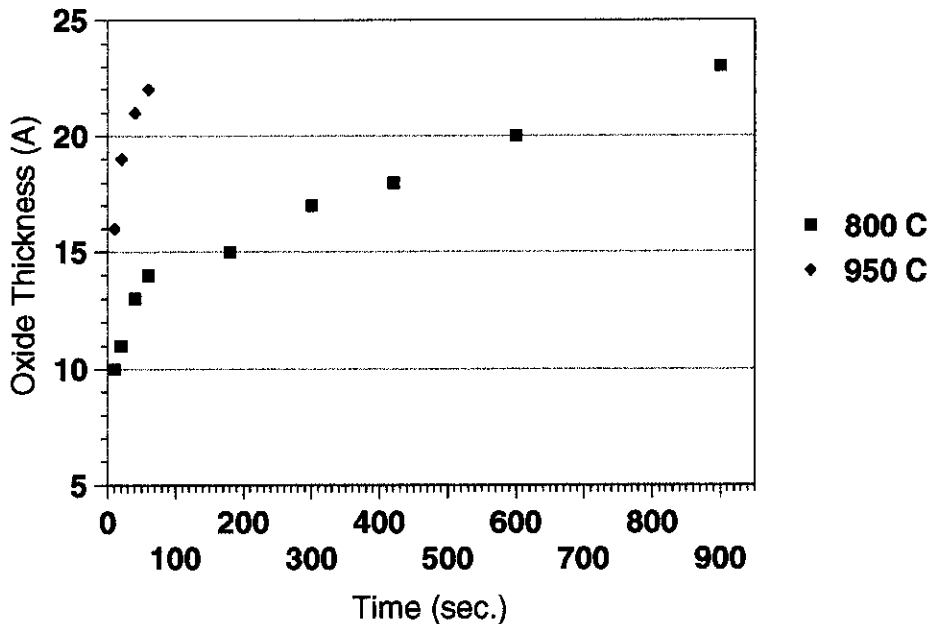


Figure 1: RT-N₂O oxidation of silicon at 800 and 950 C. The process pressure= 100 torr and N₂O flow rate = 0.5 slm

down the growth rate due the excellent diffusion barrier properties of nitrogen. Figure 2 shows growth rates of silicon dioxide, oxy-nitrides, and nitrides grown by RT-O₂, N₂O, NO and NH₃. Under identical temperature, pressure and flow rate conditions, the thinnest films are grown by RT-NH₃ followed by RT-NO, RT-O₂ and RT-N₂O. The respective nitrogen content of these films are: 57% (silicon nitride), 10-12%, 0%, and 1-2%. Films grow thicker in RT-N₂O compared to RT-O₂ since atomic oxygen is generated during the N₂O decomposition reaction.(3,4) This radical form of oxygen has higher diffusivity in silicon than O₂. The growth rates for these processes are very similar. In accordance with the diffusivity of these species in silicon, the growth rate for RT-O₂ is fastest, while RT-NO oxy-nitridation is slowest. By changing temperature and pressure, a wide range of film thicknesses may be achieved. Films as thin as 4 Å for a RT-NH₃ processes to 200 Å for RT-O₂ processes can be obtained.

In order to grow thicker oxy-nitride films than can be grown by RT-NO alone, oxygen can be mixed with NO to increase the resulting film thickness. Figure 3 shows the effect on film thickness by diluting the NO gas in oxygen. The oxy-nitride film optical thickness can be increased by 4-7 Å by diluting the NO from 100%-10% in oxygen. The advantage

of growing thicker films this way is that nitrogen may still be incorporated which improves

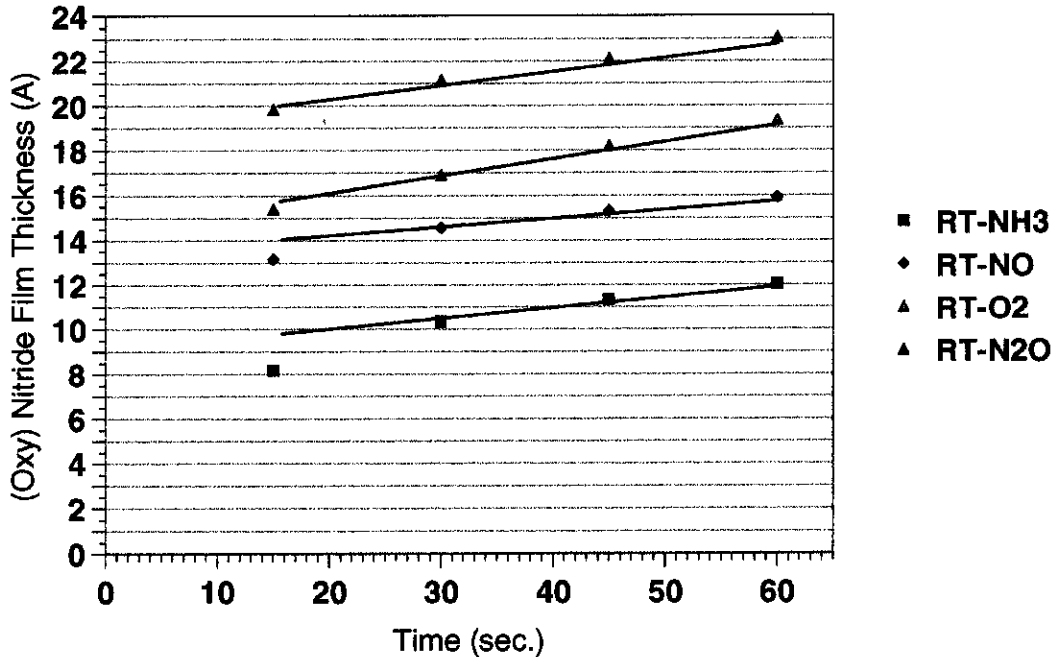


Figure 2: Growth kinetics comparison of RT-O₂, N₂O, NO and NH₃. All recipes use a process temperature of 900 C, pressure of 550 torr, and flow rate of 0.9 slm.

the films electrical and diffusion barrier properties. The amount of nitrogen in the film will scale with the percentage of NO in the gas stream. Diluting NO into oxygen is a more efficient process than re-oxidizing an RT-NO film in RT-O₂ to grow thicker films. For instance, Figure 4 shows that a 14 A RT-NO film requires a 3 min. re-oxidation in O₂ at 950 C to reach 20 A. Figure 3 shows that a 20 A oxy-nitride film grown in NO+O₂ only requires 30 sec. (30% NO) or 60 sec. (50% NO). Although these films will not have identical levels of nitrogen, they will have substantially more than an RT-N₂O film.

Nitrogen Concentration and Profile. The nitrogen content of the oxy-nitride films will depend on the reactant species used as well as the process conditions. Films grown by RT-N₂O typically incorporate 1-2 atomic percent of nitrogen. For a 20 A film, this corresponds to a nitrogen concentration of 1-2 E14 atoms/cm² as determined by nuclear reaction analysis. The nitrogen profile of RT-N₂O films has been studied by many (3,4) and shows nitrogen buildup at the SiO₂/Si interface and a decrease in nitrogen concentration as one moves away from the interface. Atomic oxygen is produced during the decomposition of N₂O during the RTP process. This very reactive species effectively remove nitrogen from the top of the oxy-nitride film during the film growth

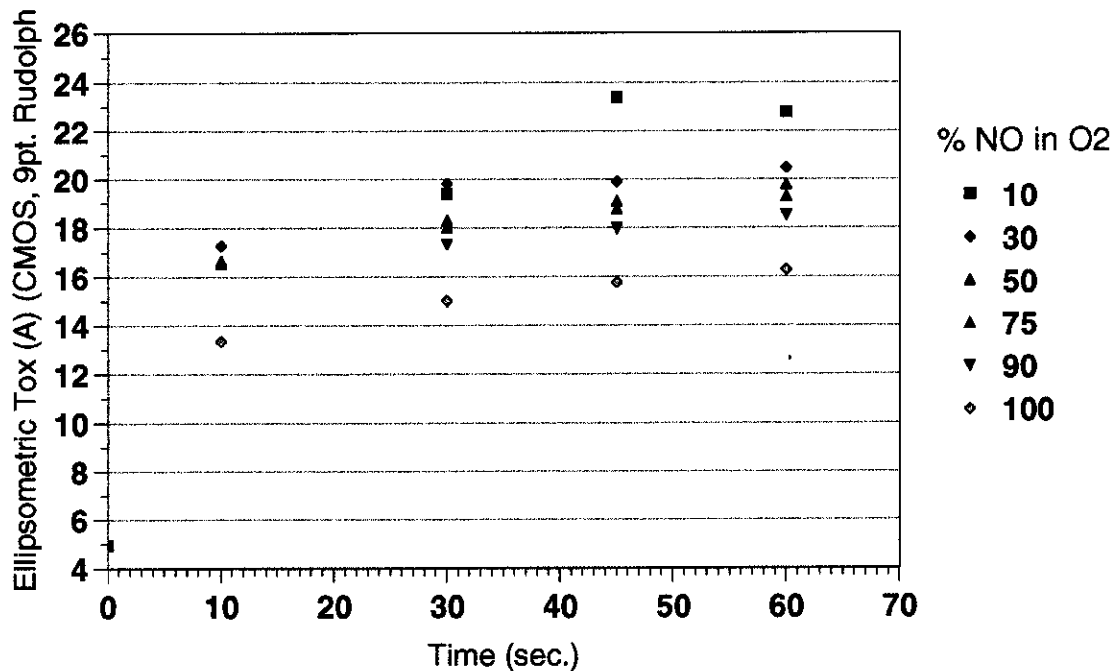


Figure 3: RT-NO + O₂ oxynitride growth on silicon. All recipes were run with a process temperature of 900 C, pressure of 740 torr and same total flow rate. All p-type monitor wafers were HF-Last cleaned before film growth.

Films grown by RT-NO have about ten times the nitrogen concentration of RT-N₂O films. Medium energy ion scattering (MEIS) analysis of RT-NO (see Figure 5) oxynitrides indicate they have 10-12% atomic nitrogen uniformly distributed throughout the film. The total nitrogen concentration as determined by nuclear reaction analysis (NRA) is about 1E 15 atoms/cm² for thin films (11-18 A optical thickness). As seen in Figure 6, the nitrogen content of these films does not change much for growth temperatures from 700 – 1000 C, even though the film's optical thickness increases from 11-18 A. The mechanism for nitrogen incorporation during RT-NO processes is not completely understood but the nitrogen content of the film does not appear to scale with thickness. Figure 7 shows the effect of RT-NO growth pressure on nitrogen content. For short growth times (i.e. 10 sec.), there is little change in nitrogen content with growth pressure. However, for longer times (30-60 sec.), increasing the growth pressure can incorporate as much as 2-3 E14 /cm² (20%) more nitrogen into the films. the films electrical and diffusion barrier properties.

