Ammonia pretreatment for high-κ dielectric growth on silicon

R. T. Brewer,[a] M.-T. Ho, K. Z. Zhang, L. V. Goncharova, D. G. Starodub,
T. Gustafsson, and Y. J. Chabal
Departments of Chemistry & Chemical Biology and Physics & Astronomy, Laboratory for Surface Modification, Rutgers University Piscataway, New Jersey 08854

N. Moumen
International SEMATECH, 2706 Montopolis Drive, Austin, Texas 78741

Thermal nitridation of $H/Si(100)$ surfaces with NH_3 gas has been studied as a pretreatment for atomic layer deposition of Al_2O_3. The chemical nature of both the nitride interface and the Al_2O_3 growth was characterized using *in situ* transmission infrared spectroscopy and medium energy ion scattering. Nitride layers thicker than $3-4$ Å provide an effective barrier against interfacial SiO_2 formation and promote the nucleation of Al_2O_3 growth. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1807024]

The implementation of high-κ dielectrics to replace SiO_2 gate oxide is urgently needed.[1,2] Appropriate high-κ dielectric materials must meet a series of requirements, such as thermodynamic stability with Si to avoid the formation of an interfacial SiO_2 layer, and thus to permit the deposition of gate oxides with the thin (<1 nm) effective oxide thickness required by the semiconductor industry road map.[3,4]

Atomic layer deposition (ALD) is a promising, industrially attractive method for depositing ultrathin gate oxides without the formation of an interfacial SiO_2 layer. However, attempts to use ALD to deposit high-κ dielectrics directly on H-terminated silicon have resulted in the formation of an unwanted SiO_2 interfacial layer.[5] On H-terminated $Si(100)$ for instance, Al_2O_3 growth cannot be initiated by replacing the hydrogen termination with a hydroxyl group. Previous experiments have shown that exposure of H-terminated $Si(100)$ to either O_2 or H_2O at elevated temperatures results in oxygen insertion into the silicon back-bond without the removal of the surface hydrogen.[6] Additionally, *in situ* IR absorption studies of Al_2O_3 ALD have revealed that SiO_2 formation is associated with the presence of metal precursor at the surface, i.e., after the initial trimethylaluminum deposition, which often only partially covers the surface.[7] While longer exposures of the metal precursor prior to ALD growth do minimize SiO_2 formation and promote the growth of high-κ dielectrics,[8] complete elimination of the SiO_2 interfacial layer has not been demonstrated.

In this letter, we investigate ammonia thermal pretreatment of H-terminated $Si(100)$ to passivate the surface against SiO_2 formation during Al_2O_3 ALD, and we monitor the surface chemical state with *in situ* infrared spectroscopy. Si_3N_4 is a well-known diffusion barrier[9] and has been used to protect materials from semiconductor dopants[10] metals,[11] water,[12] and oxygen.[13,14] Silicon nitride has also been proposed as a barrier between HfO_2 and Si to avoid silicate formation in high-κ dielectric gate stacks and thus to minimize the equivalent oxide thickness (EOT).[15] While silicon nitride diffusion barriers are often tens of nanometers thick, we find that $3-4$ Å is sufficient to prevent the formation of interfacial SiO_2 during Al_2O_3 ALD. We also find that the

silicon nitride surface promotes nucleation and linear growth similar to Al_2O_3 growth on hydrophilic SiO_2 surfaces.

$Si(100)$ samples are prepared using standard RCA cleaning techniques[16] and a 20 s 10%–20% HF dip to create a well-defined hydrogen surface termination.[17] The H-terminated $Si(100)$ samples are placed in a dry nitrogen purged ALD cell operating at atmospheric pressure and located inside the sample compartment of a Nicolet Magna infrared spectrometer.[18] Nitridation is performed by introducing a 4% NH_3/N_2 gas mixture into the reaction chamber, raising the sample temperature to the desired temperature at about 100 °C/min, and then annealing for 2 min. Al_2O_3 is deposited by alternating exposures of trimethylaluminum (TMA) and D_2O[19] (respectively 0.001 and 0.02 mole fraction in 0.81/min N_2 carrier gas, atmospheric pressure), with at least 30 min purge time between precursor exposures. The IR windows are protected during the precursor exposure by shutters and nitrogen purge. The shutters are only opened to take IR measurements between deposition cycles after the chamber is fully purged. Al_2O_3 ALD is performed between 318 and 380 °C. Temperatures are measured using a thermocouple clipped to the substrate and calibrated using an infrared optical pyrometer. The difference between the thermocouple and actual sample temperature (as measured optically) is significant (see Table I) due to convective cool-

