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Outdiffusion of La and Al from amorphous $LaAlO_3$ in direct contact with Si (001)

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We have evaluated the thermal stability of $Al_2O_3/LaAlO_3/Si$ (001) stacks with atomic force microscopy, x-ray diffraction, transmission electron microscopy, and secondary ion mass spectrometry using a back side polishing approach. Crystallization of the amorphous $LaAlO_3$ film was found to occur for rapid thermal anneals (RTA) above 935 °C for 20 s, in flowing N_2. Penetration of Al and La into the underlying Si (001) is clearly observed for RTA at or above 950 °C for 20 s in flowing N_2. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1928316]

The *International Technology Roadmap for Semiconductors (ITRS) 2003* predicts the need for the introduction of higher dielectric constant (k) gate dielectrics by 2006 to meet continued scaling requirements in metal-oxides silicon field-effect transistor (MOSFET) digital logic technology. Hafnium-based dielectrics appear to be one of the leading candidates for near term scaling of transistors.[1,2] Oxides and silicates of Column III elements of the periodic table, including La and Y, have also been examined. Lanthanum aluminate ($LaAlO_3$) has been identified as a high-k candidate beyond Hf-based dielectrics[1] due to its high k ~20–25,[3] thermodynamics stability on silicon,[4] band gap of >5 eV,[5–7] and suitable valence- and conduction-band offsets.[7] The introduction of $LaAlO_3$ is anticipated for the 45 nm node.[1]

The thermal stability of a high-k dielectric film in direct contact with the underlying Si substrate is essential because outdiffusion of metal impurity atoms into the channel region during processing can cause carrier mobility degradation.[8–10] In this letter, we present results on the evaluation of La and Al outdiffusion from amorphous $LaAlO_3$ thin films in direct contact with Si (001) during annealing conditions relevant to the highest-temperature step (implant activation) in conventional MOSFET processing.

Amorphous $LaAlO_3$ thin films ~1000 Å thick (Ref. 11) were grown on single-side polished, p-type boron-doped (001) Si ($N_A \sim 0.3–1.5\times10^{16}$ cm^{-3}) by molecular-beam deposition in an EPI 930 molecular-beam epitaxy chamber modified for the growth of oxides.[12] Prior to insertion into the deposition chamber, the substrate was Radio Corporation of America (RCA) cleaned and hydrogen-terminated with ~1% hydrofluoric acid. La (Aesar, 99.9% pure) was evaporated from a tungsten crucible in a high-temperature effusion cell, while Al (Aesar, 99.9999% pure) was evaporated from a pyrolytic boron–nitride crucible in a dual-filament effusion cell with the tip filament turned off. La, Al, and O_2 (99.994% purity) at a background pressure of 6×10^{-8} Torr, were codeposited at room temperature to form the amorphous $LaAlO_3$ dielectric film on (001) Si. The La and Al fluxes were each 2×10^{13} atoms/cm^2 s. Rutherford backscattering spectrometry (RBS) measurements (1.4 MeV He^+, 170° scattering angle) showed that the ~1000 Å thick $LaAlO_3$ films were stoichiometric with a La (1:1) Al ratio to within ±5 mol %. The films were capped *in situ* with ~100 Å of Al_2O_3 at a background molecular oxygen pressure of 3×10^{-6} Torr, in order to protect the film surface from hydroxyls.[7] This deposition process has been shown to yield an abrupt amorphous $LaAlO_3$/Si interface free of interfacial SiO_2.[13]

The $Al_2O_3/LaAlO_3/p$-Si (001) stack was rapid thermal annealed (RTA) in a flowing N_2 (>99.999% purity) ambient at 850–1040 °C for various annealing durations (10–20 s). Temperatures were calibrated using cross-referenced optical pyrometry and thermocouple measurements. Contact mode atomic force microscopy (AFM) was used to characterize the surface morphology evolution and x-ray diffraction (XRD) was used to study the crystallization of $LaAlO_3$ films as a function of RTA temperature. Cross-sectional transmission electron microscopy (TEM) images of the stack were acquired in order to study the microstructure of the stack before and after RTA.