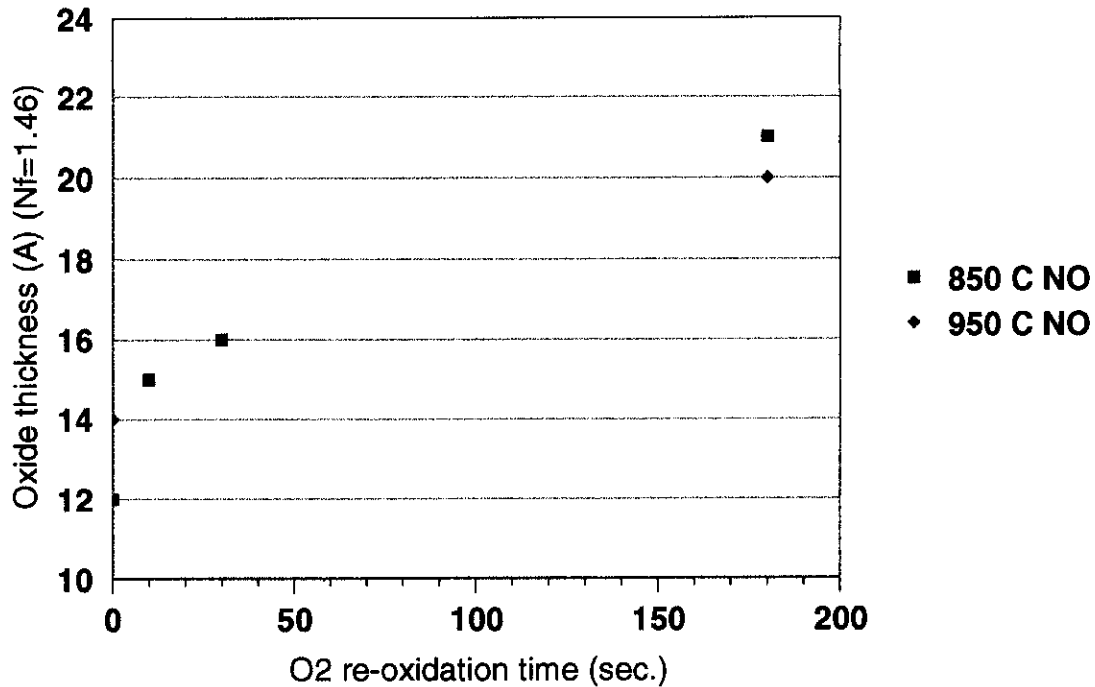


Figure 4: Re-oxidation of RT-NO oxynitride in RT-O₂. RT-NO oxidation time was 10 sec. and RT-O₂ reox was done at 950 C. Process pressure was 740 torr.

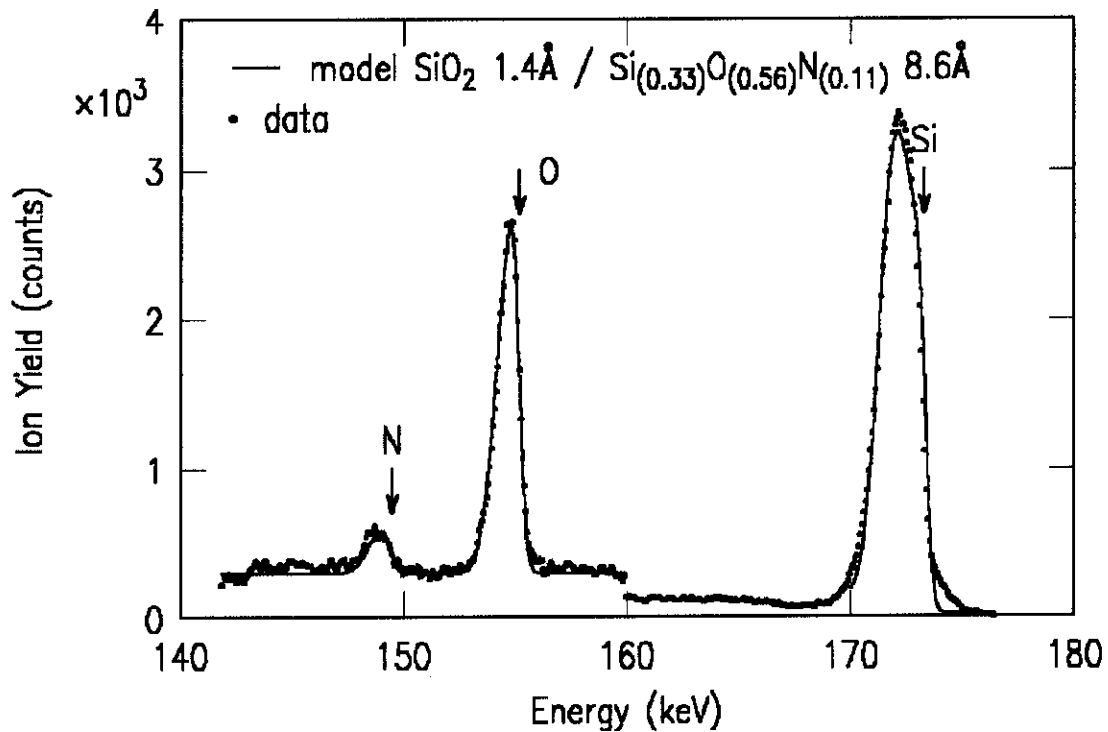


Figure 5: MEIS analysis of 11 Å RT-NO film gives 12 atomic percent of nitrogen that is uniformly distributed throughout the film. The film was grown at 750 C, 740 torr for 30 sec.

The incorporation of nitrogen into SiO₂ causes an increase in the films optical refractive index as well as its dielectric constant compared to pure SiO₂. This results in a

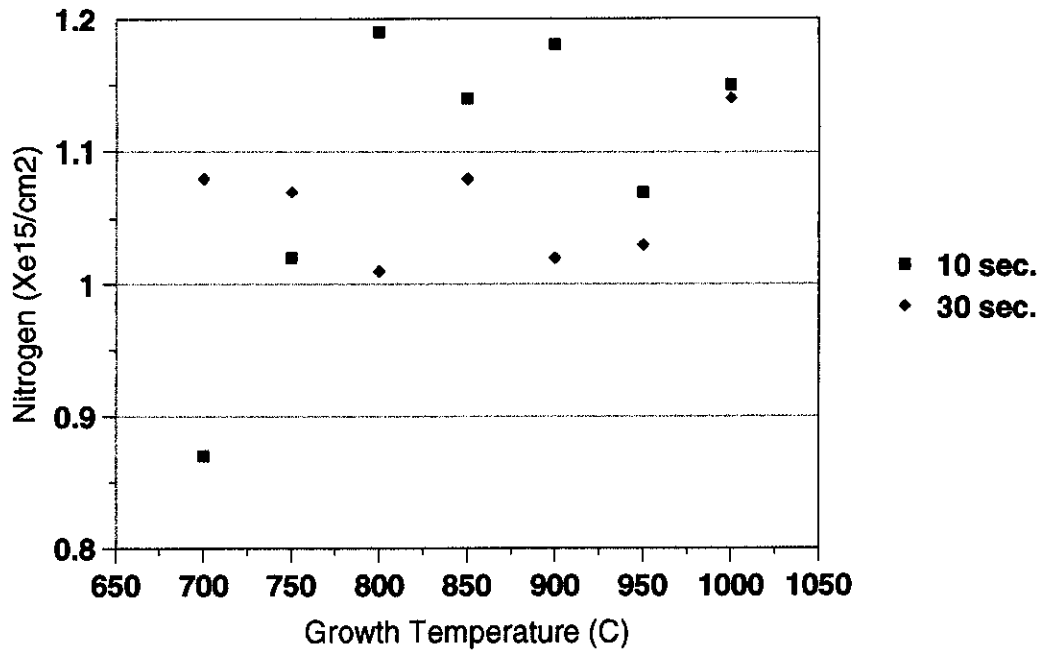


Figure 6: Nitrogen concentration of RT-NO films vs. growth temperature. All films grown at 740 torr pressure. Nitrogen sigma= 0.06 E15/cm2. Optical film thickness ranges from 10-18 A (Nf= 1.46)

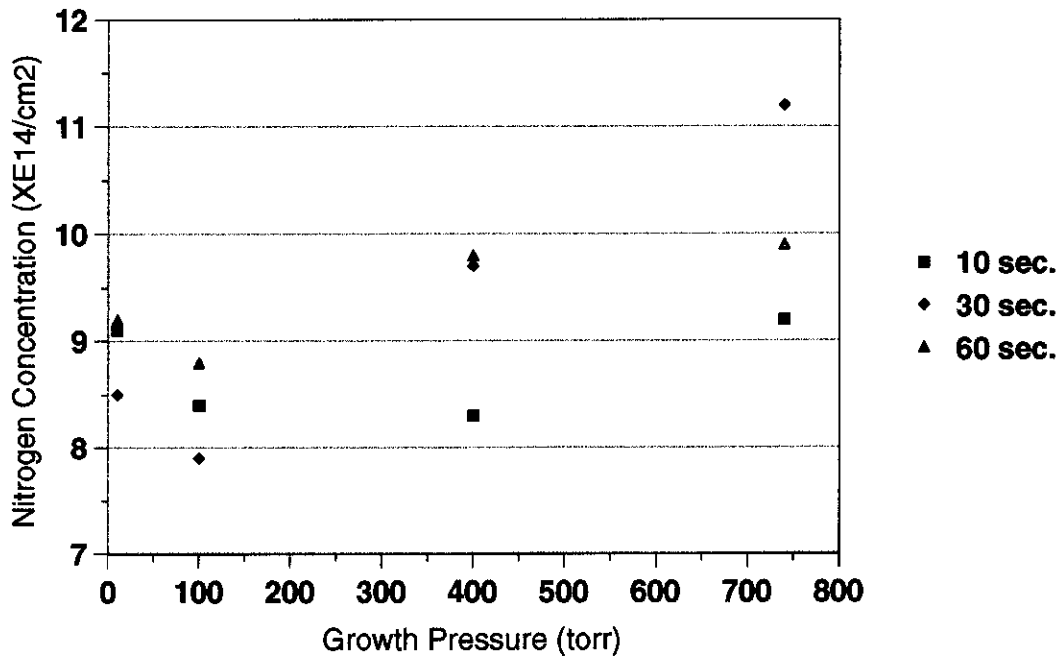


Figure 7: Nitrogen concentration vs. growth pressure for RT-NO films. All recipes use a growth temperature of 950 C and flow rate of 1 slm. Nitrogen concentration std. dev. = 0.6 E14/cm2.

discrepancy between the optically measured film thickness (Nf fixed at 1.46) and the electrical thickness derived from capacitance measurements. For lightly nitrided oxides, such as RT-N₂O, the electrical thickness measures 1-2 A thinner than optical thickness.

