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Thermal stability of lanthanum scandate dielectrics on Si(100)

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The authors have examined the thermal stability of amorphous, molecular beam deposited lanthanum scandate dielectric thin films on top of Si (100) after a 1000 °C, 10 s rapid thermal anneal. After the anneal, crystallization of $LaScO_3$ is observed. Excellent suppression of lanthanum and scandium diffusion into the substrate silicon is indicated by the back-side secondary ion mass spectrometry (SIMS) analyses. In contrast, front-side SIMS and high-resolution electron energy loss analyses of the amorphous $Si/LaScO_3/Si$ (100) stack indicated the outdiffusion of lanthanum and scandium into the silicon capping layer during the anneal. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2405418]

The traditional transistor-forming materials, silicon, silicon dioxide/oxynitride, and dual doped polysilicon, have been pushed to their fundamental material limits for complementary metal oxide semiconductor field effect transistor (C-MOSFET) technology. The continued aggressive scaling of C-MOSFETs would require the replacement of these constituents with a higher mobility channel layer, a higher-*k* gate dielectric, and a metal gate electrode.[1] For near term gate dielectric implementation in the year 2008,[1] hafnium silicates with optimized nitrogen content have been proposed. Group III or rare earth oxides and lanthanum based ternary oxides have been identified as candidates for long term implementation beyond the year 2011. Scandium (group III) based dielectrics such as scandium oxide[2] (Sc_2O_3) and rare earth scandates[3] ($GdScO_3$, $DyScO_3$, $LaScO_3$) have been studied as possible candidates for high-*k* dielectric applications due to a suitable optical band gap of 5–6 eV (Refs. 4 and 5) and a dielectric constant up to 35.[4,6] Rare earth scandates in amorphous form with a dielectric constant of ~22, energy band alignment close to those of HfO_2, good *C-V* behavior, low leakage levels comparable to HfO_2, and a predominantly amorphous phase even after a 1000 °C, 30 min annealing have been reported.[3,7]

The introduction of the high-*k* dielectric into the current C-MOSFET process flow poses significant integration challenges.[8] The high-*k* dielectric thin film should be thermally stable after a 1000 °C rapid thermal anneal (RTA), the highest temperature anneal performed in the standard C-MOSFET process flow.[9] Such high temperature anneals have been found to result in undesirable effects including amorphous to crystalline phase transformation of the dielectric, outdiffusion of metal atoms into the underlying channel, and concomitant carrier mobility degradation of the transistor.[8,10] In this letter, we have examined the thermal stability of amorphous $LaScO_3$ (*a*-LSO) dielectrics deposited on Si (100) by molecular beam deposition (MBD) after a 1000 °C RTA. Atomic force microscopy (AFM), electron energy loss spectroscopy (EELS), high-resolution transmission electron microscopy (HRTEM), and secondary ion mass spectrometry (SIMS) from the back side and the front side of the stack are utilized to evaluate the crystallinity, grain growth, and the outdiffusion of lanthanum and scandium into the silicon substrate and the capping layer. In contrast to previous studies of *a*-LSO films which were grown on ~1 nm of SiO_2 on Si,[7,11] the films in this study are free of interfacial SiO_2.[12]

$LaScO_3$ thin films were grown by molecular beam deposition in an EPI 930 molecular beam epitaxy chamber modified for the growth of oxides. The films were grown on one side of double-side polished *p*-type (001) Si (boron doped, $<1.4\times10^{15}$ boron/cm^3) that had been wet cleaned and hydrogen terminated with hydrofluoric acid (HF) before being loaded into the MBD growth chamber. The films were grown using elemental sources. Lanthanum (Aesar, 99.9% purity) and scandium (Aesar, 99.9% purity) were evaporated from tungsten crucibles in high temperature effusion cells. Lanthanum, scandium, and molecular oxygen (99.994% purity) at a background pressure of 5×10^{-8} Torr were codeposited at room temperature. The background partial pressure of oxygen of 5×10^{-8} Torr corresponds to the minimum pressure needed to fully oxidize lanthanum and scandium at these fluxes in the MBD chamber.[13] The lanthanum and scandium fluxes were each 2×10^{13} at./cm^2 s.

