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

L. F. Edge and D. G. Schlom[a)]
Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802

R. T. Brewer and Y. J. Chabal
Departments of Chemistry and Chemical Biology, Biomedical Engineering and Physics, Rutgers University, Piscataway, New Jersey 08854

J. R. Williams and S. A. Chambers
Fundamental Science Directorate, Pacific Northwest National Laboratory, Richland, Washington 99352

C. Hinkle and G. Lucovsky
Department of Physics, North Carolina State University, Raleigh, North Carolina 27695

Y. Yang and S. Stemmer
Materials Department, University of California, Santa Barbara, California 93106

M. Copel
IBM T. J. Watson Research Center, Yorktown Heights, New York 10598

B. Holländer and J. Schubert
Institut für Schichten und Grenzflächen ISG1-IT and Center of Nanoelectronic Systems for Information Technology, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

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, $< 1.4 \times 10^{15}$ B/cm^{-3}). The films for the other measurements were grown on p-type (001) Si [boron doped $(3–6) \times 10^{15}$ 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
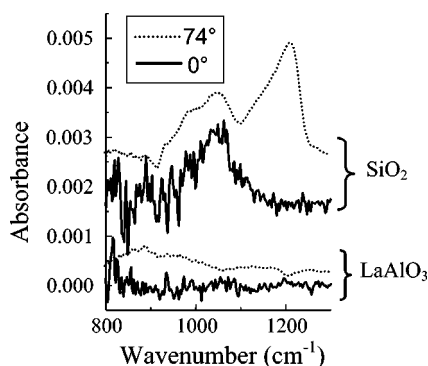
[a)]Electronic mail: schlom@ems.psu.edu

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$_2$SO$_4$:H$_2$O$_2$ 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
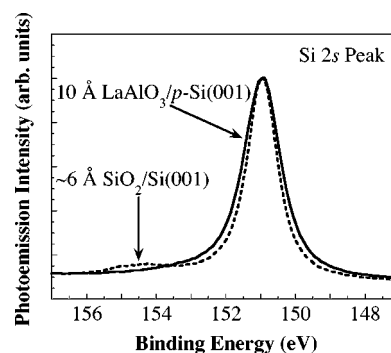
from 10-Å-thick amorphous LaAlO$_3$/Si grown in an identical way, except that the (001) Si wafer was wet cleaned and hydrogen-terminated with HF before being loaded into the MBD growth chamber. This precleaning dramatically improved the quality of the back side of the wafer, making it possible to get 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,
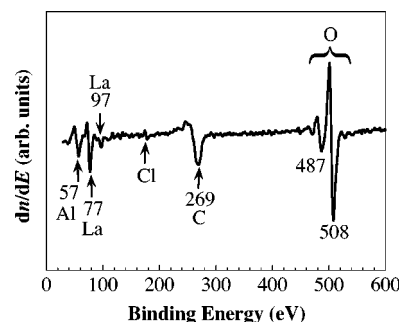

FIG. 3. AES spectra of a 10-Å-thick amorphous LaAlO$_3$ film on (001) Si showing no detectable SiO$_2$.
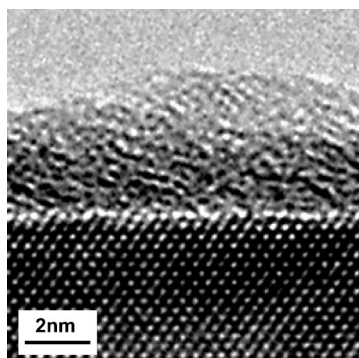
Appl. Phys. Lett., Vol. 84, No. 23, 7 June 2004

Edge *et al.* 4631

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.
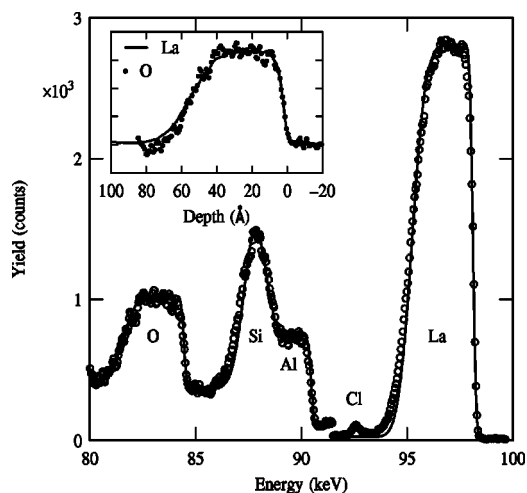
FIG. 5. MEIS energy spectrum of 40-Å-thick amorphous LaAlO$_3$ on (001) Si along with the model calculated assuming an SiO$_2$-free interface. Inset shows lanthanum and oxygen depth distributions.