For the more heavily nitrated RT-NO oxy-nitrides, this difference can be as much as 4-5 Å. The difference between the optical and electrical thickness scales with the nitrogen content of the film as shown in Figure 8.

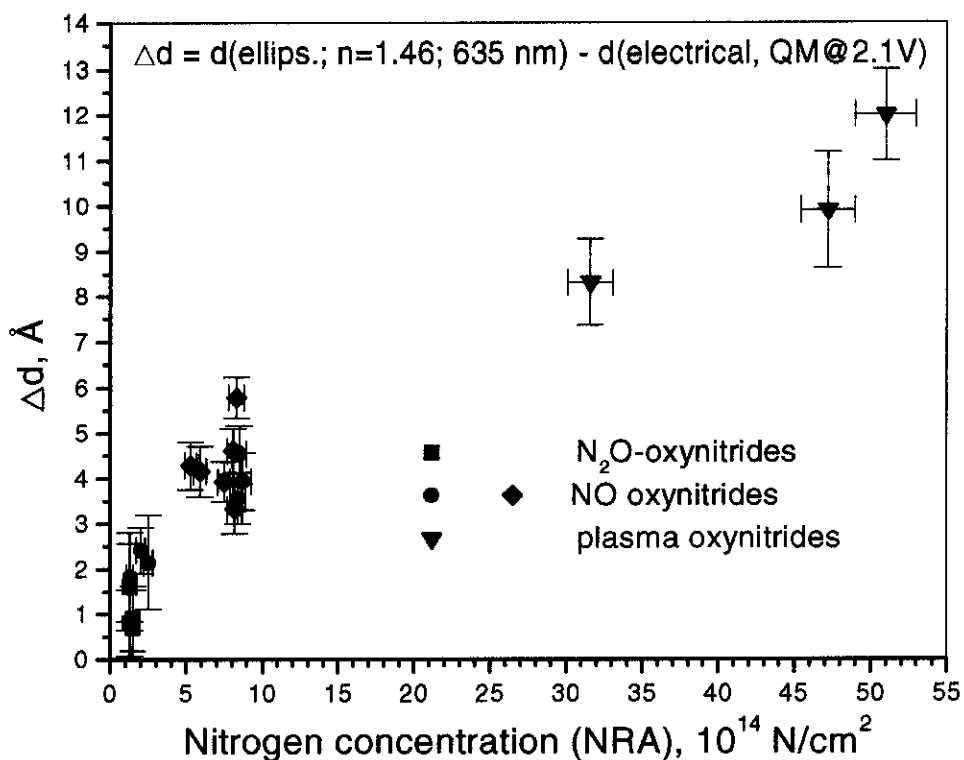


Figure 8: Difference in optical vs. electrical thickness for oxynitrides. n_f is fixed at 1.46.

Ultra-thin silicon nitride films grown by RT-NH₃ give higher nitrogen concentrations than the other films discussed. As shown in Figure 9a & b, these films can produce nitrogen concentrations from 2-6E15 atoms/cm² for an optical film thickness range from 5-12 Å ($n_f = 2.0$ fixed). This is 2-6 times higher than the nitrogen content of RT-NO films. Also, since these films are stoichiometric silicon nitride, the nitrogen is uniformly distributed throughout the film. Unlike RT-N₂O and RT-NO processes, the nitrogen content for RT-NH₃ films scales with film thickness. This enables more flexibility to tune the nitrogen content of the oxy-nitride process compared to the former processes.

Surface Morphology. The surface roughness induced by thermal growth processes can be minimized by following appropriate process considerations which promote surface passivation and avoid surface pitting and etching. Table I below and Figures 10a and b, show the rms surface roughness results from atomic force microscope (AFM) measurements for typical RT-NO and RT-NH₃ processes. Silicon nitridation in RT-NH₃ shows little or no increase in rms surface roughness. Silicon oxynitridation in RT-NO, shows about 0.3 increase in rms roughness. Both surfaces appear very smooth under AFM imaging and follow the surface contour as would be expected for thermal processes.

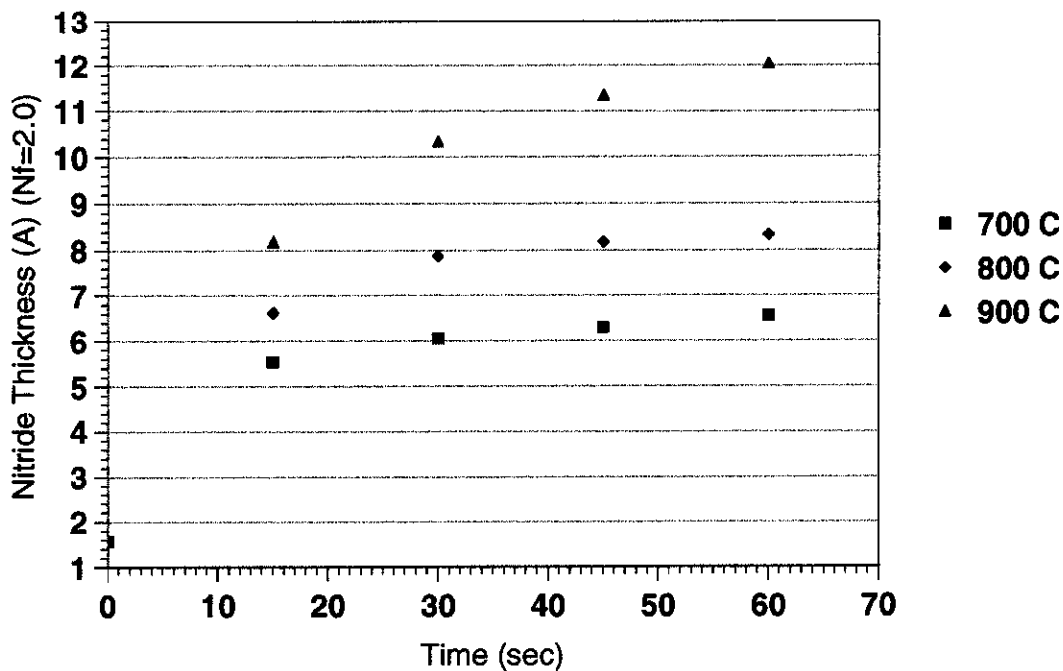


Figure 9a: Ultrathin nitridation of silicon with RT-NH₃. Results are the ellipsometric average of 49 measurements per data point. Growth pressure = 550 torr; surface is Hf-last treated.

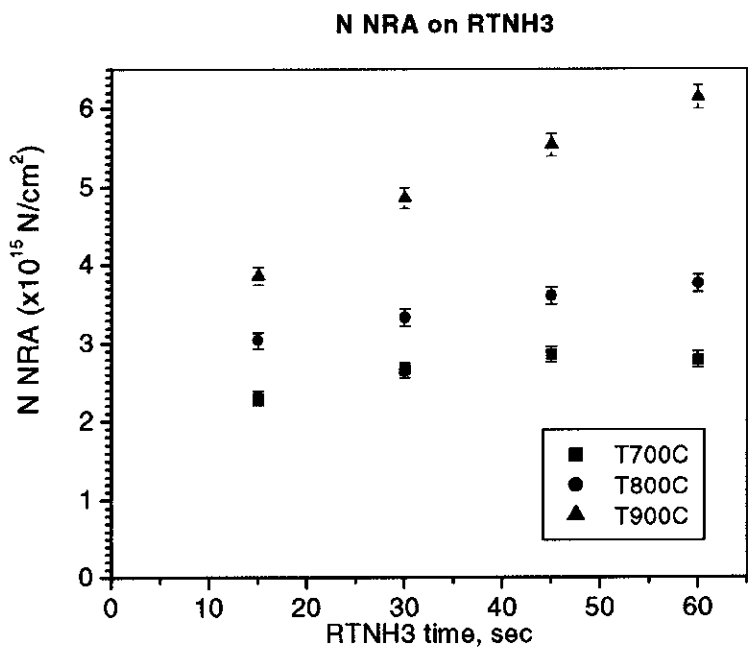


Figure 9b: Nitrogen concentration of RT-NH₃ films by NRA. Growth pressure= 550 torr. Surface was H-terminated prior to nitride growth.

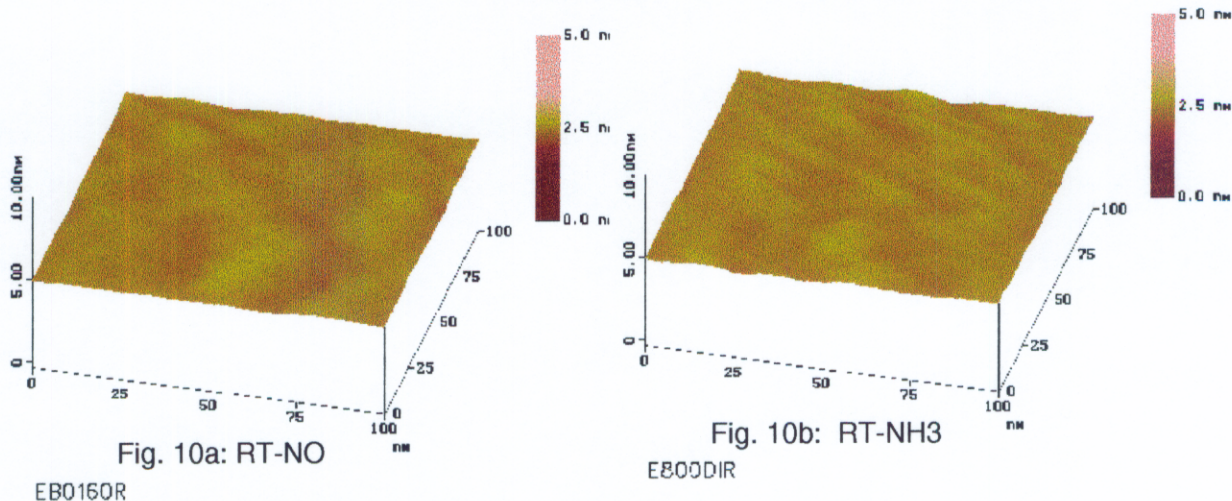


Figure 10a: AFM surface imaging of 16 Å RT-NO oxynitride on silicon (950 C, 740 torr, 10 sec.). Rms roughness = 1.07 Å.

