# Nucleation of chemical vapor deposited silicon nitride on silicon dioxide

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We have studied the early stages of silicon nitride chemical vapor deposition (CVD) on silicon dioxide using medium energy ion scattering. The growth mode consists of island nucleation followed by coalescence. Similar behavior is observed for films grown using different precursors and reactor environments, indicating that the growth mode is caused by the fundamental nonwetting nature of the nitride/oxide interface under the conditions used for CVD. © *1999 American Institute of Physics.* [S0003-6951(99)01013-X]

Downwards scaling of complementary metal-oxide-semiconductor (CMOS) devices has driven the demand for gate dielectrics with increasing capacitance. Conventionally, this need is met by decreasing the thickness of the $SiO_2$ layer used as a gate dielectric. However, scaling will encounter difficulties when the dielectric can no longer prevent electron tunneling currents.[1] An alternative to $SiO_2$ would have higher dielectric constant and larger physical thickness, thus promising a reduction in the tunneling current. Although many exotic choices have been proposed,[2,3] silicon nitride has several distinct advantages. It is compatible with existing silicon processing, easily deposited, and has roughly twice the permittivity of $SiO_2$. Unfortunately, nitride/silicon interfaces are marred by poor electrical qualities, so a nitride/oxide stack is a likely successor to a pure oxide gate.

This letter examines the nucleation of silicon nitride grown by chemical vapor deposition (CVD). The growth mode on $SiO_2$ consists of nitride islands, which merge only after 20–30 Å has been deposited. As a result, the morphology is poor, and may be detrimental to device performance. The growth mode helps explain the breakdown in oxidation resistance observed for thin CVD nitrides.[4] Previous investigators reported delayed nucleation for CVD of nitride on oxide surfaces, but nearly instantaneous nucleation on bare Si(001),[5] indicating that the growth properties are highly substrate dependent. We propose that the incubation period is associated with the island stage of growth.

Nitride films were fabricated by CVD from two different precursor chemistries: *in situ* decomposition of trisilylamine (TSA) with a 5:1 ammonia overpressure,[6] and conventional low pressure CVD from dichlorosilane and ammonia in a furnace. The TSA growth conditions were between 720 and 740 °C for 2–20 min with a TSA partial pressure of $5\times10^{-2}$ Torr. The Si(001) substrates had either freshly grown 10 Å $SiO_2$ layers or *ex situ* thermal oxides; the results were largely independent of the oxide layer, provided it was thicker than about 5 Å.

Samples were examined using medium energy ion scattering (MEIS), a high resolution form of Rutherford backscattering.[7] Samples were aligned with the $[11\bar{1}]$ axis parallel to an incident beam of 200 keV $He^+$. In this channeling configuration the ions have a low probability of backscattering from the crystalline substrate, reducing the background intensity. Due to scattering kinematics, $He^+$ ions backscattered from surface oxygen and nitrogen are detected at different kinetic energies. The backscatter peaks can be converted into a coverage ($atoms/cm^2$) by simply integrating the peak area. Alternatively, peak widths can be converted into a thickness via the stopping power, which is a well-known quantity.[8] For uniform films of known composition, e.g., thermal oxides and thermal nitrides, the coverage and the thickness agree to within 5%. A discrepancy between the coverage and the thickness indicates either a nonuniform morphology, a deviation from the expected stoichiometry, or interdiffusion. Since MEIS uses relatively energetic particles, the results are not affected by charging. A number of previous studies have successfully employed MEIS for studying oxynitride structures.[9,10]