The depth profile of La and Al within the Si substrate after RTA was determined using a back side secondary ion mass spectrometry (SIMS) approach.[14] In the case of conventional front-side dynamic SIMS analysis, the depth resolution and detection limit are severely degraded after sputtering through a thick film or an overlayer containing a high level of constituent species (La, Al) due to ion beam mixing artifacts of matrix elements. These issues can be reduced by removing sufficient substrate material from the back side of a sample with adequate precision to allow SIMS depth profiling.[15] For the current study, the back side of the $Al_2O_3/LaAlO_3/p$-Si (001) stack was polished down to ~1 μm thickness with a lateral uniformity of 1–2 Å/μm. A PHI Quadrupole SIMS instrument was used for the dynamic SIMS measurement. The stack was analyzed from the polished back side using a 5 keV O^{2+} primary beam with an

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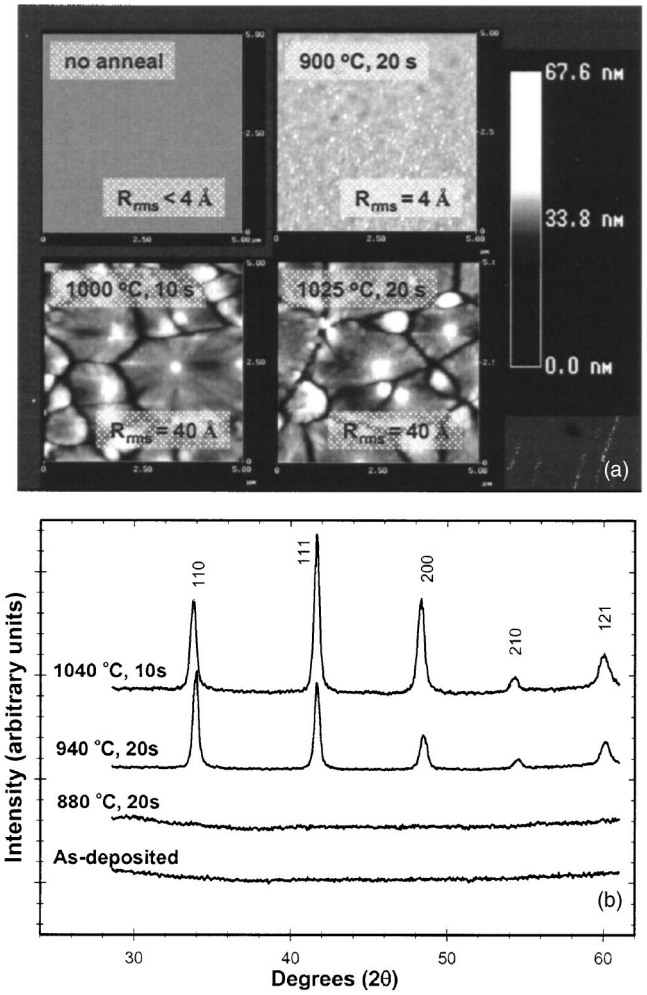

FIG. 1. (a) AFM images (area=5 μm$\times$5 μm) of the $Al_2O_3/LaAlO_3/p$-Si (001) stack before and after thermal treatments at different RTA conditions. (b) XRD spectra of the stack following RTA treatments in flowing N_2. The peaks correspond to all of the expected reflections of crystalline $LaAlO_3$ and are indexed with pseudocubic indices.