Figure 10b: AFM surface imaging of 8 Å RT-NH₃ nitride (900 C, 550 torr, 15 sec.) on silicon. Rms roughness = 0.88 Å.

Table I: AFM Surface roughness of RT-NO and NH₃ films

Surface Condition	Rms (Å)
HF-Last clean	0.78
Clean+RT-NH ₃ , 8 Å	0.88
Clean+RT-NO, 16 Å	1.07

Electrical Characteristics. Thin gate oxy-nitrides grown by RT-N₂O show similar electrical quality to N₂O furnace oxides. Figure 11 shows the C-V and I-V characteristics of a 20 Å RT-N₂O grown oxy-nitride. The C-V's and I-V's of 20 poly-gate capacitors (area= 1E-5 cm²) are tightly distributed and the electrical thickness uniformity is typically 0.1-0.2 Å 1 sigma. The leakage current, flatband voltage, charge to breakdown (Qbd) and time to breakdown (Tddb) are typical of gate quality SiO₂ films.

Films grown by RT-NO+O₂ also show good electrical characteristics. Figure 12 shows C-V and I-V data for 10% NO in O₂ and 50% NO in O₂ processes. Both processes show tight distributions of C-V's and I-V's for the 16 capacitors tested. Table II summarizes the nitrogen and electrical data for these films compared to a furnace oxide process.

There are clearly benefits to using NO + O₂ gas mixtures compared to N₂O. Increasing the concentration of NO in O₂, adds more nitrogen to the film, resulting in lower leakage and better diffusion barrier properties. Also, the increase in V_{fb}, due to fixed charge induced by nitrogen, is minimal (10-40 mV) when adding more nitrogen to the film this way. A disadvantage of the NO+O₂ gas mixtures is that as the percentage of NO in the gas mix increases, the film's growth rate drops considerably. This is an important consideration for single wafer tools where wafer throughput directly impacts manufacturability. For NO concentrations in O₂, 30% or higher, films about 15 Å (electrical thickness) or less can be grown in 60 sec. or less.

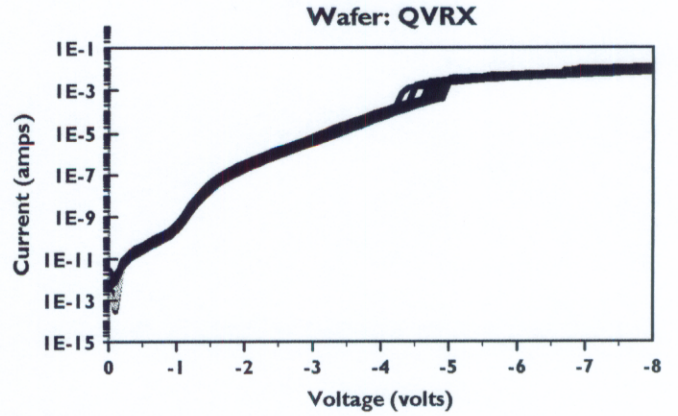
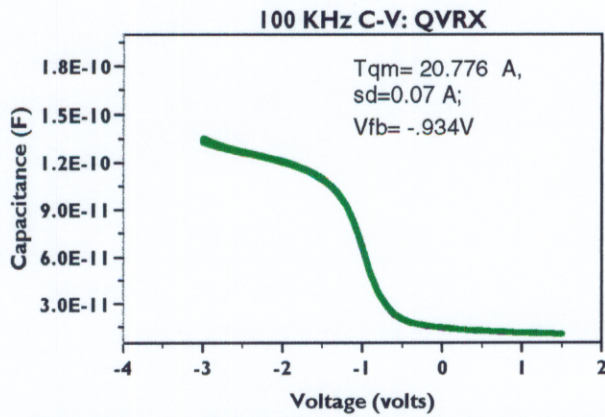
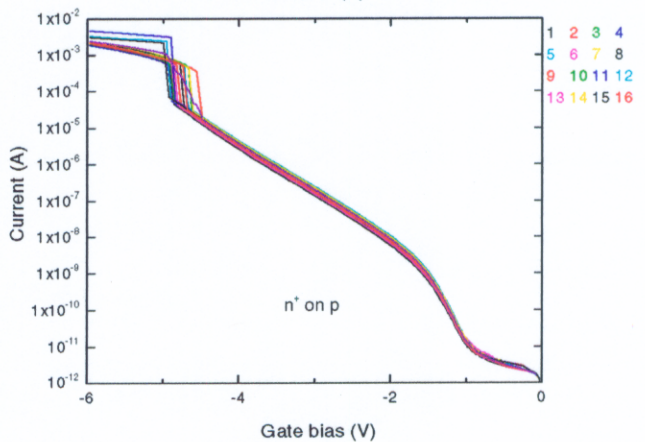
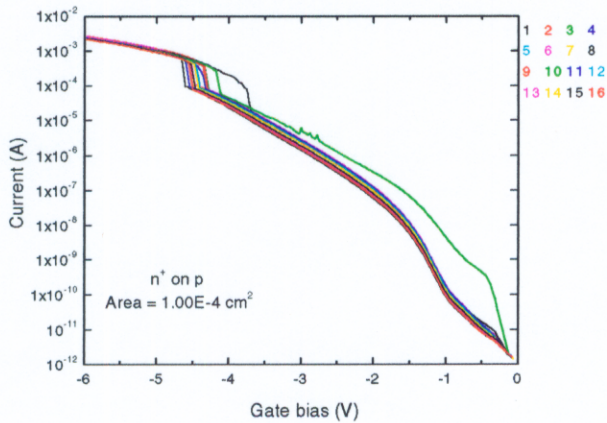
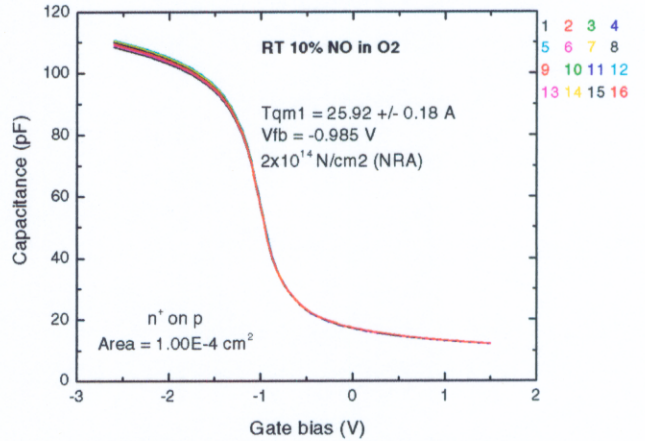
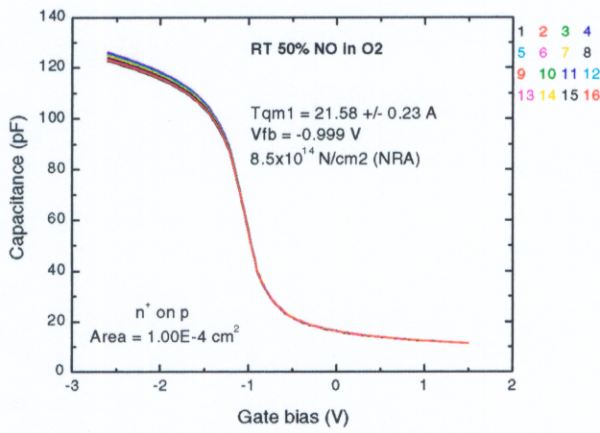


Figure 11: Electrical characteristics of 20 A RT-N2O gate oxides. 16 capacitors per wafer were tested.



(a)

(b)

Figure 12: Electrical characteristics of 50% (a) and 10% RT-NO (b) in O2 films.

Table II: Electrical and Material characteristics of Oxynitrides

Film	Electrical Thickness (A)	Elect. Thickness Std.Dev.(A)	Growth time (sec)	N NRA (XE14/cm ²)	V _{fb} (V)	Leakage reduction w/r/t SiO ₂
Furnace N ₂ O	20.88	0.11	540	1-2	-0.975	1
RT 10% NO in O ₂	24.92	0.18	80	2	-0.985	1
RT 50% NO in O ₂	21.58	0.23	420	8.5	-0.999	4.8

Since the growth rate of the RT-NO process is very slow, ultra-thin films in the 9-18 Å optical thickness range can be grown within acceptable process limits. Since this oxynitride can be grown very thin, it has potential use to serve as an interfacial oxide layer between the underlying silicon and higher dielectric constant films such as RTCVD nitrides and oxy-nitrides. As shown in Figure 13, the difference in flatband voltage for oxide/RTCVD oxy-nitride stacks using RT-N₂O vs. RT-NO bottom oxides is in the range of 8-23 mV, depending upon the post annealing conditions used on the stack. As the bottom oxide layer gets thinner, the flatband voltage of the oxide/(oxy)nitride stack increases. As shown in Figure 14, the flatband voltage for stacks with bottom oxides less than 10 Å can be as high as several hundred millivolts. With no bottom oxide, the shift can be as large as 600-700 millivolts. The leakage current of these stacks is similar whether RT-NO or RT-N₂O is used as the bottom oxide. RT-NO bottom oxides also show reasonable interface state density compared to pure SiO₂ films. Table III below shows electrical results from aluminum gate capacitors fabricated on 200 Å equivalent furnace oxide grown in O₂/HCl, RT-O₂ oxide and 11Å (optical thickness) RT-NO + Al₂O₃ stack. All films were post metal annealed in forming gas at 400 C for 30 min.