Below, we compare MEIS spectra of nitride grown by three methods: rapid thermal nitridation (RTN) of Si(001), RTN of evaporated A-Si on oxide, and CVD of nitride on oxide (Fig. 1). All of the films in Fig. 1 were grown *in situ* and contain 2.8 ML of nitrogen ($1\ ML = 6.78\times10^{14}/cm^2$). The narrowest nitrogen peak is observed for RTN of bare Si(001) using ammonia (for processing details see Ref. 10). This will serve as a benchmark for smooth, stoichiometric $Si_3N_4$. (We confirmed the stoichiometry with MEIS by comparing the nitrogen coverage and the increase in the Si surface peak. For every reacted nitrogen atom there were 0.76 Si atoms contributed by the substrate, i.e., $Si_3N_4$.) A somewhat broader peak is observed for the sample labeled ''Dep-RTN.'' The Dep-RTN sample was made by *in situ* evaporation of A-Si on an oxidized substrate, followed by a brief RTN. The deposition and RTN steps were repeated through multiple cycles until 2.8 ML of N had accumulated. The Dep-RTN layer is slightly rougher than the RTN film, but still continuous, so the peak looks almost the same as the RTN spectrum. The Dep-RTN spectrum shows that the mere

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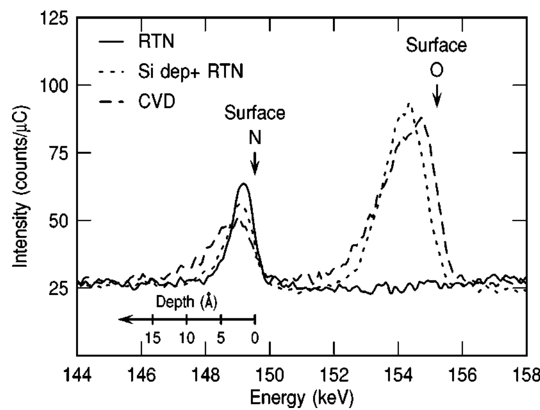


FIG. 1. Ion backscattering spectra for various 2.8 ML thick silicon nitride films. The CVD nitride has a much broader nitrogen peak, indicating that island formation occurs for this film.

presence of an oxide layer beneath the nitride is not a sufficient condition to severely alter the nitrogen peak from the RTN "benchmark." On the other hand, the nitrogen peak for the *in situ* CVD film deposited on a thermal oxide is nearly twice as broad as the RTN benchmark. Hence the nitrogen extends over roughly twice the depth in the CVD film, although the quantity of nitrogen atoms remains the same, 2.8 ML. The increase in depth distribution indicates either island formation, a strong deviation in stoichiometry, or interdiffusion. For example, if the nitride layer was silicon rich, the dilution of the nitrogen would spread the signal over a greater depth. Of these three possibilities, island formation is strongly favored by results described below.

We can obtain further information on the morphology of the nitride films from the oxygen peaks in Fig. 1. The energy of ions backscattered from surface oxygen is indicated in the figure. The leading edge of the oxygen peak of the Dep-RTN film has shifted to lower energy; there is no surface oxygen in this film. The shift in the oxygen edge occurs because ions need to penetrate the nitride layer before scattering from the underlying oxide, losing energy as a result. Assuming an ideal, smooth nitride layer, the oxygen peak should be displaced to lower energies by 0.5 keV. The observed displacement is 0.3 keV, nearly as large as expected. But the oxygen peak behaves much differently for the CVD film; the leading edge shows no shift from the position for surface oxygen. If the nitride layer was continuous, no surface oxide would be observed on an *in situ* processed film. Above, we mentioned that the broadening of the nitrogen peak could conceivably be caused by deviations in stoichiometry; now we can safely state that even if the CVD nitride is nitrogen poor, it must have islanded. Deviations in stoichiometry alone cannot explain the occurrence of surface oxide.

Distinguishing between islanding and nitride/oxide intermixing requires additional analysis. There are several reasons to favor islanding. First, if the system were prone to intermixing it would not be limited to CVD processing. Yet we do not see significant intermixing in the dep-RTN films, which required a similar thermal budget (600 ° in $NH_3$ for several minutes). Second, there is no nitrogen uptake observable with MEIS when a 20 Å oxide is exposed to $NH_3$ under the most extreme conditions used for CVD deposition in this study (740 °C, 250 mTorr, 20 min). Temperatures as great as