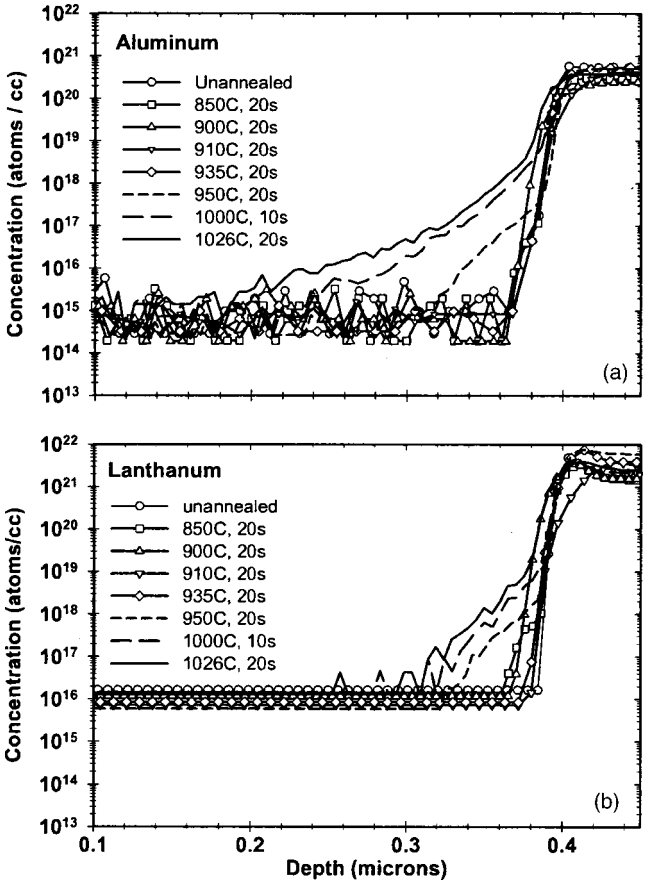

FIG. 2. Backside SIMS concentration vs depth profile for (a) Al and (b) La before and after RTA treatments of 100 Å Al_2O_3/1000 Å $LaAlO_3/p$-Si (001) stack in flowing N_2. The depth scale up to $\sim$0.4 μm corresponds to the Si substrate, followed by the 1000 Å thick $LaAlO_3$ film. SIMS results are for the same films described in Fig. 1.

incidence angle of 60°. A positive secondary ion count for La, Al, and Si was monitored as a function of depth. A stylus profilometer was utilized to determine the depth scale as a function of sputtering time. La and Al concentrations were determined from comparison with ion implanted standards.[14]

Figure 1(a) shows the surface morphology evolution of the $Al_2O_3/LaAlO_3/Si$ (001) stack evaluated by AFM as a function of the RTA conditions. After a 900 °C, 20 s, RTA in N_2, a change of the surface topography and a root-mean-square (rms) roughness (R_{rms}) of 4 Å is observed. At or above 1000 °C, 10 s RTA, a grain size of $\sim$0.5–3 μm diameter, and $R_{rms}\sim$40 Å is observed.[16]

The XRD 2θ scans of the stack before and after RTA in N_2 are shown in Fig. 1(b). Above 900 °C RTA, XRD peaks corresponding to polycrystalline $LaAlO_3$ are observed. These results are consistent with previous reports from $LaAlO_3$ films produced by atomic layer deposition,[17] pulsed laser deposition,[18] and chemical vapor deposition.[19] Since the Al_2O_3 capping layer is relatively thin compared to the $LaAlO_3$ film, no crystalline reflections of the capping layer are detected in the 2θ range analyzed.[16]

Figure 2 shows the back side SIMS concentration versus depth profile for $Al_2O_3/LaAlO_3/Si$ (001) stack before and after RTA in flowing N_2. The 1000 Å thick $LaAlO_3$ film essentially provides an infinite source of La and Al for diffusion into bulk Si.

Figure 2(a) shows the Al concentration in the silicon substrate as a function of depth at different annealing temperatures. Up to $\sim$935 °C, 20 s RTA in N_2, the penetration of Al into the Si substrate bulk is below detectible limits. However, after a 950 °C, 20 s, RTA in N_2, substantial Al penetration is observed. The concentration of Al is found to be $>10^{16}$ atoms/cm^3 up to a depth of $\sim$1000 Å from the Si/$LaAlO_3$ interface into the bulk Si (001) substrate after a 1000 °C, 10 s N_2 anneal, and would therefore be a concern for mobility degradation.[8] The penetration depth of Al is $\sim$1500 Å for the 1025 °C, 20 s, RTA. These results are generally consistent with previously reported Al interdiffusion from similar RTA treatments of Al_2O_3 films in contact with Si, and may lead to mobility degradation.[10] Additionally, our results indicate that the penetration depth is $\sim$400 Å deeper before the Al concentration in bulk silicon is reduced to $<10^{17}$ atoms/cc.