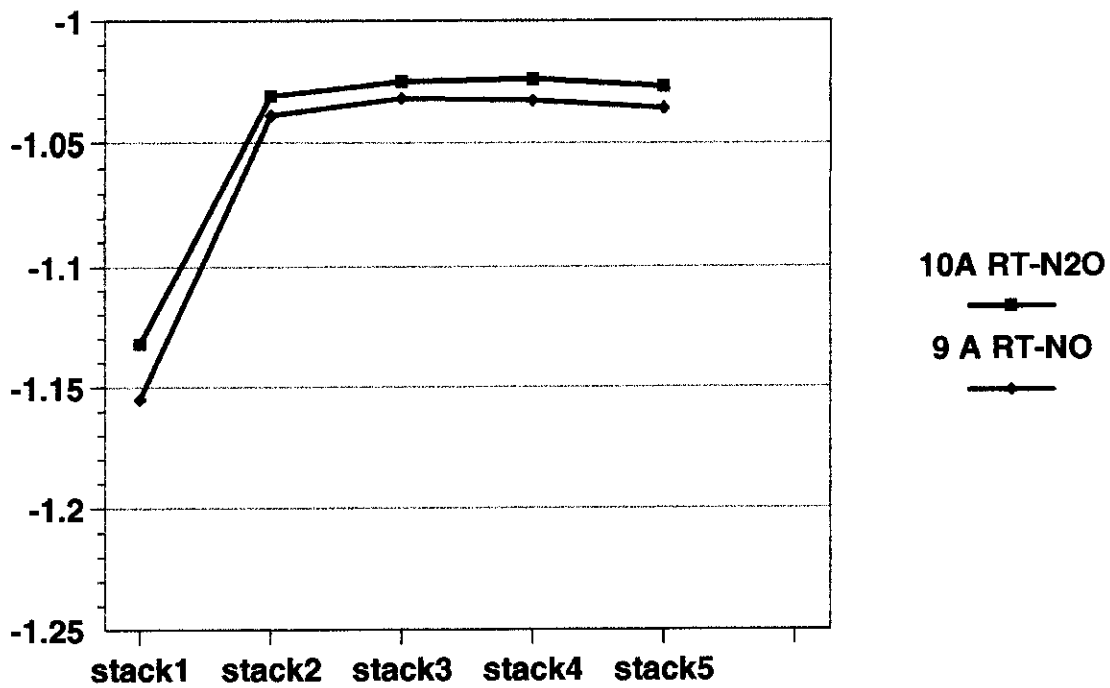


Figure 13: Effect of bottom oxide on Vfb of oxide/RTCVD oxynitride gate stack. Top oxynitride is DCS based ($N_f = 1.86$); $T_{eq} = 18-27$ A. The nitrogen concentration ranges from $1.5-4.6 \times 10^{15}$ atoms/cm².

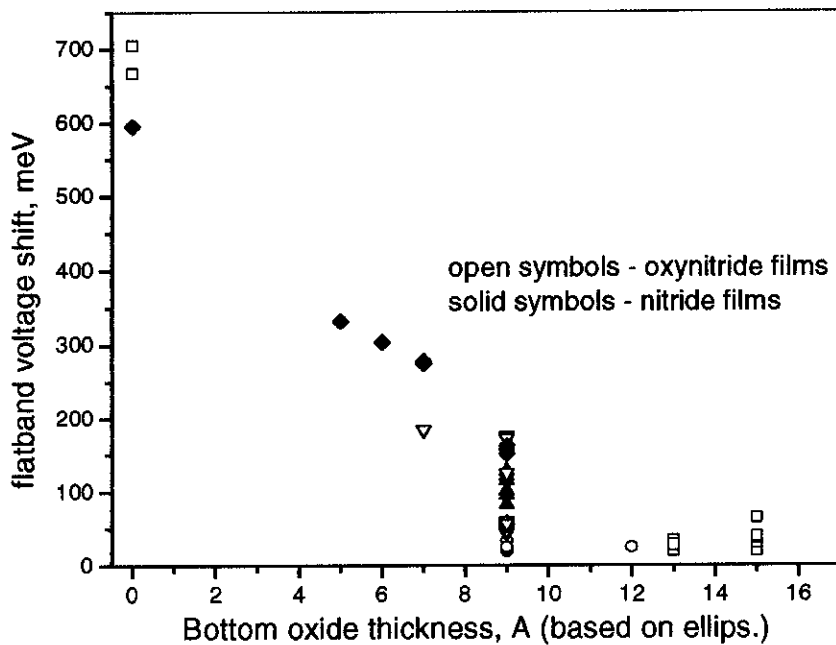


Figure 14: Effect of bottom oxide thickness on Vfb of oxide/RTCVD (oxy) nitride gate stacks. Below 9 A bottom oxide thickness, Vfb rises quickly to several hundred mV.

Table III: Electrical Characteristics of RT-NO bottom oxide in High-K stack

Film	Electrical Thickness (Å)	Elect. Thick. Std.Dev.(Å)	Interface Traps (E10/cm ²)	Carrier Lifetime (msec.)	V _{fb} (V)	Ebd (MV/cm)
Furnace O ₂ /HCl	191.6	1.77	2.62	77	-0.77	-12.322
RT-O ₂	178.7	1.003	1.82	95.2	-0.81	-10.45
RT-NO+Al ₂ O ₃	212.3	1.34	6.66	56.9	-0.46	-11.465
Al ₂ O ₃ +O ₂ anneal	208.8	1.45	5.12	30.7	1.147	-13.198

The interface state density of the bottom RT-NO film in the Al₂O₃ stack is reasonably good but about 2-3 times higher than pure SiO₂. The slight degradation in interface quality may be attributed to the high concentration of nitrogen at the silicon/oxy-nitride interface. The interface quality of the RT-NO film in this stack is also similar to that obtained by post annealing the Al₂O₃ film in oxygen (550C, 30 min.). The minority carrier generation lifetime reflects the quality of the underlying silicon beneath the oxide interface. In this case, the Al₂O₃ stack with RT-NO bottom oxide yields higher lifetime than Al₂O₃ without RT-NO but not as good as pure SiO₂. The flatband shift of the RT-NO+ Al₂O₃ stack is about +300 mV with respect to SiO₂ whereas the shift is much worse without the RT-NO bottom oxide. Breakdown field based on equivalent SiO₂ thickness is good for both Al₂O₃ cases and similar to SiO₂.

CVD Processes

Growth Kinetics. Silicon nitride can be deposited on bare silicon or SiO₂ by using silane (SiH₄) or dichlorosilane (DCS) and ammonia (NH₃). The silicon oxy-nitrides may be deposited by adding N₂O as a reactant gas to the silicon nitride process. The growth kinetics of both LPCVD and RTCVD nitrides depends on the growth surface termination. As shown in Figure 15, RTCVD silicon nitride will grow immediately on an oxide free, hydrogen terminated silicon surface. However, on an SiO₂ terminated surface, there is an incubation period where no ellipsometrically detectable film is observed, followed by linear growth kinetics. (9,10) There is little or no change in the incubation period for depositing on chemical or thermal oxides or oxy-nitrides, such as those grown by RT-N₂O or RT-NO. Annealing the SiO₂ film in ammonia at higher temperature prior to RTCVD nitride deposition shortens the incubation time by 1-2 sec. However, the incubation period can be shortened considerably by increasing the deposition rate. The rate of change is higher when pressure is increased rather than temperature. For equivalent deposition rate processes, silane based RTCVD nitride processes show 4 times longer incubation period than DCS based processes. (see Figure 16). For lower pressure processes, high NH₃ flow rates tend to shorten the incubation time. For higher pressure processes, the NH₃ flow has much less of an effect.

LPCVD silicon nitrides have similar nucleation issues on SiO₂ surfaces as RTCVD nitrides. In this case, however, since the process pressure may be 100-500 times lower than for RTCVD, the nucleation efficiency is worse. Typical LPCVD nitride processes

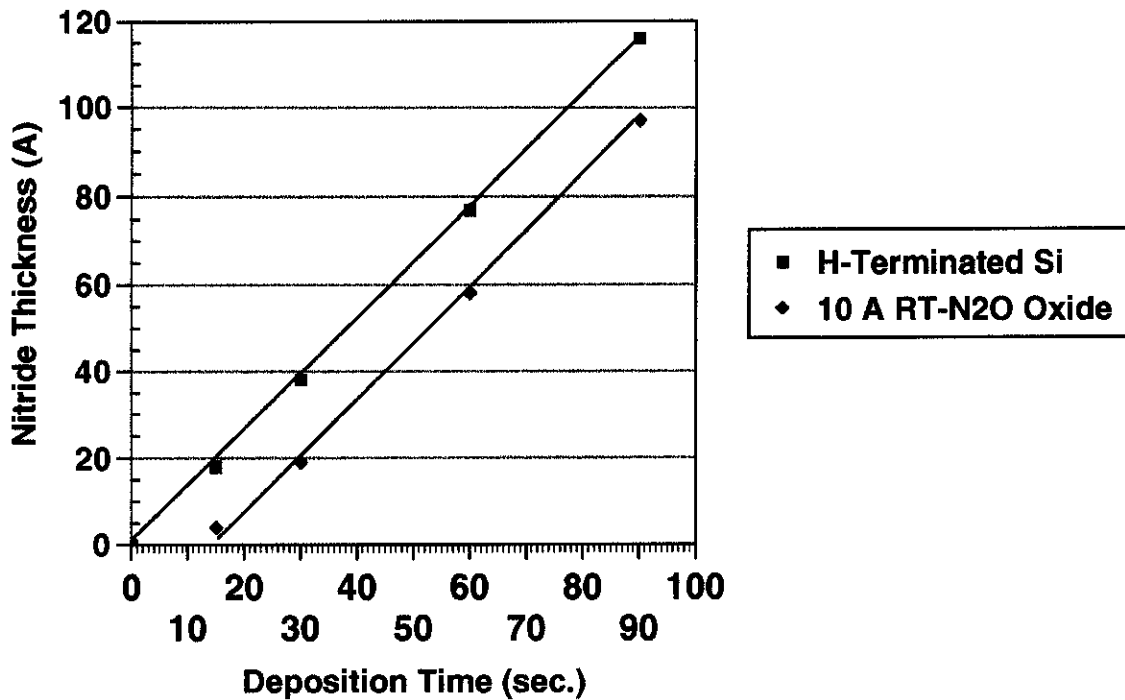


Figure 15: Deposition of RTCVD silicon nitride on H-terminated silicon vs. oxide. There is a 13 sec. incubation time for nitride growth on oxide. Growth temperature = 750 C, pressure= 100 torr, NH₃:DCS ratio = 30:1

