Thermally Driven Atomic Transport in Silicon Oxynitride and High-k Films on Silicon

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Significant research efforts are being directed to finding a gate dielectric material alternative to SiO_2 for application in MOSFET devices. Atomic-scale understanding of thermally driven atomic transport in thin dielectric films on silicon is key to determining optimal thermal processing parameters and thus identifying a suitable substitute to SiO_2. We seek such understanding by combining sample preparation in isotopically labeled gases and sample characterization by isotope-sensitive methods such as nuclear reaction analysis. In addition, X-ray photoelectron spectroscopy is used for chemical bonding characterization. This contribution focuses on a comparison between the behavior of silicon oxynitrides and a number of high-k films on silicon — namely HfO_2, $HfSi_xO_y$, Al_2O_3, $ZrSi_xO_y$, $ZrAl_xO_y$, and $GdSi_xO_y$ — upon thermal annealing in O_2.

Silicon oxynitride films were grown to 8 nm at 1090°C by RTP in $^{15}N_2O$. The films showed a uniform nitrogen concentration of about 0.015 N/(N+O) between 4 and 8 nm of depth. They were annealed in $^{18}O_2$ at the same temperature of growth for 20 to 120 min. A pure $Si^{18}O_2$ layer was observed below the original SiO_xN_y/Si interface. Significant nitrogen loss and redistribution were observed. Extensive oxygen exchange took place throughout the oxynitride film, with maxima at the sample surface and original SiO_xN_y/Si interface. It was found that most probably the defects responsible for the migration of nitrogen and oxygen atoms are intersticialcies. A second set of oxynitride samples was prepared by ion beam nitridation of silicon at 20 eV followed by annealing in O_2 at 1050°C. Before annealing, nitrogen amounts ranged from the equivalent to about 1/30 to 1 monolayer. SiO_2 growth was strongly retarded by the presence of nitrogen. Once again, nitrogen loss was observed, which based on the thermodynamics of the Si-N-O system we attributed to exchange for oxygen.

Hafnium oxide films about 6 nm-thick deposited on an oxynitride buffer on silicon were found to incorporate oxygen from the gas phase upon annealing at 800°C for 10 to 60 s. Oxidation of the Si substrate was observed at the highest thermal budgets. Oxygen incorporation was minimized by annealing in Ar:N_2 prior to exposition to O_2. A complex interface consisting of Hf, Si, N, and O was observed after annealing. The oxynitride buffer did not prevent Hf from reaching the silicon substrate, even upon annealing in inert gas. Oxygen exchange was also observed in about 10 nm-thick **hafnium silicate** deposited on silicon. An interfacial layer was observed by TEM in the as-deposited sample. RTP was performed at 1000°C for 10 to 60 s in N_2 or O_2. As before, annealing in N_2 before annealing in O_2 enhanced resistance to oxygen exchange. After about 30% of the oxygen had been uniformly substituted, SiO_2 started to grow at the interface with silicon. These films also showed silicon migration to the sample surface. Even so, hafnium silicate presented the higher thermal stability among the materials studied. **Aluminum oxide** films 6.5 nm-thick deposited on an oxide buffer on silicon were submitted to RTP in vacuum or in O_2 betwen 600 and 800°C for up to 60 s. We observed aluminum loss, silicon transport to the sample surface, oxygen exchange, and oxidation of the substrate. XPS revealed formation of Si-Al-O compounds near the sample surface at and above 700°C in O_2. No such instabilities were observed upon annealing in vacuum. **Zirconium silicate** films 9 nm-thick were annealed at 600°C for 30 min in vacuum or in O_2. The interface with silicon was seen to be rather stable, i.e. no SiO_2 formation took place at that temperature. The surface region suffered from accumulation of silicon in the form of precipitates, which were partially or totally oxidized in the presence of O_2. Similar behavior was found for about 8 nm-thick **zirconium aluminate** films sputtered on silicon upon thermal annealing at 600° for 10 min. **Gadolinium silicate** films 8 to 10 nm-thick on silicon were submitted to annealing in vacuum or O_2 at up to 800°C for up to 120 s. Oxygen diffused into the film eliminating vacancies; silicon diffusion was not observed. Annealing in O_2 at the highest temperature resulted in an interfacial layer seen by TEM. Annealing in vacuum prior to exposition to O_2 reduced oxygen incorporation.

To different extents, all the materials investigated were transparent to oxygenic species. Silicon oxynitrides offered the highest resistance to diffusion. Annealing of SiO_xN_y in O_2 resulted in significant exchange between oxygen in the gas phase and oxygen originally in the samples, with maxima close to 100% at the surface of the films and at the original SiO_xN_y/Si interface. Nitrogen loss accompanied oxygen exchange. In the high-k films, oxygen from the gas phase was initially found with maximum concentration at the surface; with annealing time, this evolved to a uniform distribution along the films. Such exchange, however, did not involve more than 30% of the original oxygen amount. Annealing in vacuum or inert gas before exposition to O_2 was generally seen to improve high-k resistance to oxygen diffusion. This is consistent with film densification and annealing of defects resulting from the deposition processes. Other observations include aluminum loss from Al_2O_3, diffusion of hafnium from HfO_2 into the silicon substrate, and diffusion of silicon in $HfSi_xO_y$, Al_2O_3, $ZrSi_xO_y$, and $ZrAl_xO_y$. All observations are remarkably different from those corresponding to pure silicon oxide films on silicon, which show no incorporation of oxygen from the gas phase to the bulk region.

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