Figure 2(b) shows the corresponding La profile where significant penetration is observed at RTA temperatures $\geqslant$950 °C. The penetration of La was $\sim$400 Å for the highest-temperature RTA condition examined here of 1025 °C, 20 s. These results are consistent with the relative masses of the diffusing species, *viz*. Al diffusing deeper into the Si substrate compared to La, as well as recent reports on the silicidation of La upon thermal treatments.[20–22] We also note that Si diffusion into the $LaAlO_3$ cannot be ruled out in

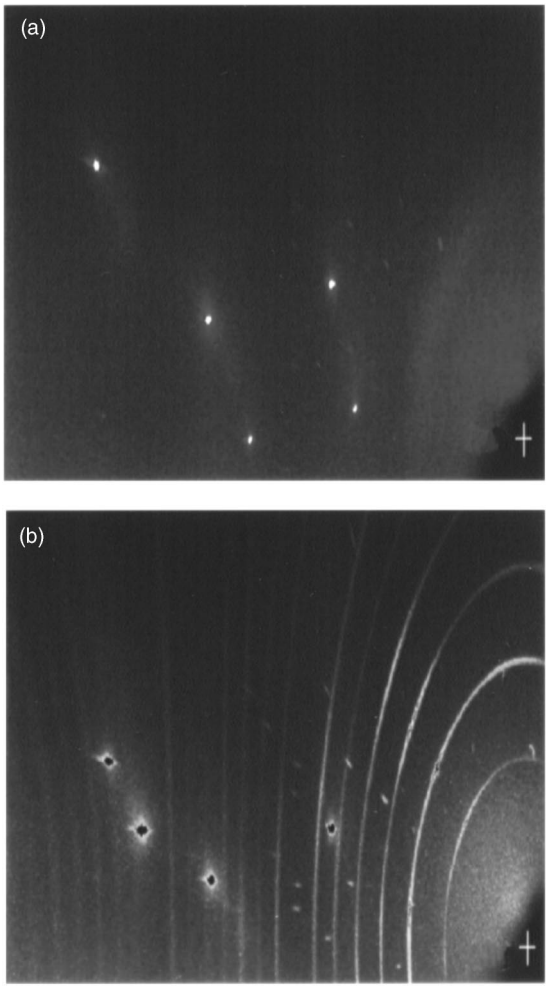

FIG. 3. 2D XRD image of $Al_2O_3/LaAlO_3/p$-Si (001) stack after; (a) 935 °C, 20 s and (b) 950 °C, 20 s anneal in N_2. Only diffraction spots associated with the Si substrate are evident in (a), while the characteristic rings are observed from crystallized $LaAlO_3$ in (b).

our back side SIMS studies reported here; such Si diffusion has been reported for oxidized La deposited on Si resulting in La-silicate formation,[21,22] and more recently for similarly annealed $LaAlO_3$ from XPS depth profiles[23] and nuclear reaction profiles.[24]

The La and Al penetration into the Si substrate at or below 935 °C, 20 s, RTA in N_2 is close to the limit of detection of the SIMS technique and appears to be consistent with a lack of detectible crystallization of $LaAlO_3$ from these thermal annealing budgets. This can be seen in the two-dimensional (2D) XRD images shown in Fig. 3 where evidence of $LaAlO_3$ crystallization is clear only after anneals at (or above) 950 °C, 20 s in N_2.

We find that for RTA anneals above 935 °C, 20 s, in N_2, crystallization is detected for the $Al_2O_3/LaAlO_3/Si$ (001) stack. We also find that La and Al metal diffusion into the Si substrate is observed for RTA treatment at or above 950 °C. Further studies are underway to examine the effects of annealing on metal gate electrode candidates on $LaAlO_3$.

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