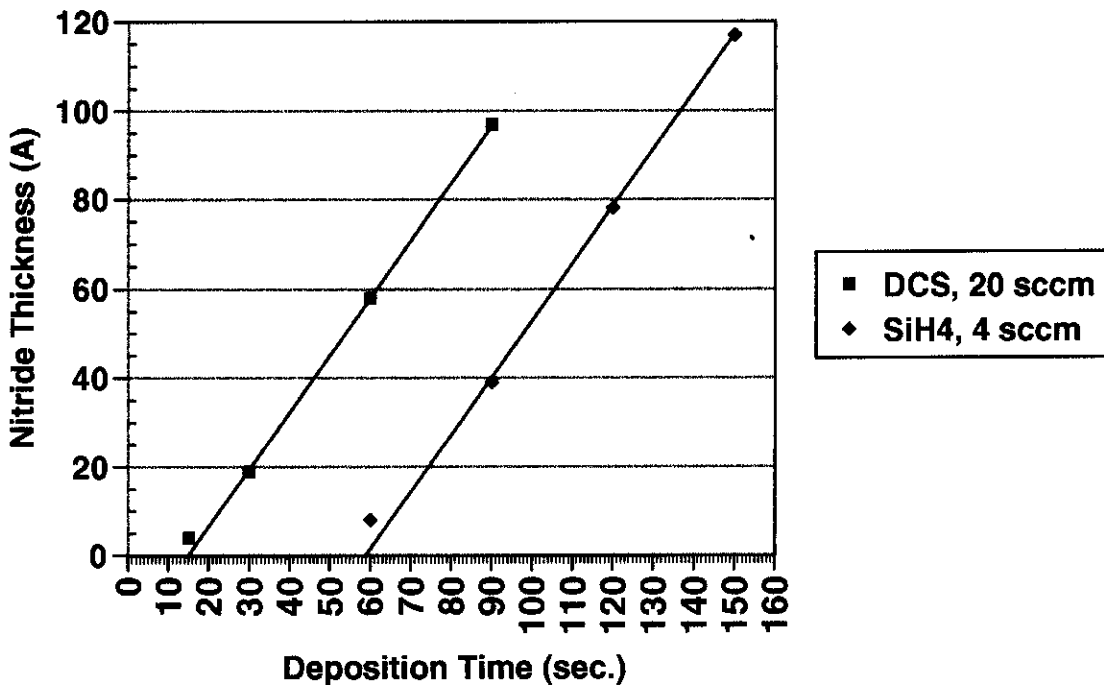


Figure 16: Growth kinetics of RTCVD nitride on oxide: SiH₄ vs. DCS based; equivalent deposition rate of 78 Å/min. for each process. Bottom oxide is 10 Å N₂O. Growth pressure= 100 torr, temperature = 750 C, NH₃ flow rate = 0.6 slm.

operate at 200-300 mtorr, while RTCVD processes are in the 10-100 torr range. While incubation times for RTCVD nitride processes can be 10-60 sec., those for LPCVD processes can be several minutes.

RTCVD oxy-nitride processes tend to nucleate more efficiently than silicon nitride processes. The addition of N_2O as a reactant gas along with NH_3 and SiH_4 or DCS reduces the surface tension of the depositing film on the SiO_2 surface. This reduction in surface tension enables the film to nucleate more efficiently even though the deposition rate may be less than a similar RTCVD nitride process. A previous study by D'Emic, Gusev, et al. (10) discusses these effects in more detail.

Nitrogen Content and Profile. The nitrogen and oxygen concentrations of RTCVD nitrides and oxy-nitrides can be changed by changing the process conditions. By adding N_2O to the reaction mix of SiH_4 (or DCS) and NH_3 , nitrides effectively become oxy-nitrides. The amount of nitrogen in the film (and thus its refractive index) can be effectively tuned by changing the ratio of $NH_3:N_2O$ in the reactant gas mixture. The higher refractive indices can be achieved by operating at lower pressures (e.g. 10 torr) and switching from SiH_4 to DCS as a source gas. Figure 17 shows how the nitrogen content of oxide/oxy-nitride stacks changes with the refractive index of the top (oxy) nitride film. For stacks with an equivalent SiO_2 thickness in the 22-25 Å range and 15 Å bottom oxide, the nitrogen content can be tuned from 1 to 3.5 E15 N/cm² for a corresponding refractive index changes in the top film from 1.5 (oxy-nitride) to 1.94 (nitride). The nitrogen concentration is uniform throughout the deposited film.

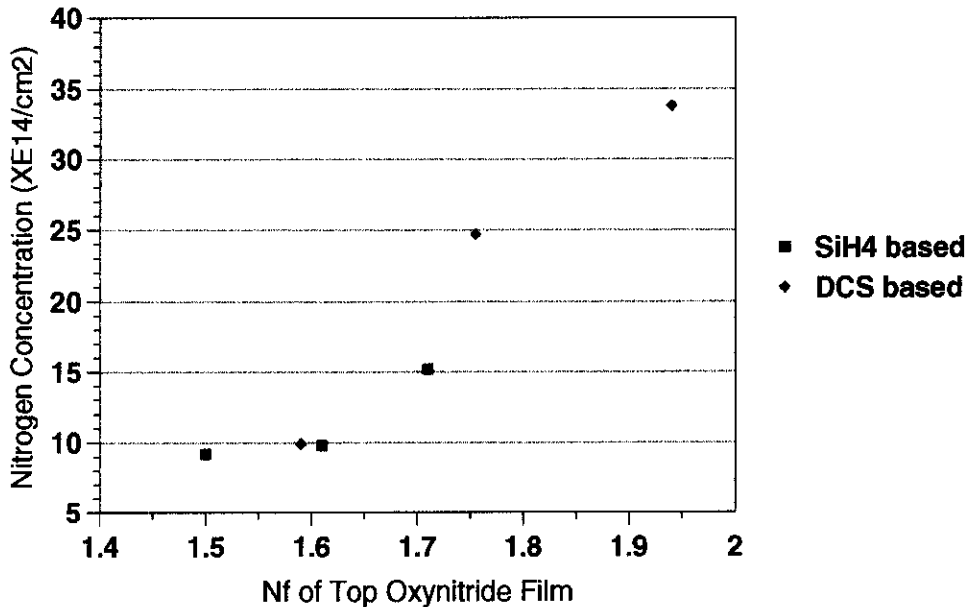


Figure 17: Nitrogen concentration of oxide/oxy-nitride stacks for different top oxynitrides. The bottom oxide is 15 Å RT- N_2O in each case and the equivalent SiO_2 electrical thickness is 22-25 Å for the stacks.

Post annealing these nitrides and oxy-nitrides in RT-N₂O, increases the film's thickness and removes nitrogen from the film. Atomic oxygen, generated in the RT-N₂O process, rapidly removes nitrogen while oxidizing the remaining silicon to SiO₂. For example, a 10A RT-N₂O + 15 A DCS oxy-nitride stack has a total nitrogen content of 4.6E15 N/cm² and an equivalent SiO₂ oxide thickness of 20 A. An exposure to RT-N₂O at 850 C for 30 sec., increases the equivalent oxide thickness of the stack to 27 A and reduces the nitrogen level by half (2.3E15/cm²). The amount of thickness increase and nitrogen loss scales with increasing temperature and duration of the RT-N₂O anneal. Table IV below shows how the nitrogen:oxygen ratio (as determined by MEIS analysis) in a 27 A RTCVD nitride film drops with RT-N₂O annealing temperature. The annealing time was 10 sec. at 740 torr pressure. While this scheme may be effective to form N/O or O/N/O structures, the loss of nitrogen will reduce the stacks ability to serve as a diffusion barrier as well as other benefits associated with high nitrogen content.

Table IV: Composition of RTCVD nitride films after RT-N₂O annealing

RT-N ₂ O Temp. (C)	Ox (monolayer)	Ox (A)	N (monolayer)	N (A)	N:O
800	6.5	9.5	13.2	15.8	1.66
900	9.0	13.1	10.0	11.5	0.88
950	10.4	15.1	9.2	10.6	0.70

Surface Morphology. The morphology of LPCVD and RTCVD nitride and oxy-nitride films differ from RT-N₂O, NO and NH₃ films primarily because these are deposition processes which involve the formation and coalescence of nuclei, whereas the latter are thermal growth processes. Copel and others (11) have studied the initial stages of CVD nitride growth on SiO₂ by medium ion energy scattering (MEIS). Here, the width of the nitrogen peaks is an indication of the completeness of the nitride surface coverage. As shown in Fig. 18, thermal nitridation in NH₃ shows the peak width is linear with film thickness. For a given amount of nitrogen on the surface, RTCVD nitride films deposited on SiO₂ show broader nitrogen peaks than thermal nitride films grown in NH₃, indicating less complete surface coverage of the RTCVD film compared to the thermal film. LPCVD films deposited on SiO₂ show the largest deviation from the ideal line, indicating the least surface coverage for the same nitrogen levels as the RTCVD and thermal nitride films. The arrows indicate corrections made for nitride surface oxidation in air.

Surface roughness measurements by atomic force microscopy also support this data. Figure 19 shows RTCVD nitride thickness on a 10 A oxide vs. deposition time. There is no film detected by ellipsometry for 9 sec. or less deposition time. Although the Rms surface roughness is fairly constant throughout the early and later stages of nitride growth, the Rmax value drops from 12 A (for 6 sec. time) to about 9 A (for 1 min.). The inflection point, where the Rmax value begins to level off is between 20- 30 sec., or 15-30 A measured by ellipsometer. AFM images of these different stages of nitride growth (Figures 20a-e) show that even after only 6 sec. deposition time (0 A measured by ellipsometer), silicon nitride nuclei approximately 100 A in width can be observed. This topography changes little as the film grows thicker. At 15 A nitride thickness, the most

