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# Ammonia pretreatment for high-$\kappa$ dielectric growth on silicon

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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-$\kappa$ dielectrics to replace $SiO_2$ gate oxide is urgently needed.[1,2] Appropriate high-$\kappa$ 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-$\kappa$ 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-$\kappa$ 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-$\kappa$ 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 0.8 l/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-teminated 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 (~850 $cm^{-1}$).

| Temperature (°C) | | | |
|---|---|---|---|
| TM | Optical | MEIS N density (atoms/$cm^2$) | Calculated $Si_xN_y$ thickness (Å) |
| 350 | 439 | | 0.7 |
| 400 | 496 | | 1.2 |
| 500 | 605 | $2.0\times10^{15}$ | 3.3 |
| 600 | 715 | | 5.5 |
| 700 | 826 | $3.9\times10^{15}$ | 7.5 |

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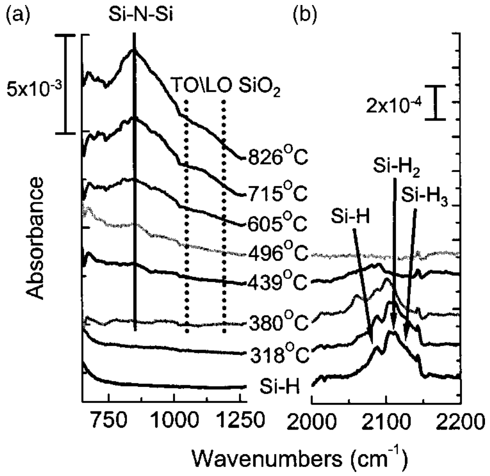

FIG. 1. IR transmission absorbance spectra from hydrogen terminated Si(100), taken *in situ* at 45° incidence angle, as the surface was exposed to a 4% $NH_3/N_2$ gas mixture (atmospheric pressure) for 2 min at the indicated temperature. The reference spectrum for (a) is from the H-terminated Si(100)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

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-$\kappa$ 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 the 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.

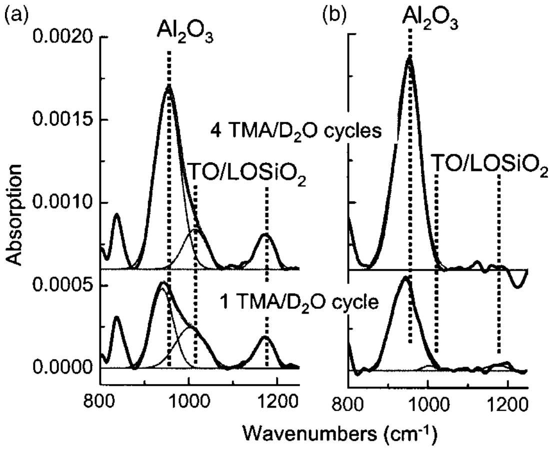

FIG. 2. IR absorbance spectra of $Al_2O_3$ grown by ALD at 330 °C on a nitrided silicon surface, prepared by $NH_3$ exposure of a H-terminated Si(100) surface at (a) 495 °C and (b) 605 °C, at atmospheric pressure. The reference spectrum is the respective nitrided surface in both cases.

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 $TMA/D_2O$ 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

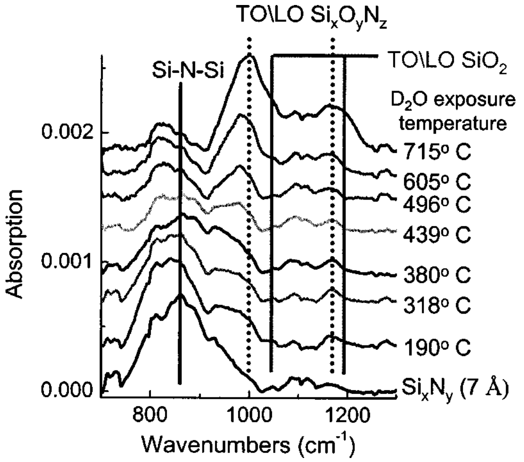

FIG. 3. IR absorbance spectra showing the oxidation of 3-Å-thick $Si_xN_y$ on Si(100) as a function of the $D_2O$ exposure temperature. The reference is the H-terminated surface.

$NH_3$ 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.

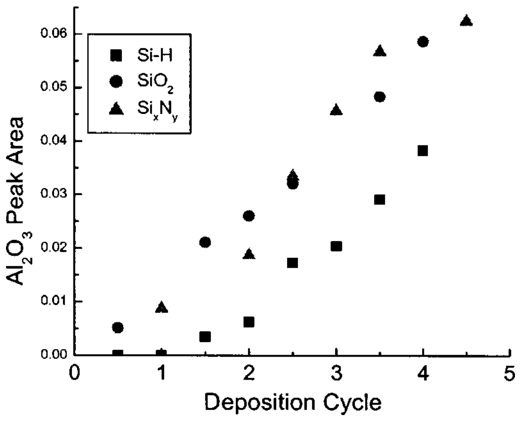

FIG. 4. Peak areas of the $Al_2O_3$ longitudinal optical (LO) absorption band (assumed proportional to film thickness) as a function of the TMA/$D_2O$ deposition cycle for different surfaces: Si–H, $SiO_2$ and $Si_xN_y$.

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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