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# Thermal stability and diffusion in gadolinium silicate gate dielectric films

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Gadolinium silicate films on Si(100) annealed in oxygen and vacuum at temperatures up to 800 °C were analyzed by Rutherford backscattering and narrow resonance nuclear profiling. Oxygen diffused into the film eliminating oxygen vacancies, but Si diffusion, previously observed in Al and Y oxides and in La and Zr silicate films, was absent. Higher-temperature annealing in oxygen resulted in the formation of an interfacial layer observable in high-resolution electron micrographs. $Gd_{0.23}Si_{0.14}O_{0.63}$ films crystallize at temperatures between 1000 and 1050 °C. These observations combined with recent electrical measurements show that gadolinium silicate films may be a good candidate for the replacement of $SiO_2$ in deep submicron metal–oxide–semiconductor gates. [DOI: 10.1063/1.1412284]

The search for a high-dielectric constant ($\kappa$) replacement for the silicon dioxide gate insulator in deep submicron metal–oxide–semiconductor technology is underway in a number of laboratories around the world. Most of the effort has focused on insulators that are "thermodynamically stable" on Si substrates; i.e., when heated in contact with silicon will not directly react to form silicide, metal, or silicon oxide.[1,2] Candidate materials include oxides such as $Al_2O_3$, $HfO_2$, $ZrO_2$, $Y_2O_3$, or $La_2O_3$, and silicates such as $ZrSiO_4$ and $HfSiO_4$.[2–4] It is generally assumed that other lanthanide oxides, such as $Gd_2O_3$,[5–7] or their silicates,[8] are also thermodynamically stable. However, even a thermodynamically stable film can react if excess oxygen in the film or from the ambient, or Si from the substrate, diffuse through the film and react with each other. These processes can lead to the formation of silicon dioxide which can undergo subsequent reactions, which are not thermodynamically forbidden, with the metal oxide or silicate.[9,10] It is thus important to determine the extent to which oxygen and silicon are mobile in the insulator during high-temperature processing.

Previous work[8] has shown that gadolinium silicate films with $\kappa$ as high as 16 have promising electrical properties that may make them a very good replacement for $SiO_2$ as the gate insulator. In this letter, we investigate the motion of Si and $O_2$ in gadolinium silicate films to show that their stability against diffusion could be superior to that of other high-$\kappa$ dielectrics. Films ~8–10 nm thick were deposited by electron-beam evaporation of pressed powder ($Gd_2O_3$–$SiO_2$) targets onto Si(100) substrates previously cleaned using an RCA HF last process. After cleaving, some pieces were annealed in a vacuum furnace, some were annealed at ambient pressure in dry $N_2$ or $O_2$, and others were annealed in $7\times10^3$ Pa of dry $O_2$ 98.5% enriched in $^{18}O_2$.

Gd and Si areal densities were determined by Rutherford backscattering spectrometry (RBS) of 0.7 MeV $He^+$ ions, detected at a scattering angle of 168° with a sample tilt of 70°. The spectrum of the as-deposited film used for these studies is shown in Fig. 1. The areal density of $^{16}O$ oxygen was determined by nuclear reaction analysis using 0.85 MeV deuterons to induce the $^{16}O(d,p)^{17}O$ reaction,[7] whereas the areal density of $^{18}O$ was determined by the $^{18}O(p,\alpha)^{15}N$ reaction.[11] The narrow resonance of the $^{18}O(p,\alpha)^{15}N$ reaction at 151 keV ($\Gamma_R = 100\,\mathrm{eV}$) was used to profile the $^{18}O$ concentration and the narrow resonance of the $^{29}Si(p,\gamma)^{30}P$ reaction at 414 keV ($\Gamma_R \leq 100\,\mathrm{eV}$) was used to perform narrow resonance profiling of $^{29}Si$.[11]