[1] D. A. Muller, T. Sorsch, S. Moccio, F. H. Baumann, K. Evans-Lutterodt, and G. Timp, Nature (London) **399**, 758 (1999).
[2] C. A. Billman, P. H. Tan, K. J. Hubbard, and D. G. Schlom, in *Ultrathin SiO$_2$ and High-K Materials for ULSI Gate Dielectrics*, edited by H. R. Huff, C. A. Richter, M. L. Green, G. Lucovsky, and T. Hattori (Materials Research Society, Warrendale, PA, 1999), Vol. 567, pp. 409–414.
[3] A. I. Kingon, J.-P. Maria, and S. K. Streiffer, Nature (London) **406**, 1032 (2000).
[4] D. G. Schlom and J. H. Haeni, MRS Bull. **27**, 198 (2002).
[5] B.-E. Park and H. Ishiwara, Appl. Phys. Lett. **79**, 806 (2001).
[6] B.-E. Park and H. Ishiwara, Appl. Phys. Lett. **82**, 1197 (2003).
[7] X.-B. Lu, Z.-G. Liu, Y.-P. Wang, Y. Yang, X.-P. Wang, H.-W. Zhou, and B.-Y. Nguyen, J. Appl. Phys. **94**, 1229 (2003).
[8] L. F. Edge, D. G. Schlom, S. A. Chambers, E. Cicerrella, J. L. Freeouf, B. Holländer, and J. Schubert, Appl. Phys. Lett. **84**, 726 (2004).
[9] S. Stemmer and D. G. Schlom, in *Nano and Giga Challenges in Microelectronics*, edited by J. Greer, A. Korkin, and J. Labanowski (Elsevier, Amsterdam, 2003), pp. 129–150.
[10] *International Technology Roadmap for Semiconductors: 2003* (Semiconductor Industry Association, San Jose, CA, 2003).
[11] S. Guha, E. Cartier, M. A. Gribelyuk, N. A. Bojarczuk, and M. C. Copel, Appl. Phys. Lett. **77**, 2710 (2000).
[12] G. D. Wilk and R. M. Wallace, Appl. Phys. Lett. **76**, 112 (2000).
[13] J. Kwo, M. Hong, A. R. Kortan, K. L. Queeney, Y. J. Chabal, R. L. Opila, D. A. Muller, S. N. G. Chu, B. J. Sapjeta, T. S. Lay, J. P. Mannaerts, T. Boone, H. W. Krautter, J. J. Krajewski, A. M. Seregent, and J. M. Rosamilia, J. Appl. Phys. **89**, 3920 (2001).
[14] S. Stemmer, D. O. Klenov, Z. Chen, D. Niu, R. W. Ashcraft, and G. N. Parsons, Appl. Phys. Lett. **81**, 712 (2002).
[15] W. Tsai, R. J. Carter, H. Nohira, M. Caymax, T. Conard, V. Cosnier, S. DeGendt, M. Heyns, J. Petry, O. Richard, W. Vandervorst, E. Young, C. Zhao, J. Maes, M. Tuominen, W. H. Schulte, E. Garfunkel, and T. Gustafsson, Microelectron. Eng. **65**, 259 (2003).
[16] J. Kwo, M. Hong, B. Busch, D. A. Muller, Y. J. Chabal, A. R. Kortan, J. P. Mannaerts, B. Yang, P. Ye, H. Gossmann, A. M. Sergent, K. K. Ng, J. Bude, W. H. Schulte, E. Garfunkel, and T. Gustafsson, J. Cryst. Growth **251**, 645 (2003).
[17] M. Ritala, K. Kukli, A. Rahtu, P. I. Räisänen, M. Leskelä, T. Sajavaara, and J. Keinonen, Science **288**, 319 (2000).
[18] E. P. Gusev, M. Copel, E. Cartier, I. J. R. Baumvol, C. Krug, and M. A. Gribelyuk, Appl. Phys. Lett. **76**, 176 (2000).
[19] S. Guha, E. Cartier, N. A. Bojarczuk, J. Bruley, L. Gignac, and J. Karasinski, J. Appl. Phys. **90**, 512 (2001).
[20] S. J. Wang, C. K. Ong, S. Y. Xu, P. Chen, W. C. Tjiu, J. W. Chai, A. C. H. Huan, W. J. Yoo, J. S. Lim, W. Feng, and W. K. Choi, Appl. Phys. Lett. **78**, 1604 (2001).
[21] S. J. Wang and C. K. Ong, Appl. Phys. Lett. **80**, 2541 (2002).
[22] H. Li, X. Hu, Y. Wei, Z. Yu, X. Zhang, R. Droopad, A. A. Demkov, J. Edwards, K. Moore, W. Ooms, J. Kulik, and P. Fejes, J. Appl. Phys. **93**, 4521 (2003).
[23] J. Y. Dai, P. F. Lee, K. H. Wong, H. L. W. Chen, and C. L. Choy, J. Appl. Phys. **94**, 912 (2003).
[24] L. Yan, H. B. Lu, G. T. Tan, F. Chen, Y. L. Zhou, G. Z. Yang, W. Liu, and Z. H. Chen, Appl. Phys. A: Mater. Sci. Process. **77**, 721 (2003).
[25] L. F. Edge and D. G. Schlom (unpublished).
[26] The nominal film thicknesses given were calculated from the fluxes of the molecular beams (measured by a quartz crystal microbalance) assuming the amorphous LaAlO$_3$ films had the density of crystalline LaAlO$_3$. The areal density (atoms/cm^2) of lanthanum and aluminum in the films was confirmed by RBS. The thicknesses of the amorphous LaAlO$_3$ films were also measured by x-ray reflectivity and show 1.5–2 times the thicknesses determined assuming the density of crystalline LaAlO$_3$. These differences will be discussed elsewhere.
[27] J. Lettieri, J. H. Haeni, and D. G. Schlom, J. Vac. Sci. Technol. A **20**, 1332 (2002).
[28] B. B. Stefanov, A. G. Gurevich, M. K. Weldon, K. Raghavachari, and Y. J. Chabal, Phys. Rev. Lett. **81**, 3908 (1998).