Thermal stability of amorphous $LaScO_3$ films on silicon

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The thermal stability of amorphous $LaScO_3$ thin films deposited by molecular-beam deposition directly on (001) Si was investigated by high-resolution transmission electron microscopy (HRTEM), transmission infrared absorption spectroscopy (IRAS), and x-ray diffraction (XRD). IRAS indicated that the as-deposited films contained <0.1 Å of SiO_2 at the interface between $LaScO_3$ and silicon. XRD studies showed that the films remained amorphous after annealing in N_2 at 700 °C, although HRTEM showed structural order on an ~1 nm length scale even in the as-deposited films. By 800 °C, the $LaScO_3$ had started to crystallize and formed a ~5 nm thick Sc-deficient interlayer between it and silicon. © *2006 American Institute of Physics*.
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The scaling of the SiO_2 gate dielectric in metal-oxide-semiconductor field-effect transistors (MOSFETs) is approaching its fundamental limit, estimated to be 7 Å.[1] To transcend this limit, new gate dielectric materials must be developed to replace SiO_2. The first high-K MOSFETs to enter the market are anticipated[2] to utilize amorphous gate dielectrics with K ranging from 10 to 20 and will later be replaced with materials having K greater than 20. One of these higher K candidate materials is $LaScO_3$.[3–10] $LaScO_3$ is being investigated as a high-K gate dielectric due to its high K (ranging from 22 to 32),[3–10] high optical band gap (5.5 eV for amorphous films[7,11] and 5.7–5.8 eV for epitaxial films),[7,10,11] and high band offsets for amorphous films (2.0 eV for electrons and 2.5 eV for holes).[12,13] All of these properties meet the requirements for an alternative gate dielectric as suggested by ITRS.[2]

One of the areas that have not been investigated is the thermal stability of amorphous $LaScO_3$ thin films directly in contact with silicon. Determining the thermal stability is a critical parameter for the integration of the high-K gate dielectric into the MOSFET structure. The high-K gate dielectric must remain stable in contact with silicon in the annealing temperature range of ~900–1000 °C.[14–16]

In this letter, we investigate the growth and thermal stability of amorphous $LaScO_3$ thin films deposited directly on (001) Si by molecular-beam deposition (MBD). The films were characterized using high-resolution transmission electron microscopy (HRTEM), transmission infrared absorption spectroscopy (IRAS), and x-ray diffraction (XRD).

The ~30 nm thick[17] $LaScO_3$ thin films were grown by MBD in an EPI 930 molecular-beam epitaxy chamber modified for the growth of oxides.[18] The films were grown on one side of double-side polished p-type (001) Si (boron doped, $<1.4\times10^{15}$ B/cm^3) that had been wet cleaned and hydrogen terminated with hydrofluoric (HF) acid before being loaded into the MBD growth chamber. The films were grown using elemental sources. 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 our MBD chamber.[19] The lanthanum and scandium fluxes were each 2×10^{13} at./cm^2 s. The films were annealed in N_2 (99.999% purity) at a pressure of 1 atm by rapid thermal annealing (RTA) at temperatures between 700 and 1000 °C for 10 s. HRTEM images were acquired using a field-emission TEM

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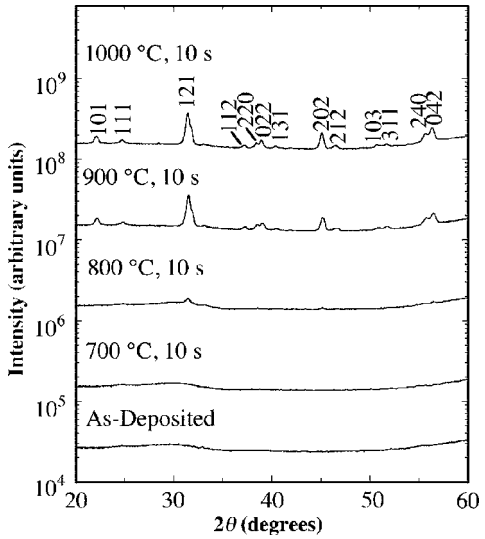

FIG. 1. XRD of 30 nm thick $LaScO_3$ thin films deposited on (001) Si after annealing in N_2 at 700, 800, 900, and 1000 °C for 10 s. The peaks correspond to crystalline $LaScO_3$, an orthorhombic perovskite.