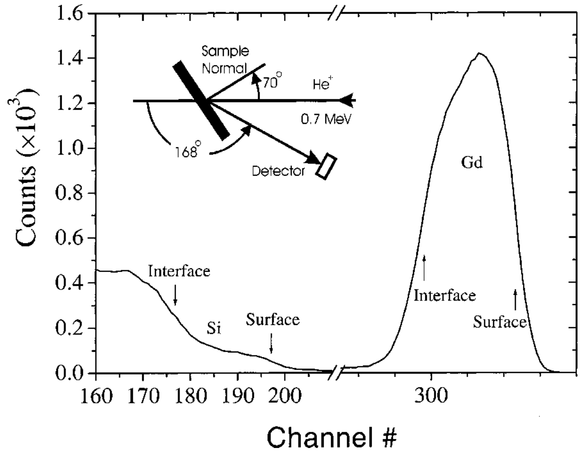

FIG. 1. Gd and Si signals in the RBS spectrum of an as-deposited $GdSi_{1.4}O_{4.3}$ film obtained with 0.7 MeV $He^+$ ions using the geometry shown in the inset.

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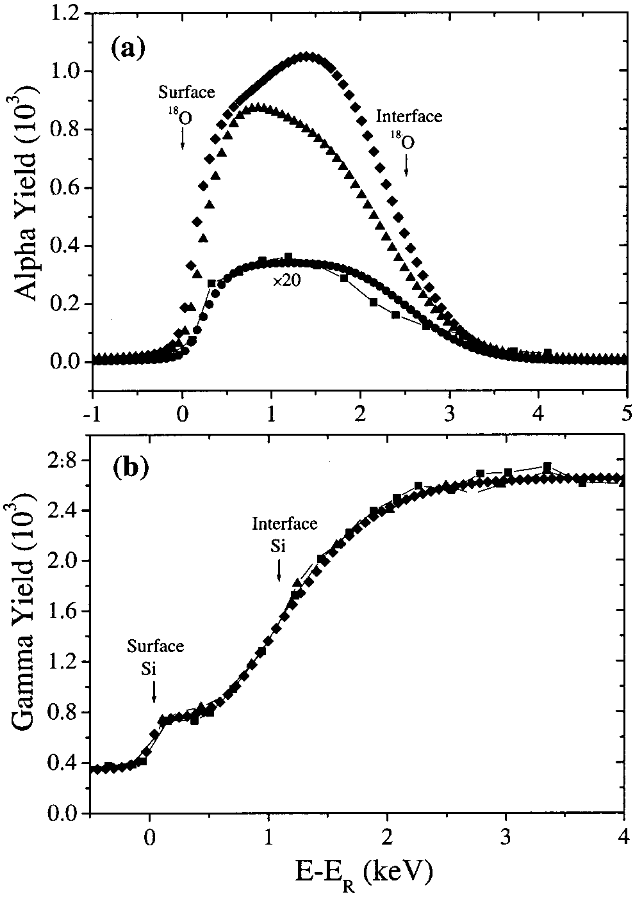

FIG. 2. (a) Alpha yield of the nuclear reaction $^{18}O(p,\alpha)^{15}N$ around the resonance at 151 keV. (b) Gamma yield of the nuclear reaction $^{29}Si(p,\gamma)^{30}P$ around the resonance at 414 keV. Samples were annealed 2 min in vacuum and/or 1 min in $^{18}O_2$; (■■■) as deposited, (●●●) 800 °C vacuum, (▲▲▲) 800 °C vacuum+800 °C $^{18}O_2$, and (◆ ◆ ◆) 800 °C $^{18}O_2$.