TABLE I. Summary of Si_xN_y growth by annealing H-terminated Si (100) in 4% NH_3/N_2. The temperatures are measured using a thermocouple (TM) clipped to the sample and by infrared optical pyrometry. The nitride thicknesses were calculated using the measured MEIS nitrogen areal density and assuming the Si_xN_y has the density of bulk Si_3N_4 (3.3 g/cm^{-3}), then estimating other film thicknesses grown at other temperatures by comparing the nitride LO mode absorption intensity ($\sim$850 cm^{-1}).

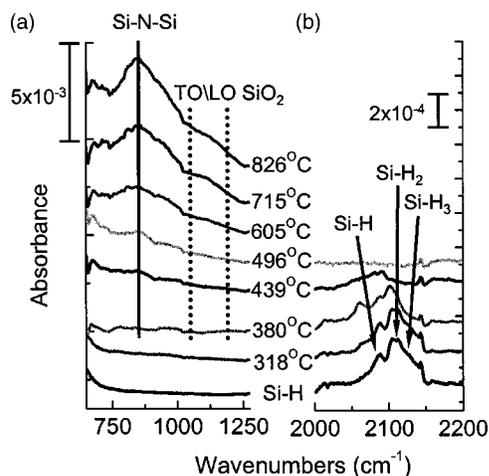| Temperature (°C)		MEIS	Calculated
TM	Optical	N density (atoms/cm^2)	Si_xN_y thickness (Å)
350	439		0.7
400	496		1.2
500	605	2.0×10^{15}	3.3
600	715		5.5
700	826	3.9×10^{15}	7.5

[a]Electronic mail: rhett.t.brewer@intel.com

FIG. 1. IR transmission absorbance spectra from hydrogen terminated Si(100), taken *in situ* at 45° incidence angle, as the surface was exposed to a 4% NH_3/N_2 gas mixture (atmospheric pressure) for 2 min at the indicated. temperature. The reference spectrum for (a) is from the H-terminated Si(100) surface and for (b) it is from the sample exposed to NH_3 at 825°C.

FIG. 2. IR absorbance spectra of Al_2O_3 grown by ALD at 330 °C on a nitrided silicon surface, prepared by NH_3 exposure of a H-terminated Si(100) surface at (a) 495 °C and (b) 605 °C, at atmospheric pressure. The reference spectrum is the respective nitrided surface in both cases.

ing of the thermocouple in the atmospheric pressure nitrogen purge ambient.

Exposure of Si to NH_3 at high temperatures is a standard process for growing Si_xN_y,[20,21] which has been shown to be an effective oxygen diffusion barrier[9,13,15] thus preventing interfacial SiO_2 formation. However, its thickness should be minimized to attain low EOT because its dielectric constant (~7), while larger than SiO_2, is still lower than other high-κ materials like HfO_2 and Al_2O_3 (25 and 9, respectively).[1]

We first monitor the formation of Si_xN_y from the exposure of H-terminated Si(100) to a 4% NH_3/N_2 gas mixture as a function of temperature using *in situ* transmission IR spectroscopy (see Fig. 1). There is no decrease of the Si–H stretching modes, ~2100 cm^{-1} [Fig. 1(a)] or growth of the Si–N–Si phonon modes, ~840 cm^{-1} (Ref. 22) [Fig. 1(b)] until the temperature reaches 380 °C, at which point we observe a small reduction in the Si–H stretching modes. At ~440 °C, we observe a drastic reduction in the surface hydrogen (only traces of the mono-hydride remain), accompanied by the formation of Si–N–Si bonds. Further increases in the 4% NH_3 exposure temperature result in larger Si–N–Si peak absorption areas, which we assume to be proportional to the thickness of the Si_xN_y layer. Evidently, the H-terminated surface is inert to NH_3 at low temperatures and the surface only begins to react at temperatures where hydrogen begins to desorb from the surface. At no time during our experiment do we observe Si–NH$_x$ absorption modes because the temperatures at which NH_3 reacts with the H-terminated surface are above the NH_x decomposition temperatures observed for NH_3 absorption on porous Si.[23]