For the AFM analysis, an uncapped 5 nm thick $LaScO_3$ film on Si (100) was subjected to *ex situ* RTA at 1000 °C, 10 s in a flowing N_2 ambient. Contact mode AFM analysis was done before and after RTA to study the changes in surface morphology and grain growth in the $LaScO_3$ thin films.

Both conventional front-side SIMS and back-side SIMS were used to study the outdiffusion properties of the $LaScO_3$ dielectrics. Before SIMS analysis, air-exposed 10 nm thick $LaScO_3$ thin films were capped with ~100 nm thick layer of amorphous silicon (*a*-Si) by e-beam evaporation at room temperature. A capping layer prior to the back-side SIMS analysis was found to improve the depth resolution of the technique.[14] The *a*-Si/*a*-LSO/Si stack was then submitted to

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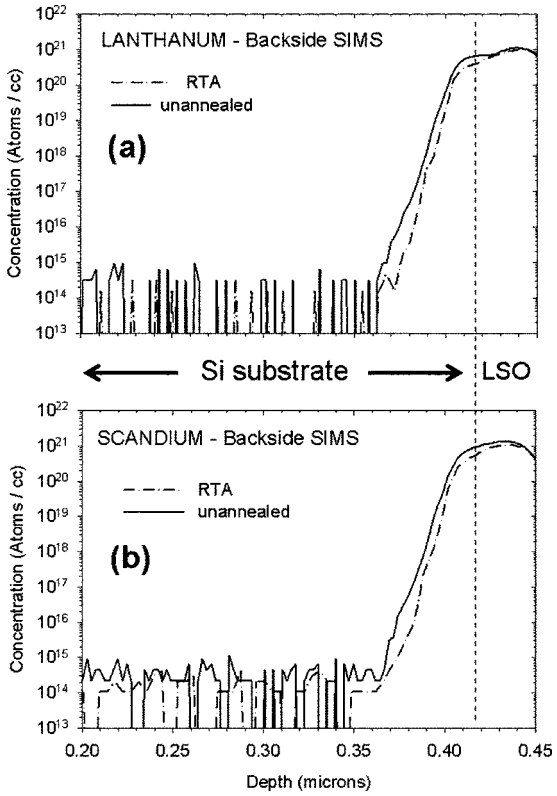

FIG. 1. Back-side SIMS analysis of 100 nm *a*-Si/10 nm LSO/Si (100) stack, before and after 1000 °C, 10 s N_2 RTA. The concentration vs depth profiles of lanthanum are shown in (a) and those of scandium in (b). The silicon substrate was polished to less than 0.5 μm thickness prior to SIMS profiling.

a RTA treatment at 1000 °C for 10 s in flowing N_2. An O_2^+ primary ion beam was used as the probe at incident energy of ~5.5 keV on a CAMECA IMS-6F. The beam current was varied between 30 and 120 nA in order to optimize detection limit and depth resolution and to minimize charging effects during the SIMS analysis. The sputtered lanthanum and scandium secondary ions were quantified by comparing to ion implanted calibration standards, and detection limits of $1\times10^{15}/\text{cm}^2$ were obtained for both La and Sc. For back-side SIMS, the substrate Si (100) was polished to less than 0.5 μm thickness and probed from the polished side for studying metal outdiffusion. Front-side SIMS was also used to study the outdiffusion of lanthanum and scandium into the overlying silicon capping layer. Due to ion-beam mixing (knock-on) effects associated with front-side SIMS, however, the lanthanum and scandium front-side diffusion profiles into the Si (100) substrate could be misleading.[15]

Surface morphology of an uncapped 5 nm thick $LaScO_3$ film on Si (100) was evaluated using AFM (not shown). In the case of as-deposited $LaScO_3$, no evidence of grains is seen and the root mean square roughness is ~2 Å. After the 1000 °C, 10 s N_2 RTA sub-0.2-μm grains were seen and the roughness increased to ~2.6 Å. These results are consistent with the x-ray diffraction analyses performed on uncapped ~30 nm $LaScO_3$ thin films (not shown), where the films remain amorphous up to 700 °C and crystallize above 800 °C anneals.[12] The amorphous to crystalline phase transformation could play a vital role in the overall performance of the transistor like mobility and bias temperature instability.[16]