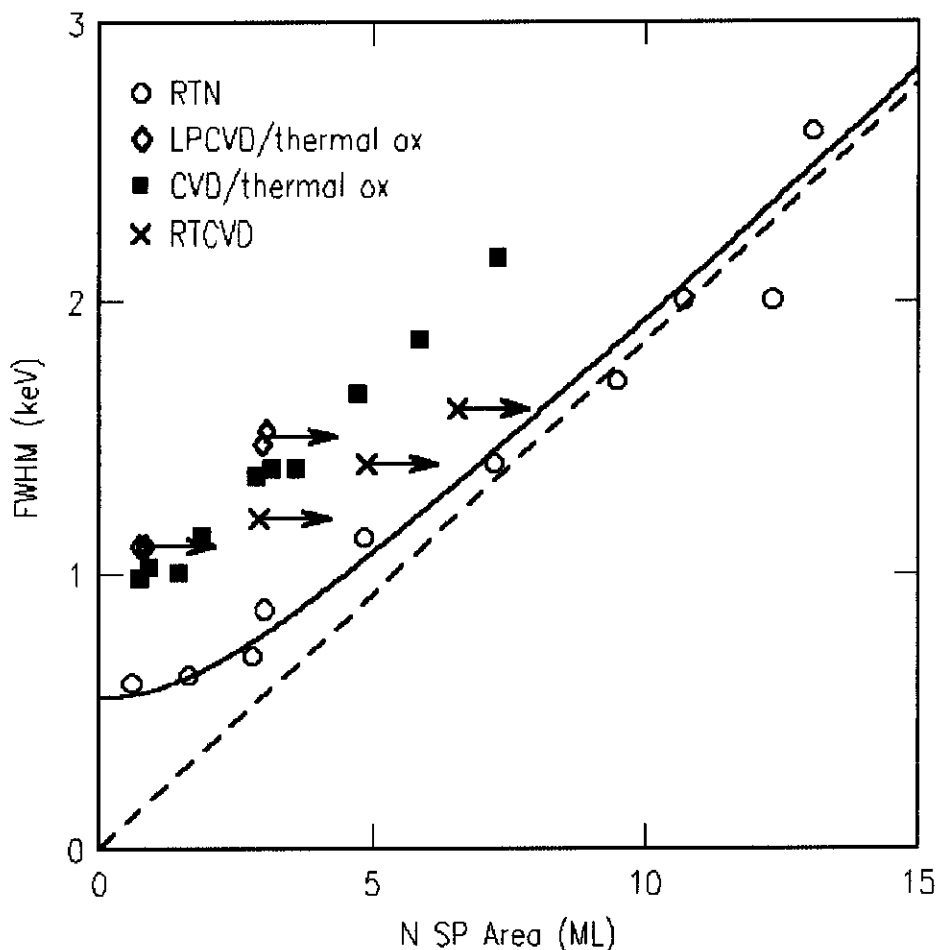


Figure 18: Nitrogen surface coverage of RTN, LPCVD and RTCVD nitrides on SiO₂, as determined by MEIS.

contrast is observed. As the film grows thicker, the contrast diminishes indicating a smoother, more continuous film. The Rms and Rmax values drop slightly during the deposition and the film seems most continuous after 15-30 Å.

Electrical Characteristics. When ultra-thin LPCVD or RTCVD nitride films are deposited on an oxide or oxy-nitride layer, the resulting gate stack shows reasonable C-V and I-V electrical characteristics provided the CVD film is thick enough. Figure 21a shows a 25 Å RTCVD nitride film deposited on top of a 10 Å oxide. Although, the C-V and I-V distributions for the 16 capacitors tested are reasonably tight, the leakage current of the stack is more than ten times higher than a furnace oxide of similar electrical thickness (i.e. 26.2 Å-stack, 24.7 Å oxide). This excessive leakage may be attributed to the nucleation problems described above. Thinning the top nitride film results in even leakier stacks with C-V's and I-V's that are spread in distribution. Figure 21b shows the C-V and I-V distributions of capacitors made from a 17 Å RTCVD nitride (same recipe as 25 Å nitride) on top of a 10 Å oxide. This electrical data is consistent with the MEIS and AFM data for ultra-thin nitrides on oxides. Below a nitride thickness of 20 Å, the nitride films on oxide surface are rougher (higher Rmax) and provide incomplete surface coverage as seen by MEIS data. The AFM, MEIS and electrical data all support the

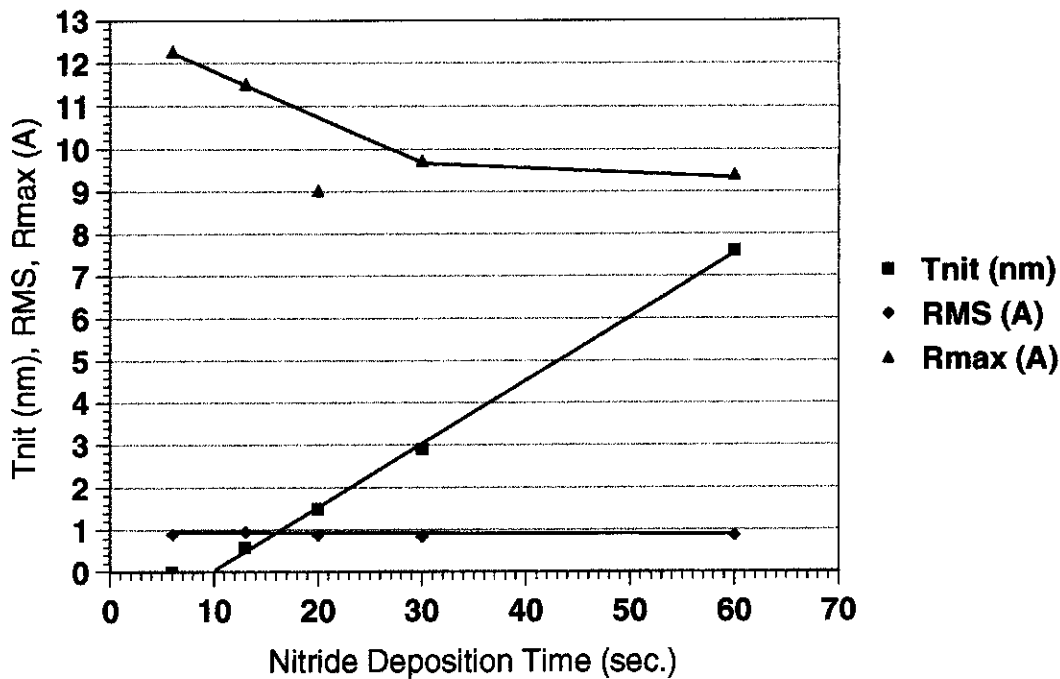


Figure 19: Surface roughness of initial stages of RTCVD nitride deposition on SiO₂. 10 Å RT-N₂O bottom oxide was used. The nitride thickness was measured by ellipsometry with fixed Nf= 1.94.

premise that CVD nitride films that are deposited less than 20 Å on bottom oxides show signs of discontinuity.

The electrical properties of oxide/RTCVD oxy-nitride stacks may be tuned by changing the top oxy-nitride composition. The flatband voltage of the oxide/oxy-nitride gate stack increases with increasing refractive index of the top oxy-nitride. Table V below shows how the flatband voltage of a 10 Å oxide/15 Å oxy-nitride increases with the refractive index of the oxy-nitride.

Table V: Flatband voltage vs. Nf of top RTCVD oxynitride in oxide/oxynitride stacks

Top Oxy-nitride Refractive Index	V _{fb} of Oxide/Oxy-nitride Stack (V)
1.6	-1.013
1.75	-1.095
1.86	-1.132

The higher flatband shifts associated with the higher refractive index oxy-nitride films are likely due to the higher nitrogen content of these films which incorporates more fixed charge and traps into the gate stack. Higher nitrogen concentration in the top oxy-nitride film also changes the fermi level with respect to the polysilicon gate. This can also give rise to higher flatband shifts.

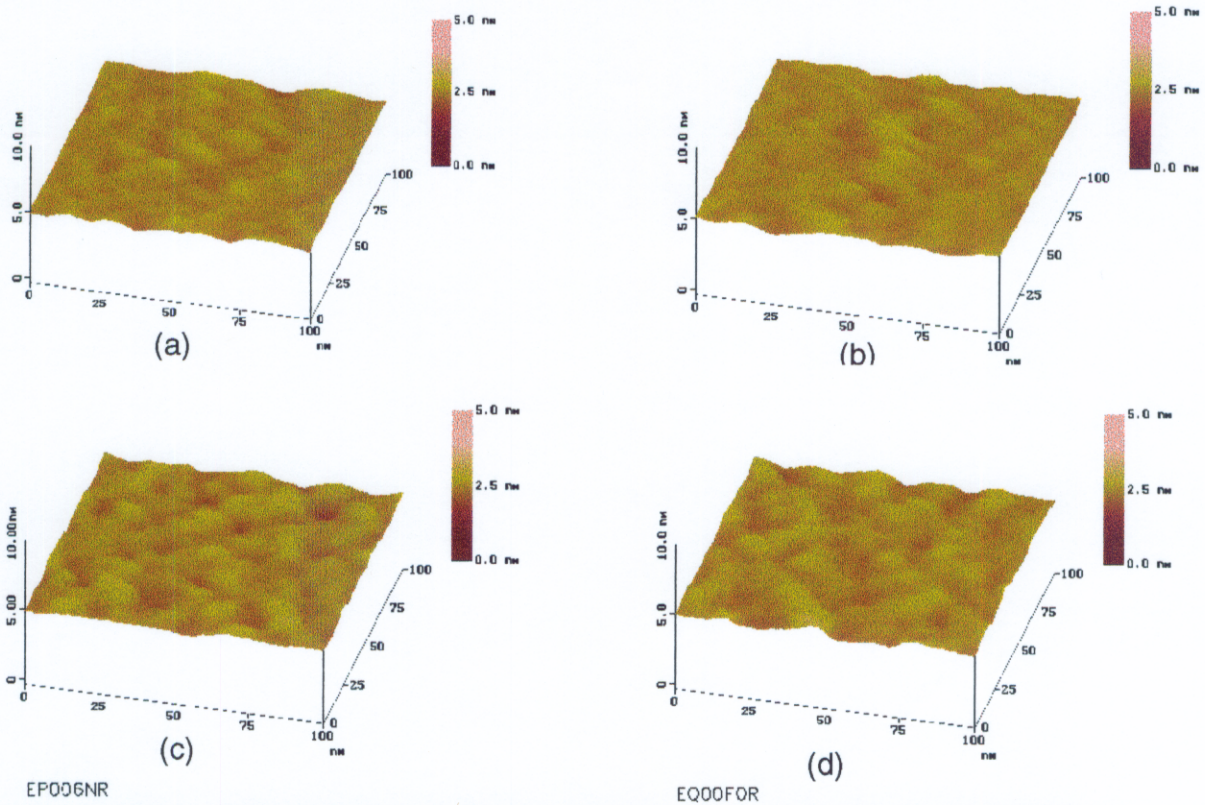


Figure 20a-d: AFM images of RTCVD nitride on 10 Å SiO₂. (a) 0 Å ellipsometric thickness; 6 sec. deposition, (b) 6 Å thickness; 13 sec. deposition, (c) 15 Å thickness; 20 sec. deposition, (d) 29 Å thickness; 30 sec. deposition.