We use the Si–N–Si mode IR absorption area as a quantitative measurement of Si_xN_y thickness by calibrating it with medium energy ion scattering (MEIS) for two Si_xN_y films grown by exposing an H-terminated Si(100) surface to 4% NH_3/N_2 at 605 and ~825 °C. The MEIS spectra are best modeled by a thick SiO_xN_y layer on a thin Si_xN_y layer, in contrast to the IR data which do not exhibit a strong SiO_xN_y peak at 950 cm^{-1}.[22] This apparent discrepancy indicates that the as grown, predominantly Si_xN_y film is heavily oxidized to form oxynitride during the transfer from the growth to MEIS chamber. We used the MEIS measured areal density of
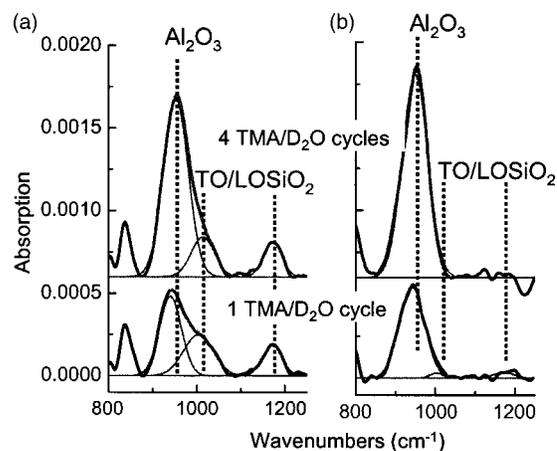
nitrogen and assumed a film density of bulk Si_3N_4 (3.3 g/cm^3) to determine the thickness of the Si_xN_y layers grown at 605 and 825 °C. The Si_xN_y thickness for the films grown at other temperatures were determined by scaling the intensity of the Si–N–Si IR absorption peak at 850 cm^{-1} to the values measured at these two points (Table I). These values represent a lower limit on the film thickness because these thin Si_xN_y films may be less dense than bulk Si_3N_4. Combining Si_xN_y density and Si–N–Si IR peak measurement uncertainties, the thickness of the 605 °C NH_3 nitride film could be as high as 4.1 Å (3.3 Å in Table I), so we estimate our thickness measurements to be within 1 Å.

ALD Al_2O_3 film thicknesses are extracted from MEIS Al areal densities. We find that as a result of the very large exposures used in our experiments, and possible incomplete purging between growth cycles, some chemical vapor deposition may take place resulting in a higher growth rate (up to 5 Å per cycle) than what was reported (~1.8 Å per cycle) for pure (and possibly incomplete) ALD growth.[24] Our results are therefore characteristic of fully saturated layers and observations of interfacial silicon oxidation processes are intrinsic to the materials system, rather than a result of incomplete precursor surface coverage. However, for all the studies presented in the following, great care is taken to maintain consistent growth conditions to ensure meaningful comparisons.

The effectiveness of NH_3 grown Si_xN_y in preventing SiO_2 formation is first studied by growing ALD Al_2O_3 on Si_xN_y surfaces at various temperatures and measuring the formation of interfacial SiO_2 with transmission IR spectroscopy. Figure 2 shows the absorption spectra after one and four cycles of TMA/D$_2$O exposures, at 331°C, on Si(100) H-terminated surfaces that had been pretreated with a 4% NH_3/N_2 exposure at ~495 and 605°C for Figs. 2(a) and 2(b), respectively. We note Al_2O_3 growth during the first exposure cycle on Si_xN_y (evident from the Al_2O_3 absorption peak 850 cm^{-1}), which is not observed under identical deposition conditions on H-terminated Si(100). From the TO and LO absorption modes of SiO_2 (1020 and 1175 cm^{-1}, respectively), it is clear that ~1 Å (average thickness) of SiO_2 is formed on the 1.2-Å-thick Si_xN_y grown at 495 °C [Fig. 2(a)], while no measurable SiO_2 (<0.1 Å) is formed on the 3.3-Å-thick Si_xN_y grown at 605 °C [Fig. 2(b)]. We conclude that
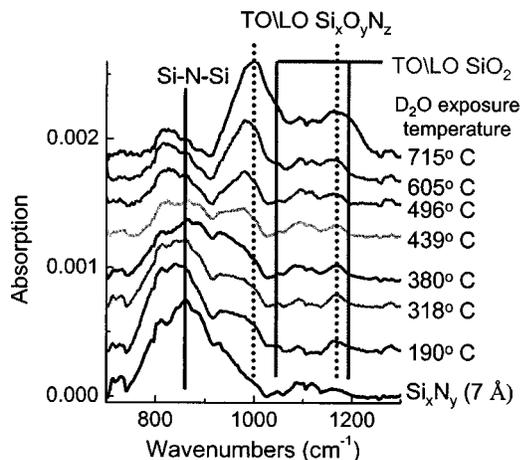
FIG. 3. IR absorbance spectra showing the oxidation of 3-Å-thick Si_xN_y on Si(100) as a function of the D_2O exposure temperature. The reference is the H-terminated surface.

