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Suppression of subcutaneous oxidation during the deposition of amorphous lanthanum aluminate on silicon

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Amorphous $LaAlO_3$ thin films have been deposited by molecular beam deposition directly on silicon without detectable oxidation of the underlying substrate. We have studied these abrupt interfaces by Auger electron spectroscopy, high-resolution transmission electron microscopy, medium-energy ion scattering, transmission infrared absorption spectroscopy, and x-ray photoelectron spectroscopy. Together these techniques indicate that the films are fully oxidized and have less than 0.2 Å of SiO_2 at the interface between the amorphous $LaAlO_3$ and silicon. These heterostructures are being investigated for alternative gate dielectric applications and provide an opportunity to control the interface between the silicon and the gate dielectric. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1759065]

The continued scaling of SiO_2 in metal-oxide-semiconductor field-effect transistors (MOSFETs) is approaching the fundamental thickness limit of 7 Å.[1] Below this thickness, SiO_2 is predicted to no longer be an effective gate insulator.[1] One way to circumvent this problem is to replace SiO_2 with a gate dielectric having a higher dielectric constant such as $LaAlO_3$.[2–4] Amorphous $LaAlO_3$ thin films on silicon have an estimated dielectric constant of 20–27[5–7] and an optical band gap of 6.2 ± 0.1.[8] The band offsets between amorphous $LaAlO_3$ and silicon were recently measured to be 1.8 ± 0.2 eV and 3.2 ± 0.1 eV for the conduction and valence bands, respectively.[8] It has also been shown that single crystalline $LaAlO_3$ is stable in contact with silicon under standard MOSFET processing conditions of 1026 °C for 20 s.[9] These known properties make $LaAlO_3$ a promising candidate material to replace SiO_2 in MOSFETs.

One of the major challenges[10] in producing an alternative gate dielectric is the ability to grow very thin alternative gate dielectrics on silicon without forming unwanted SiO_2 at the interface during deposition and without the need to cap the film *in situ* to prevent such SiO_2 formation upon air exposure after growth.[11–16] Only a few groups have reported the growth of gate dielectrics on silicon without substantial formation of interfacial SiO_2 without capping the film before exposure to air.[17–24] The thinnest of these films was 22 Å of amorphous Al_2O_3 on silicon.[18]

In this letter, we present the growth of amorphous thin films of $LaAlO_3$ directly on (001) Si by molecular beam deposition without the formation of SiO_2 at the interface. The films were deposited by codeposition of lanthanum, aluminum, and oxygen at the minimum partial pressure of oxygen required to fully oxidized the metal species. This minimum oxygen pressure was established by detailed oxidation experiments of the constituents of $LaAlO_3$, which are reported elsewhere.[25] Even after prolonged air exposure of films as thin[26] as 10 Å there was no formation of SiO_2 or SiO_x at the interface within the maximum sensitivity of our methods (~0.2 Å).

Amorphous $LaAlO_3$ films of thickness[26] equal to 10 and 40 Å were grown by molecular beam deposition (MBD) in an EPI 930 MBE chamber modified for the growth of oxides.[27] The films for transmission infrared absorption spectroscopy were grown on one side of double-side polished *p*-type (001) Si (boron doped, $<1.4\times10^{15}$ B/cm^{-3}). The films for the other measurements were grown on *p*-type (001) Si [boron doped $(3-6)\times10^{15}$ B/cm^{-3}] with one side polished. The native SiO_2 on the silicon wafer was thermally desorbed in ultrahigh vacuum at a substrate temperature of

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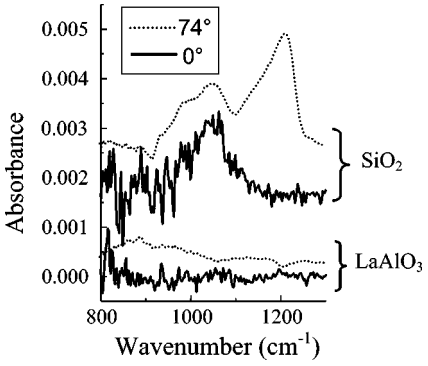

FIG. 1. Transmission infrared absorption spectra of ~4 Å SiO_2/Si, using H/Si as reference, and 10 Å amorphous $LaAlO_3$/Si, using the sample after removal of the $LaAlO_3$ film and H-terminating the surface for reference (keeping the back surface constant). Data are taken at normal incidence and 74° in both cases.