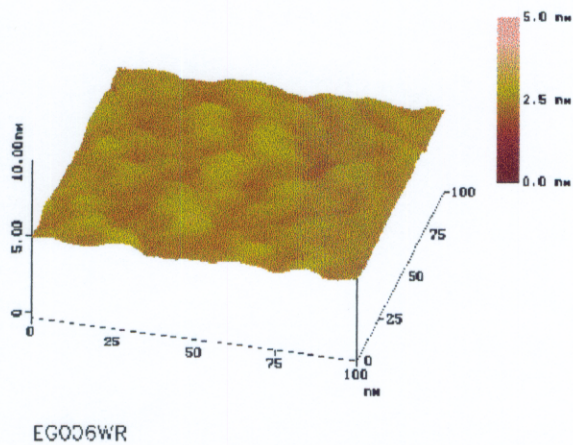


Figure 20e: AFM image of 76 Å RTCVD nitride (60 sec. deposition) on 10 Å SiO₂.

Post annealing of oxide/(oxy) nitride gates stacks by RT-N₂O can reduce the flatband shift. Table VI below shows the effect of post annealing a 10 Å oxide/15 Å DCS oxy-nitride (N_f= 1.86) on the stacks nitrogen concentration and flatband shift from C-V data.

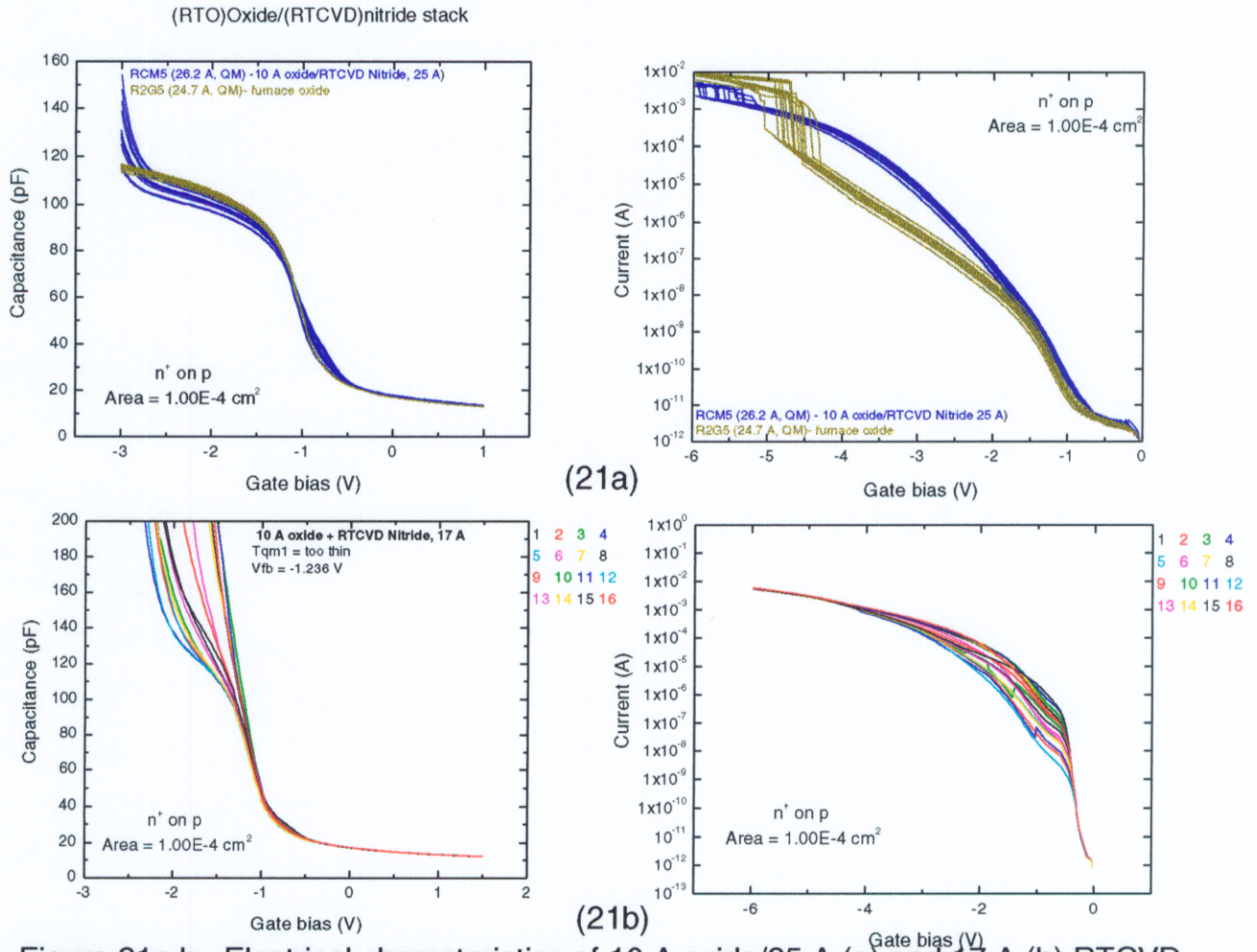


Figure 21a,b: Electrical characteristics of 10 A oxide/25 A (a) and 17 A (b) RTCVD nitride gate stacks.

Note that post annealing the stack in N_2O removes nitrogen and correspondingly reduces the flatband voltage shift. RT- N_2O anneals that are more aggressive than 800 C, 30 sec. do not remove any more nitrogen from the stack nor reduce V_{fb} any further. This is evidence that the V_{fb} shift correlates with the amount of nitrogen in the top oxy-nitride film. Post annealing in RT- N_2O oxidizes the top surface of the oxy-nitride very rapidly for mild conditions.

Figure 22 shows the C-V and I-V characteristics of a 10 A oxide/14 A oxy-nitride stack which was post annealed in N_2O . The C-V and I-V distributions are tight for the 16 capacitors tested indicating good electrical thickness uniformity. The flatband shift is only 20-30 millivolt compared to furnace oxides DCS and SiH_4 based oxy-nitrides used in oxide/oxy-nitride gate stacks show no difference in leakage current.

Table VI: Change in flatband voltage and nitrogen content of oxide/oxyntiride stacks with annealing condition.

Post annealing condition	Nitrogen by NRA (XE14 N/cm ²)	Vfb of stack (V)	Tqm (A) of Gate Stack
RT-N ₂ , 850 C, 30 sec.	46	-1.132	19.795
RT-N ₂ O, 800 C, 10 sec.	31	-1.031	24.654
RT-N ₂ O, 800 C, 30 sec.	25	-1.025	25.553
RT-N ₂ O, 850 C, 10 sec.	27	-1.024	25.868
RT-N ₂ O, 850 C, 30 sec.	23	-1.027	27.007

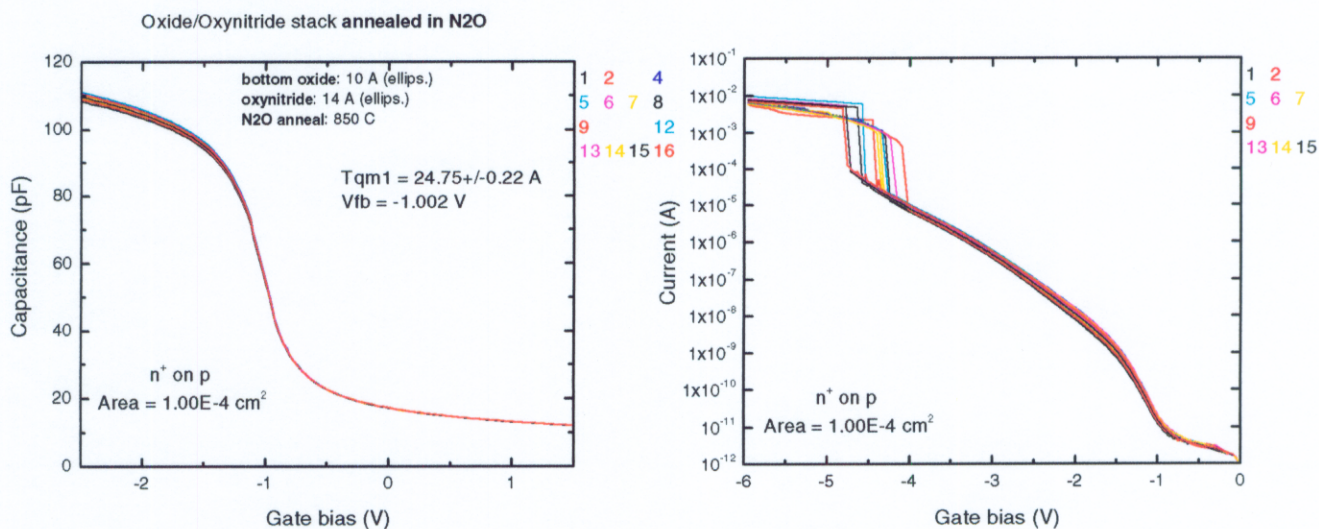


Figure 22: Electrical characteristics of oxide/RTCVD oxyntiride gate stack.

SUMMARY

In the ultra-thin regime, there are clearly marked differences among rapid thermally grown (oxy) nitrides grown in N₂O, O₂, NO, NO+O₂ and NH₃. In general, the thinner the film can be grown, the higher its nitrogen content and vice versa. Films can be grown thinnest by RT-NH₃ and have a high nitrogen concentration that scales with film thickness. RT-NO films can be grown thicker, but the nitrogen content for ultra-thin films becomes saturated at about 1E15 atoms/cm². Films grown in NO+ O₂ mixtures can be tailored

thicker than RT-NO films and the range of thickness and nitrogen concentrations depends on the NO dilution in O₂. All three of these processes have uniform nitrogen distributions throughout the film. RT-N₂O films can be grown thicker than the others, but have about ten times less nitrogen than RT-NO films and a non-uniform distribution. The morphology of these thermally grown films is quite smooth based on AFM measurements. Electrical results indicate that the addition of NO to O₂ in the gas stream results in lower leakage films compared to pure SiO₂.

Ultra-thin LPCVD and RTCVD nitride films show nucleation problems when depositing about 20 Å or less on SiO₂. This is confirmed by MEIS, AFM, and leakage current data. Films this thin are likely discontinuous, and thus allow for many leakage paths. The nucleation problem is worse for LPCVD than RTCVD nitrides likely because the process pressure is much lower. RTCVD oxy-nitrides show more efficient nucleation on SiO₂ surfaces because reduced surface tension lowers the energy barrier height for nucleation and coalescence. The nitrogen concentration in RTCVD oxy-nitride films can be easily tuned by changing process gas flow ratio's, pressure and source gas type. Oxide/(oxy)nitride gate stacks show good electrical characteristics so long as the top (oxy)nitride is not too thin. As the top film gets too thin, the film may become discontinuous, which will lead to higher electrical leakage. Thin top films can easily be made thicker by post annealing in RT-N₂O. While this may restore electrical integrity, it will also remove nitrogen from the stack.

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