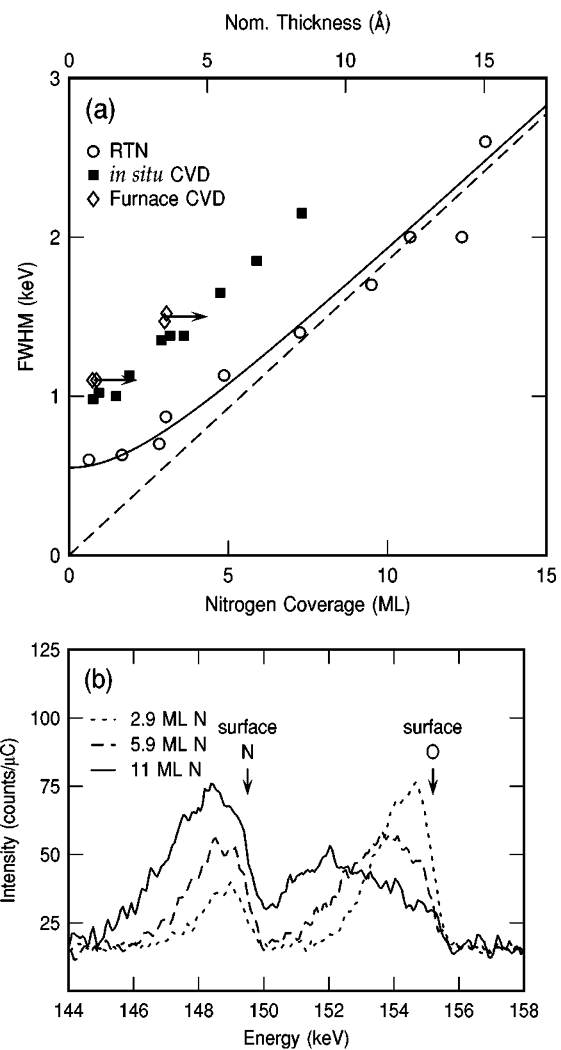


FIG. 2. Nitride peak evolution with increasing thickness. (a) Nitrogen peak width plotted as a function of coverage for CVD nitrides and thermal nitrides. (b) Ion backscattering spectra for several thicknesses of *in situ* CVD nitride grown on $SiO_2$. Even for the thickest nitride, areas of $SiO_2$ remain exposed.

900–1000 °C are required for significant nitridation of the oxide. This indicates that the oxide is stable against nitridation for our growth conditions. Finally, we may consider the possibility of the oxide layer reacting with and admixing into the nitride, but this is unlikely due to the enormous thermodynamic stability of $SiO_2$, which should prevent reaction to form an oxynitride. In our view, island formation is the most likely hypothesis to explain the results.

Since the nitrogen peak shape is an indicator of the morphology, we can use the full width at half maximum (FWHM) to compare films [Fig. 2(a)]. After deconvolving the detector resolution, the FWHM of the RTN films closely matches the stopping power for $Si_3N_4$ (dashed curve) with a small discrepancy below 1 keV. If we quadratically add a constant inelastic broadening of 0.55 keV to the stopping power, the RTN results can be modeled quite accurately (smooth curve).[10] However, the results for the CVD films strongly depart from the RTN benchmark. Both the films grown *in situ* using TSA as well as the *ex situ* films grown with conventional chemistry show similarly increased widths for coverages below 10 ML. [For $Si_3N_4$ with density of 3.44 g/cm$^2$, 1 ML of nitrogen is the equivalent of 1.15 Å of ni-

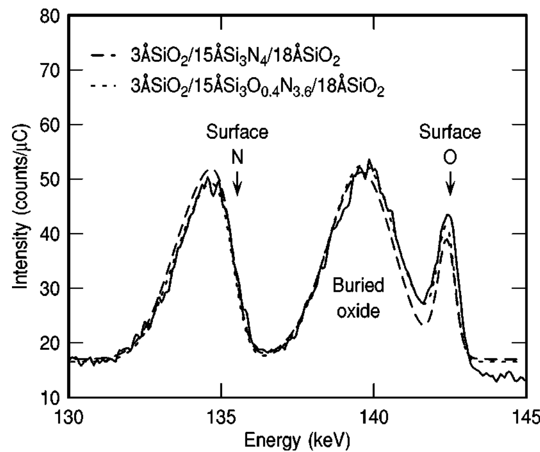


FIG. 3. Ion backscattering spectrum for a furnace-grown CVD nitride on a thermal oxide layer. A model assuming stoichiometric $Si_3N_4$ (dashed curve) underestimates the valley between the surface oxide and the underlying oxide film. A model incorporating oxygen in the nitride is more successful (dotted curve), indicating either penetration of oxygen into the nitride or the presence of inhomogeneities such as oxidized pinholes.