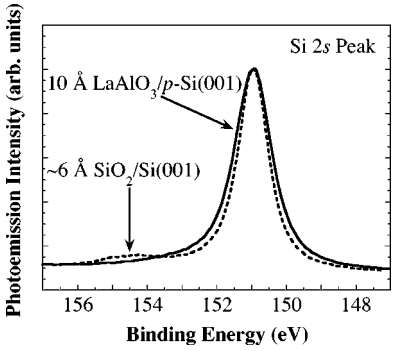

FIG. 2. High-energy resolution XPS core-level spectra of the Si 2*s* region for a 10-Å-thick amorphous $LaAlO_3$ film on (001) Si in comparison with ~6 Å of SiO_2 on (001) Si.

900 °C, as measured with a pyrometer. The films were grown using elemental sources. Lanthanum, aluminum, and molecular oxygen (99.994% purity) at a background pressure of 6×10^{-8} Torr, were codeposited with the substrate at a thermocouple temperature of ~100 °C. The lanthanum and aluminum fluxes were each 2×10^{13} atoms/cm^2 s. Several ~1000-Å-thick amorphous $LaAlO_3$ films were analyzed by Rutherford backscattering spectrometry (RBS) (1.4 MeV He+, 170° scattering angle). These measurements revealed that the films were stoichiometric with a 1:1 La:Al ratio to within ±0.05 mol %.

The samples were grown at Penn State and then shipped in air to the other laboratories for additional measurements. Transmission infrared absorption spectroscopy was performed at Rutgers with a Nicolet Magna interferometer operated at 4 cm^{-1} resolution.[28] The x-ray photoelectron spectroscopy (XPS) core level spectra were obtained at PNNL with a GammaData SES 200 analyzer using monochromatic Al $K\alpha$ x rays at a normal emission geometry. The Auger electron spectroscopy (AES) spectra were obtained at NCSU using a Phi model 11-010 Auger electron spectrometer operated with a beam diameter and current that would minimize sample damage. High-resolution transmission electron microscopy (HRTEM) images were acquired at UCSB using a 200 kV TEM (JEOL 2010). The medium-energy ion scattering (MEIS) analysis was completed at IBM with 100 keV protons channeling at normal incidence and the backscattered protons were detected with a toroidal electrostatic analyzer at a scattering angle of 110°.

Figure 1 compares the transmission infrared absorption spectra (taken at both 74° and 0° incidence angles) of a 10-Å-thick $LaAlO_3$ film deposited on silicon with the absorption spectra of a 4-Å-thick SiO_2 layer on silicon [made by wet chemical treatment of hydrogen-terminated (001) Si in 4:1 H_2SO_4:H_2O_2 at 80 °C for 10 min]. The transverse optical mode at ~1050 cm^{-1} and the longitudinal optical mode at ~1210 cm^{-1} are the signatures of the 4-Å-thick SiO_2 film. Clearly, there is no evidence of these modes in the absorption spectra of the $LaAlO_3$ film. However, difficulties related to the ill-defined back surface of the $LaAlO_3$ wafer limit the signal-to-noise ratio, placing an upper limit of 0.2 Å for a possible interfacial SiO_2 layer. To alleviate this problem, transmission infrared absorption spectra were also taken from 10-Å-thick amorphous $LaAlO_3$/Si grown in an identical way, except that the (001) Si wafer was wet cleaned and hydrogen-terminated with HF before being loaded into the MBD growth chamber. This precleaning dramatically improved the quality of the back side of the wafer, making it possible to get a much better baseline and signal-to-noise ratio for the infrared measurements. With this sample, we also see no evidence for interfacial SiO_2, and can now set an upper limit for interfacial SiO_2 of 0.07 Å.

Figure 2 shows the Si 2*s* peak measured by XPS from a 10-Å-thick film of amorphous $LaAlO_3$/Si along with that of ~6 Å of SiO_2/Si. There is clearly no peak at ~155 eV characteristic of SiO_2 in the $LaAlO_3$ spectrum, showing there is no detectable SiO_2 at the interface. We estimate the detection limit to be ~3 Å of SiO_2. The Si 2*p* was not analyzed because the La 4*d* peaks from the amorphous $LaAlO_3$ thin film overlap the position where photoemission from SiO_2 would be observed.