Figure 1 shows the back-side SIMS analysis of the

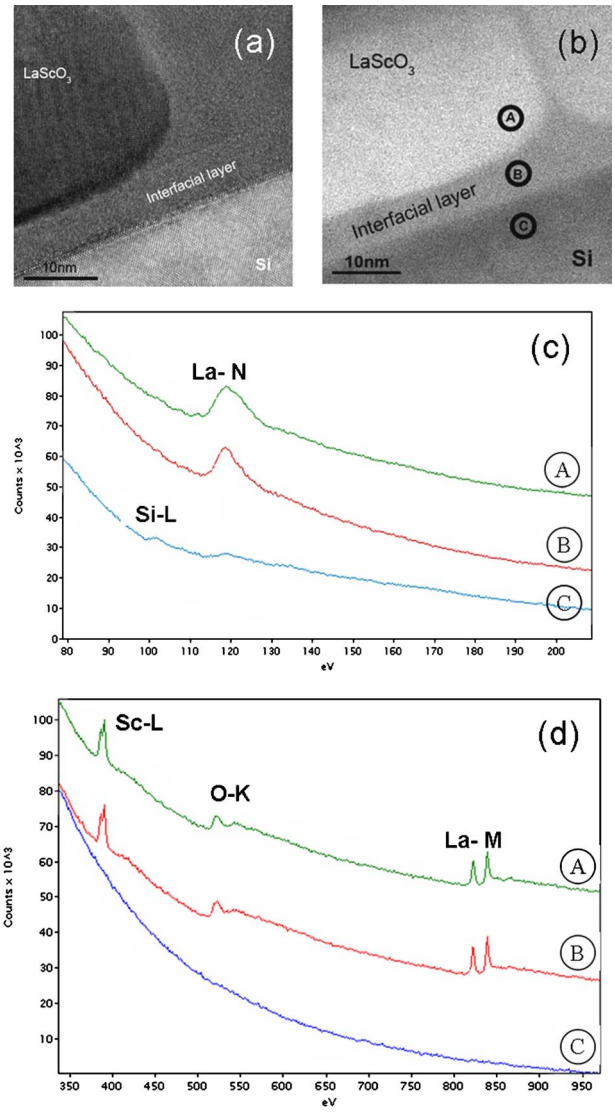

FIG. 2. (Color online) (a) HRTEM image of an ~30 nm LSO/Si (100) stack after 1000 °C, 10 s N_2 RTA, showing an amorphous interfacial layer. (b) High-resolution annular dark field (HRADF) STEM image taken from the area shown in (a). The labeled points designate the location of EELS measurements shown in (c) and (d). EELS spectra were vertically displaced for comparison.

100 nm *a*-Si/10 nm *a*-LSO/Si (100) stack, before and after the 1000 °C, 10 s N_2 RTA. Given the depth resolution of the SIMS analysis (~10 nm), the scandium and the lanthanum penetration into silicon substrate are below the detection limits. Similar rigorous annealing treatments have previously been found to result in substantial metal outdiffusion from both Al_2O_3 (Ref. 17) and $LaAlO_3$ (Ref. 10) high-*k* dielectrics into the substrate Si (001).

That previous work[10,17] suggests that the extent of metal outdiffusion from a high-*k* dielectric film appears to be correlated to (1) the amorphous to crystalline phase transformation in the high-*k* dielectric and (2) the presence of an interfacial layer between the high-*k* dielectric thin film and the silicon substrate. Even though evidence of crystallization is seen in the annealed $LaScO_3$ films here, a concomitant metal outdiffusion is not detected by the SIMS results, suggesting the presence of an interfacial "barrier" layer in the stacks after the high temperature RTA.[12] The HRTEM image of an (uncapped) annealed 30 nm LSO/Si (100) stack [Fig. 2(a)] shows the amorphous nature of the interfacial layer, and the