tride. We have used this to compute the nominal thickness of the nitride films as if they were smooth layers and included it as the top axis in Fig. 2(a).] The poor morphology of the CVD films can also be qualitatively observed in the shape of the oxygen peak [Fig. 2(b)]. If the nitride films were continuous, the oxygen peak would shift to lower energy and gradually broaden with increasing nitride thickness. Instead, a sharp leading edge can be seen at 155.2 keV due to surface oxygen. At the highest coverage shown, 11 ML, more than 20% of the surface is still oxygen terminated. At this stage of growth the nitride islands have largely merged and cover the remainder of the surface. With further increases in the nitride thickness, the leading edge of the oxygen peak continues to decrease.

An example of a relatively thick nitride/oxide stack grown in a conventional CVD furnace is shown in Fig. 3. (To clearly separate the nitrogen and oxygen peaks, the scattering angle has been changed from 60° to 70.5°. This shifts the peaks to lower energies than in previous spectra.) The oxygen signal consists of two peaks: a narrow surface peak at 142.5 keV, and a broader peak at 139.7 keV due to the underlying oxide layer. There is a valley between the peaks corresponding to the depth where the nitride resides. If the sample is modeled as 15 Å of pure $Si_3N_4$ sandwiched between the oxide layers, the depth of the valley is overestimated (dashed curve). To accurately model the spectrum, some oxygen must be included in the nitride, changing the stoichiometry to $Si_3O_{0.4}N_{3.6}$ (dotted curve). Although the spectrum is modeled as a homogeneous alloy, this is a mere convenience. The sample could be modeled equally well as an inhomogeneous film consisting of $Si_3N_4$ covering 90% of the sample and the remainder composed of oxidized pinholes. Either the nitride layer has not completely coalesced or, alternatively, the inadvertent postgrowth oxidation has penetrated from the surface throughout the film.

Surface oxidation poses a major difficulty in interpreting results for ultrathin *ex situ* films. The data collected for thicker *ex situ* samples, such as shown in Fig. 3, give an indication of the extent of the inadvertent postgrowth oxidation. Assuming that thinner nitrides undergo a similar degree of oxidation, we can attempt to correct the *ex situ* data for the adventitious oxygen, which is typically 2 ML. This is not sufficient oxidation to be the sole cause of the nitrogen peak broadening reported in Fig. 2(a). If the 2 ML of surface oxide results from conversion of the nitride, it would replace 1.3 ML of nitrogen. A correction for the oxidation can be made simply by displacing the *ex situ* data in Fig. 2(a) to greater nitrogen coverages by 1.3 ML, as indicated by the arrows. This would bring the *ex situ* results into agreement with the *in situ* results, but a substantial shift in the data would be required to match up with the RTN results.

In the early stage of growth, CVD silicon nitride forms islands on silicon dioxide, which eventually coalesce. Unfortunately, the coalescence does not take place until the film is thicker than roughly 20 Å, which may limit the usefulness for ultrathin gate insulators. Both nitride and oxide have low surface energies, thus the difference in surface free energies should be a weak influence in determining morphology. It is more probable that interface formation is responsible for the growth mode. This is not altogether surprising, since the oxide surface has arranged its bond topology to minimize the surface energy; presumably this topology must be rearranged to minimize the energy of the oxide/nitride interface. As a consequence, there would be an energy barrier to wetting, but little energy gained from de-wetting. One might hope to alter the growth properties by using lower temperatures, but restricting the growth kinetics will slow down the deposition to unacceptable rates. Alternatively, it may be worth investigating energy assisted methods of deposition such as plasma processes,[11–13] providing the damage can be reduced to acceptable levels.

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