The same sample was then analyzed by AES. Figure 3 shows the AES spectrum, which shows no detectable SiO_2 at the interface between amorphous $LaAlO_3$ and silicon. There is a trace amount of chlorine present in the film. The chlorine is probably from the lanthanum source. Comparing this AES trace with studies of SiO_2 formation by remote plasma-assisted oxidation, we estimate the sensitivity of AES to be <3 Å of SiO_2 under a 10-Å-thick amorphous $LaAlO_3$ film.

A cross-sectional TEM specimen was made from the same 10 Å sample analyzed by XPS and AES. Figure 4 shows the HRTEM cross sectional image. No SiO_2 or SiO_x is evident at the interface between the $LaAlO_3$ film and the silicon and there are no contrast changes across the sample,

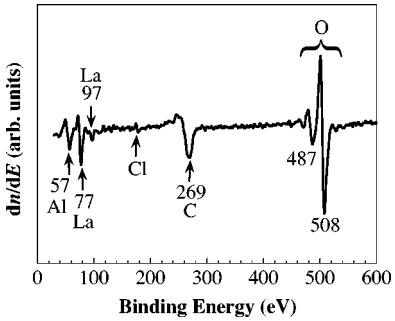

FIG. 3. AES spectra of a 10-Å-thick amorphous $LaAlO_3$ film on (001) Si showing no detectable SiO_2.

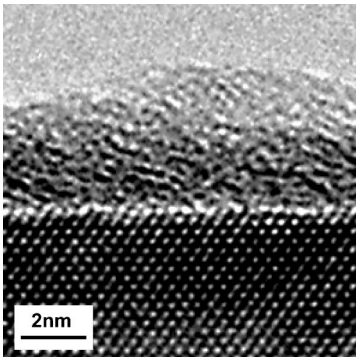

FIG. 4. Cross-sectional HRTEM image of 10 Å of amorphous $LaAlO_3$ on (001) Si showing no interfacial layer between the $LaAlO_3$ film and silicon.

which indicates that there are no gross compositional variations across the sample.

The MEIS spectrum of a 40-Å-thick $LaAlO_3$ film on silicon, deposited in the same way as the other amorphous $LaAlO_3/Si$ samples, shows well separated lanthanum, aluminum/silicon, and oxygen backscatter peaks (Fig. 5). When the lanthanum and oxygen peaks are plotted on the same depth scale after corrections for cross section and concentration (see the inset), we see that the two elements have nearly identical depth distributions, indicating the near total absence of interfacial SiO_2. Quantitative modeling confirmed this conclusion, to an upper limit of 2 Å of interfacial SiO_2. We note that the masses of aluminum and silicon are similar, making it difficult to discriminate between the two species in a buried layer using MEIS. Thus, although we can put tight constraints on the quantity of interfacial SiO_2, there is a reduced sensitivity to interfacial $LaSiO_x$ at the interface between the amorphous $LaAlO_3$ and Si. The ability to avoid subcutaneous oxidation provides an opportunity to controllably introduce SiO_2 at the interface and study its effect on the electrical properties of the dielectric stack as a function of the interfacial SiO_2 thickness.

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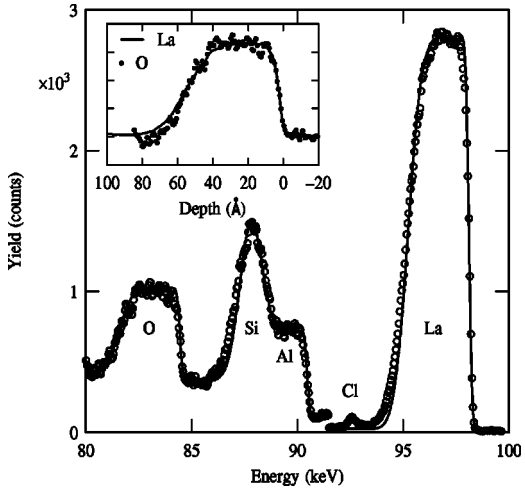

FIG. 5. MEIS energy spectrum of 40-Å-thick amorphous $LaAlO_3$ on (001) Si along with the model calculated assuming an SiO_2-free interface. Inset shows lanthanum and oxygen depth distributions.

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