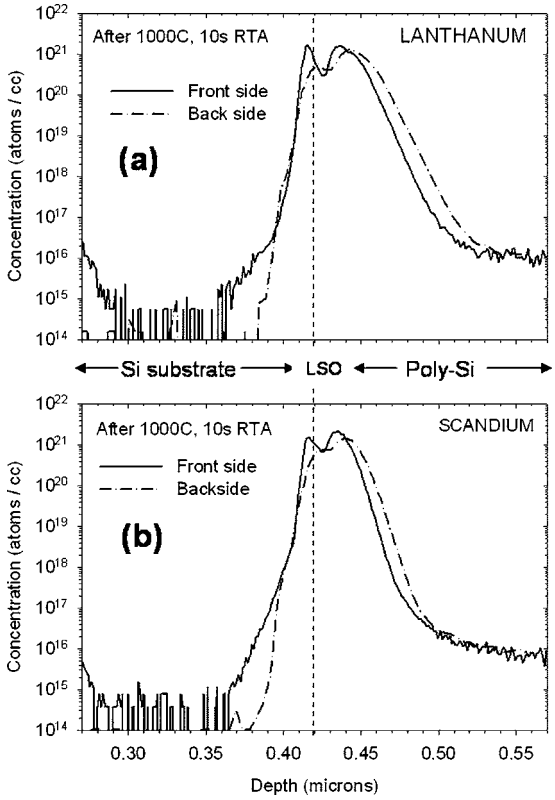

FIG. 3. Front-side SIMS analysis of 100 nm *a*-Si/10 nm LSO/Si (100) stack after the 1000 °C, 10 s N_2 RTA. For comparison of the depth resolution and the ion-beam mixing effects, the corresponding back-side SIMS profiles displayed in Fig. 2 are included.

associated high-resolution annular dark field (HRADF) scanning transmission electron microscopy (STEM) image [Fig. 2(b)] indicates weaker average atomic number contrast of the amorphous interfacial layer relative to the one of the overlying crystallized $LaScO_3$ film and appears to be consistent with a relatively lower density. High-resolution EELS [Fig. 2(c)] detected no silicon in the amorphous interfacial layer within detectible limits (<10 at. %), even with long spectra acquisition times and larger collection angles. EELS analysis [Figs. 2(c) and 2(d)] also indicated that both La and Sc contents in the interfacial layer are lower than in the crystallized region, which is consistent with the HRADF results.

Figure 3 shows the front-side SIMS profiles for a 100 nm *a*-Si/10 nm *a*-LSO/Si (100) stack after the RTA. For comparison, the corresponding back-side SIMS profiles are reproduced. The *a*-Si cap transforms to a polycrystalline capping layer upon the RTA anneal.

Both of the front-side SIMS profiles indicate outdiffusion of lanthanum and scandium into the overlying silicon capping layer, and the concentrations are $>10^{17}$ at./cm^2 up to a distance of ~50 nm into the silicon capping layer from the LSO/silicon cap interface. The outdiffusion of metal atoms from the high-*k* dielectric into the capping layer is important with respect to the gate stack stability.[8,9] Such outdiffusion could affect the desired work function of the metal gate electrode and cause unwanted reactions with the top electrode after the high temperature RTA.[1,8,9]

A comparison of the front-side SIMS profiles (Fig. 3) with that of the back-side SIMS profiles (Fig. 1) clearly highlights the ion-beam mixing (knock-on) artifact. While the back-side SIMS profiles do not show any change in the slope of the profiles in the Si (100) substrate, the front-side SIMS profiles for both lanthanum and scandium exhibit a shoulder with a concurrent increase in metal concentrations between 0.35 and 0.40 μm depth scales. These results highlight the merits of back-side SIMS over the conventional front-side SIMS technique in obtaining realistic concentration profiles of the metal/impurity species in bulk substrates.

In conclusion, we have examined the 1000 °C thermal stability of MBD $LaScO_3$ high-*k* dielectric on top of Si (100). After the 1000 °C, 10 s RTA, crystallization of uncapped $LaScO_3$ films is observed, consistent with previous reports.[12] The outdiffusion of lanthanum and scandium into the Si (100) substrate is completely suppressed, and this may be attributed to growth of amorphous metal-deficient interfacial layer as indicated by HRTEM and EELS measurements. The role of capping layers and the film morphology evolution with annealing remains to be established, however. We also observe the outdiffusion of lanthanum and scandium into the polycrystalline silicon capping layer. MOSFET performance evaluations are required to further qualify $LaScO_3$ as an alternate high-*k* gate dielectric material for the long term implementation.

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