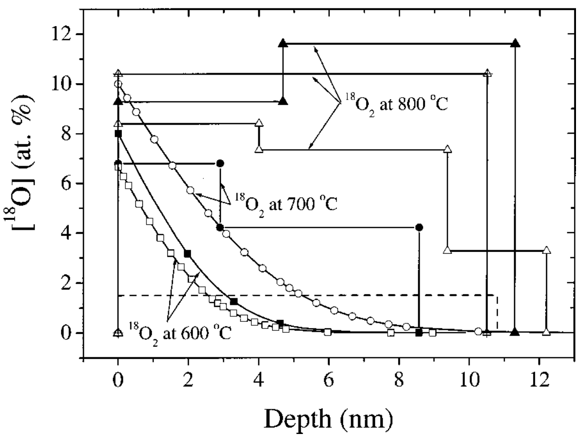

FIG. 3. Concentration profiles of $^{18}O$ obtained using SPACES simulations of narrow nuclear resonance data: open symbols, preannealing in vacuum at 800 °C for 2 min followed by annealing in $^{18}O_2$ for 1 min; cross-centered symbol, preannealing in vacuum at 700 °C for 2 min followed by annealing in $^{18}O_2$ for 1 min; solid symbols, no preannealing in vacuum, annealing in $^{18}O_2$ for 1 min; and dashed line, annealing only in vacuum at 800 °C (expanded × 10).

As deposited, the film composition was determined to be $GdSi_{1.4}O_{4.1}$. After annealing 2 min in vacuum at 800 °C followed by 1 min in $^{18}O_2$ at 800 °C, the integrated intensity of the $^{18}O$ peak increased while the $^{16}O$ signal remained constant so that the composition of the sample was that of a pseudobinary alloy consisting of 27% $Gd_2O_3$ and 73% $SiO_2$ ($GdSi_{1.4}O_{4.3}$). During this oxygen annealing there was no evidence for a change in Si or Gd ($1.3\times 10^{15}\,cm^{-2}$) concentration in the films.

To better quantify the change in O and Si profiles, two sets of samples were prepared, one set annealed for 1 min in $^{18}O_2$ at 600, 700, or 800 °C, and the other annealed at the same temperatures after a 2 min vacuum anneal at 800 °C. A final sample was annealed 2 min in vacuum at 700 °C and 1 min in $^{18}O_2$ at 800 °C to determine the sensitivity of oxygen diffusion to the vacuum annealing temperature. No significant changes were discernable in the Si and Gd RBS signals after annealing. Typical excitation curves for the $^{18}O(p,\alpha)^{15}N$ and $^{29}Si(p,\gamma)^{30}P$ reactions obtained on the $GdSi_{1.4}O_{4.3}$ sample are shown in Fig. 2. The $^{18}O$ excitation curves in Fig. 2(a) were converted into profiles with subnanometer depth resolution using the program SPACES.[12] The results shown in Fig. 3 indicate that oxygen does diffuse in the films and that the diffusion rate is lower as a result of the densification of the film, if the sample is first annealed in vacuum at 800 °C. Comparing the samples annealed in $^{18}O_2$ at 800 °C after vacuum anneals at 700 or 800 °C demonstrates that the higher-temperature vacuum anneal is more effective in reducing the oxygen diffusion.

The annealing has no effect on the $^{29}Si$ excitation curves of Fig. 2(b); apparently, silicon does not diffuse in these gadolinium silicate films, during either oxygen or vacuum annealing, at temperatures up to 800 °C. To corroborate this, the samples were examined by x-ray photoelectron spectroscopy using a Mg K$\alpha$ x-ray source at a low takeoff angle of 30°, where the measurements are surface sensitive or at 65°, in the bulk-sensitive mode. A single Si 2$p$ line, characteristic of fully oxidized silicon, was observed and its position (103 eV) and width (1.69 eV) did not vary with the takeoff angle or annealing over the full range of annealing conditions described above.

Si readily diffuses into metals such as Y, and subsequent oxidation results in the formation of a silicate layer.[13] Vacuum annealing of very oxygen-deficient zirconium silicate films ([Zr]+[Si]=[O]/1.5) on Si resulted in Si–Si precipitates accumulating at the sample surface as a result of silicon diffusion from the substrate.[14]

Si has also been shown to incorporate during the deposition of lanthanum and yttrium oxide films formed by atomic-beam deposition using La or Y and O beams[15] or during e-beam deposition of lanthanum oxide from pressed powder targets.[16] In the latter films, which were initially oxygen rich ([O]>3/2[La]+2[Si]), further Si diffusion was observed after annealing at temperatures as low as 750 °C. The diffusion of silicon from the substrate is not universally observed in aluminum oxide films[10] and may not occur in all zirconium or hafnium silicate films.[1] More experiments need to be performed to determine the factors determining Si diffusion in high-$\kappa$ films, but the apparent tendency of gadolinium silicate films to have a slight oxygen deficiency, rather than a pronounced excess or deficiency, may be a significant advantage.