(FEI Tecnai-F30U) operating at 300 kV, equipped with a UTWIN objective lens (Cs=0.52 mm). The nanochemistry of the annealed films was analyzed by high-resolution electron energy loss spectroscopy (EELS) in a JEOL 2100F TEM/scanning transmission electron microscopy (STEM) equipped with Gatan Enfina at 200 kV. Before the transmission IRAS measurements were completed, the backside of the wafer was H terminated (by local ~10%–20% HF etching), and the reference sample was a silicon wafer with both sides H terminated. This procedure made it possible to measure both the $LaScO_3$ phonons and any interfacial SiO_2. The IRAS was performed in transmission with a Nicolet 7600 spectrometer with 4 cm^{-1} resolution.[20] The XRD scans were acquired using a Bruker D5000 diffractometer equipped with a Highstar area detector. The XRD scans were collected using 1.2 kW and a 36 h collection time. Several 100 nm thick $LaScO_3$ thin films were analyzed by Rutherford backscattering spectrometry (RBS) (1.4 MeV He^+, 170° scattering angle). RBS indicated that the films are stoichiometric with a ratio of La:Sc=1±0.05 (not shown).

Figure 1 shows the XRD patterns of the $LaScO_3$/Si films as a function of annealing temperature. The $LaScO_3$ films remain amorphous (as measured by XRD) up to 700 °C, but start to crystallize to polycrystalline $LaScO_3$ by 800 °C. This result is in good agreement with Zhao *et al.*[6] who also reported a crystallization temperature of 800 °C for $LaScO_3$ deposited on SiO_2 on silicon. The peaks seen in the XRD spectrum correspond to the expected peaks for polycrystalline $LaScO_3$ with an orthorhombic perovskite structure with intensity ratios consistent with approximately randomly oriented $LaScO_3$ grains.[21] No secondary phases were detected by XRD for the annealing temperatures investigated.

Figure 2 shows cross-sectional HRTEM images as a function of annealing temperature. Figure 2(a) shows the abrupt interface between the as-deposited amorphous $LaScO_3$ thin film and (001) Si. Structural order on an ~1 nm length scale is evident. This structural order is also visible in the $LaScO_3$ film annealed at 800 °C for 10 s (Fig. 2(b)). This structural order was also detected by x-ray absorption spectroscopy (XAS) for films deposited and annealed under similar conditions.[22] Also visible in Fig. 2(b) is a ~5 nm thick

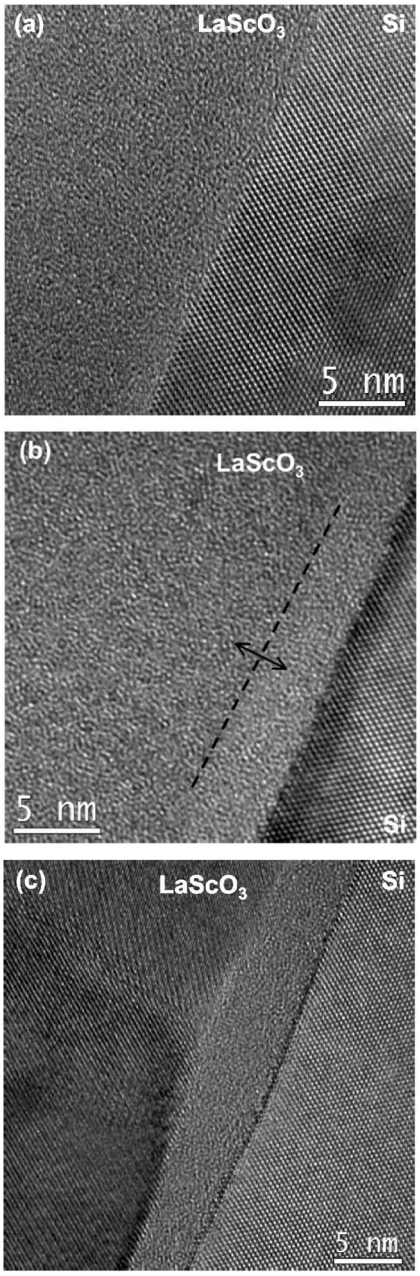

FIG. 2. Cross-sectional HRTEM images of the $LaScO_3$/Si interface from the same films studied by XRD in Fig. 1. The annealing conditions are (a) as deposited, (b) 800 °C for 10 s in N_2, and (c) 1000 °C for 10 s in N_2.

interlayer between the $LaScO_3$ thin film and silicon. Figure 3(c) shows the film annealed at 1000 °C for 10 s. By 1000 °C, large crystalline grains of $LaScO_3$ exist in the film, as does a ~5 nm thick amorphous interlayer. No silicon was detected in the interfacial amorphous layer within the EELS detection limit, indicating no or minimal reaction between the $LaScO_3$ thin film and the silicon substrate. The EELS analysis also revealed less Sc content in the amorphous interlayer than in the outer crystalline region, suggesting outdiffusion of Sc during the annealing. The presence of the Sc-deficient interlayer between crystalline grains as well as with the silicon substrate is surprising considering the stoichiometric and uniform composition of the deposited film, but the result was confirmed on multiple samples.