NH_3 thermal Si_xN_y films must be between 3 and 4 Å thick before they are continuous and that a continuous Si_xN_y is effective in preventing the formation of interfacial SiO_2.

The ability of a continuous Si_xN_y layer to prevent interfacial SiO_2 formation is further investigated by exposing a 3-Å-thick Si_xN_y film to the ALD oxidant, D_2O, at increasing temperatures (Fig. 3). It is clear that, while Si_xN_y is oxidized by D_2O even at 190 °C to form $Si_xO_yN_z$, there is no SiO_2 formation up to 605 °C. In contrast, an H-terminated Si(100) surface first treated with TMA at 330 °C (half of our standard Al_2O_3 ALD cycle) and then exposed to D_2O at 380 °C results in the formation of over 1 Å SiO_2.

Finally, the nucleation of Al_2O_3 on Si_xN_y is examined by comparing the rate of Al_2O_3 growth for the first four cycles of TMA/D_2O exposure to the growth rate of Al_2O_3 on H-terminated Si(100) surfaces and on SiO_2 surfaces, prepared by dipping an H-terminated Si(100) sample into a solution of 1 HCl:1 H_2O_2:4 H_2O at 80 °C for 10 min.[25] In Fig. 4, the Al_2O_3 absorption phonon area (950 cm^{-1}), which is proportional to Al_2O_3 film thickness, is plotted as a function of TMA/D_2O exposure cycle. On the OH-terminated SiO_2 surface we observe linear growth of Al_2O_3 from the first TMA/D_2O exposure cycle, confirming that there is no barrier to Al_2O_3 nucleation.[24] Al_2O_3 deposition under the same conditions on the Si_xN_y surface proceeds as fast as
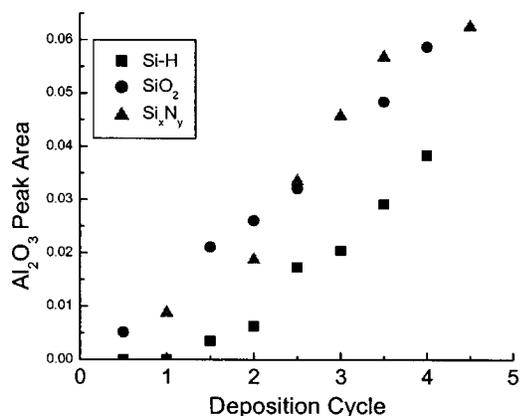
growth on hydrophilic SiO_2, indicating that the Si_xN_y surface is reactive to TMA and does not pose a barrier to Al_2O_3 nucleation and growth. In contrast, the first cycle of TMA/D_2O on the H-terminated surface, even at these very large precursor exposures, results in no measurable Al_2O_3 because of the low reactivity of the H-terminated Si(100) surface with TMA.

In conclusion, we have demonstrated that interfacial SiO_2 formation is prevented by Si_xN_y films only 3–4 Å thick during ALD growth of Al_2O_3. Immediate growth of Al_2O_3 during the first TMA/D_2O exposure cycle demonstrates that there is no nucleation barrier to Al_2O_3 growth on the Si_xN_y surface.

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FIG. 4. Peak areas of the Al_2O_3 longitudinal optical (LO) absorption band (assumed proportional to film thickness) as a function of the TMA/D_2O deposition cycle for different surfaces: Si–H, SiO_2 and Si_xN_y.