To determine the effect of annealing at temperatures higher than 800 °C, a 30-nm-thick $Gd_{0.23}Si_{0.14}O_{0.63}$ film was annealed in $O_2$ for 2 min at 900 °C. The high-resolution

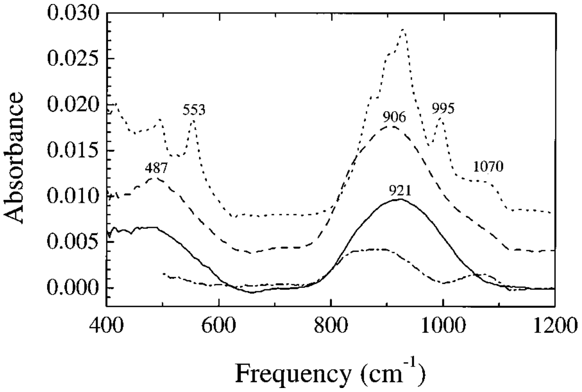

FIG. 4. Fourier transform infrared spectra of the 30-nm-thick $Gd_{0.23}Si_{0.14}O_{0.63}$ sample: (——) as deposited; (----) after annealing at 900 °C in $O_2$ for 120 s; (·····) after crystallization at 1050 °C in $O_2$ for 15 s; and (—·—·—·—) difference, first two spectra.

transmission electron microscope photograph of the annealed film has a single distinct 3.5-nm-thick interfacial layer between the Si and the amorphous film. Electron energy-loss spectra of the Gd $N_{4,5}$ peak were obtained using a Philips CM20 STEM equipped with a field-emission gun and an energy-loss imaging filter (Gatan Model 678). No gadolinium was detected in the interfacial layer. To shed more light on the nature of this layer, Fourier transform infrared spectroscopy was performed on this sample at normal incidence. In the spectrum obtained by subtracting the spectrum of the as-deposited film from that of the annealed film, two characteristic peaks centered around 875 and 1068 cm$^{-1}$ were evident, as shown in Fig. 4. Bands at 1070, 900, and 850 cm$^{-1}$ in aluminosilicate,[17] or alkali silicate,[18] glasses have been attributed to Si–O stretching vibrations of $SiO_{4/2}$ tetrahedra involving zero, three, or four nonbridging oxygens, respectively. Thus, our spectra indicate that significant numbers of the $SiO_{4/2}$ tetrahedra in the interfacial layer have one or more nonbridging oxygens per tetrahedron.[17]

High-resolution transmission electron microscopy revealed that films annealed in $O_2$ at 1000 °C remained amorphous but for those annealed for 15 s at 1050 °C the layer above the interfacial layer had crystallized. In Fig. 4 the spectrum of the film annealed at 1050 °C showed further peaks characteristic of a crystalline film. If 15 s anneals at 1050 °C are required to anneal implants using conventional device processing sequences, the anneals would have to be done in an oxygen-free environment on films with a higher silicon dioxide fraction than those studied here, but more work needs to be done to study the effect of these anneals on the electrical properties of the interface.

In conclusion, it has been shown that gadolinium silicate films deposited by e-beam evaporation are not susceptible to Si diffusion during either vacuum or oxygen annealing. Oxygen diffuses through the films, eliminating any oxygen deficiency and resulting in pseudobinary alloys of $Gd_2O_3$ and $SiO_2$. Subsequently, extra oxygen can diffuse through the films to the oxide/Si interface, allowing some flexibility in engineering the electrical properties of the interface.

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