Figure 3 shows the transmission IRAS spectra as a function of annealing temperature. Upon annealing above 800 °C, the $LaScO_3$ longitudinal optical (LO) mode, origi-

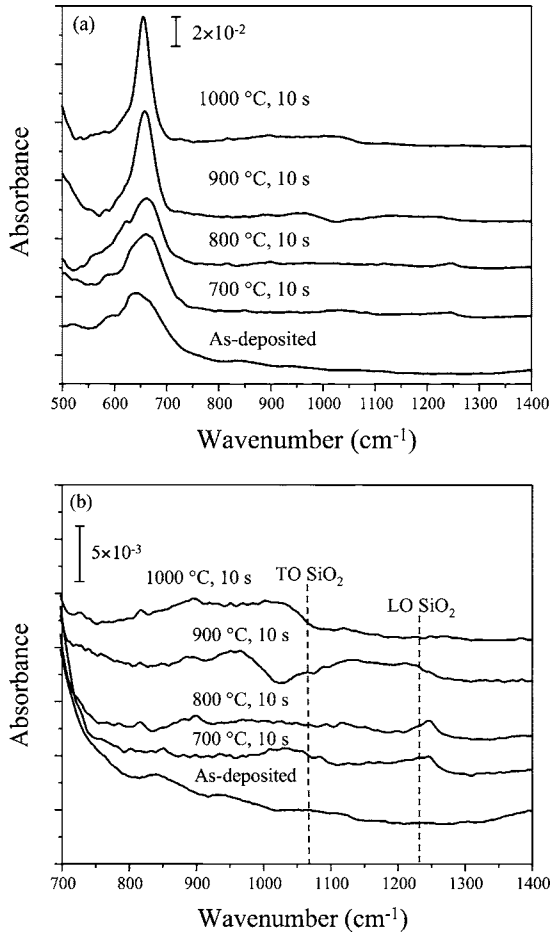

FIG. 3. Transmission infrared absorption spectra taken at 74° incidence angle from the same 30 nm thick $LaScO_3/Si$ (001) films studied in Figs. 1 and 2 as a function of annealing temperature. The absorbance intensity scale is indicated next to the vertical bar. All spectra are referenced to H-terminated (001) Si. (b) Shows a blow-up of the SiO_2 absorption region using a more sensitive absorbance scale.

nally very broad and located at $\sim 634\ cm^{-1}$, sharpens and shifts to $662\ cm^{-1}$ (shown in Fig. 3), reflecting the transition from the amorphous to the polycrystalline state as observed by XRD. The crystallinity observed at 800 °C by XRD is not easily observed in the IR spectrum, suggesting that crystallites do not represent a large fraction of the sample.

The $700-1400\ cm^{-1}$ region is shown at a higher magnification in Fig. 3(b). This is the region that would indicate if SiO_2 is present in the films. For typical SiO_2 films, both transverse optical (TO) and LO modes are observed to shift with film thickness: from ~ 1050 to $1062\ cm^{-1}$ for the TO modes and from 1220 to $1252\ cm^{-1}$ for the LO modes as the films increase from 6 to 32 Å.[23] The absence of any SiO_2 features for the as-deposited film suggests that <0.1 Å of SiO_2 is present initially. Upon annealing, a clear feature appears at $1249\ cm^{-1}$, which could correspond to the LO mode of an ~ 30 Å thick SiO_2 film. There is, however, no clear corresponding TO mode expected at $1060\ cm^{-1}$. While a broadband is apparent at $1030\ cm^{-1}$ for the sample annealed at 700 °C, it is absent in the sample annealed at 800 °C. Assuming that this band corresponds to SiO_2, its integrated area would correspond only to a 2 Å thick SiO_2 layer, not to a 30 Å thick layer as implied by the mode at $1249\ cm^{-1}$. Moreover, the $1249\ cm^{-1}$ feature is only present for the samples annealed at 700 and 800 °C, not at room temperature or when the film is crystallized. Therefore, while the origin of this mode is still under investigation, it cannot be assigned to SiO_2. It is most likely involved with a vibration of an oxygen atom, but not in a Si–O–Si configuration.

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