# The role of the OH species in high-k/polycrystalline silicon gate electrode interface reactions

Theodosia Gougousi,[a] M. Jason Kelly, and Gregory N. Parsons
*Department of Chemical Engineering, North Carolina State University, Campus Box 7905, Raleigh, North Carolina 27695*

(Received 20 February 2002; accepted for publication 17 April 2002)

In this letter, reactions occurring at the interface between polycrystalline silicon (poly-Si) and $LaSiO_x$ high-dielectric-constant (high-k) insulating layers are characterized using x-ray photoelectron spectroscopy. Dielectrics were formed by sputter deposition of metal on silicon, followed by oxidation at 900 °C. Amorphous silicon was deposited on top by plasma-enhanced chemical vapor deposition from silane, followed by anneal at 650–1050 °C. We show that if the dielectric layer is exposed to sufficient water vapor before polysilicon deposition, annealing at 1050 °C for 10 s is sufficient to completely oxidize ~25 Å of deposited silicon. Minimal reaction is observed without deliberate water exposure. This demonstrates the importance of the dielectric surface condition in determining reactivity of high-k/polysilicon interfaces. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1485122]

Significant work is currently focused on high dielectric constant insulators as possible replacements to $SiO_2$ in metal oxide semiconductor devices.[1] Several high-k candidate materials have been proposed. However, there are still serious obstacles such as fixed charge, poor carrier mobility, and instability when in contact with silicon.[2,3] Several factors influence the Si-dielectric interface reactivity, and significant effort has been devoted to understanding it.[4–7] However, there is very little documented work on the reactions occurring in the upper interface, between the dielectric and the gate material. In this letter we offer some insight into the role $H_2O$ plays on the poly-Si/$LaSiO_x$ interface reactivity.

We prepared $LaSiO_x$ dielectrics by La metal sputtering on Si ⟨100⟩ substrates and *ex situ* high temperature furnace annealing in the presence of an oxidizing agent ($N_2O$) using the tools and procedures published previously.[8] Approximately 330 Å of La was deposited, resulting in thick (>500 Å) $LaSiO_x$ films. Prior to deposition, the substrates were cleaned in J.T. Baker Clean 100, rinsed in de-ionized (DI) water, and dipped in buffered oxide etch. Films were characterized using x-ray photoelectron spectroscopy (XPS) and infrared absorption spectroscopy. The XP spectra were obtained using a Riber LAS3000 equipped with a single pass cylindrical mirror (MAC2) analyzer and a Mg $K\alpha$ ($h\nu = 1253.6$ eV) nonmonochromatic x-ray source at a 90° take-off angle with 0.1 eV step size. Charge compensation was performed by setting the adventitious C 1$s$ peak to a binding energy of 285.0 eV. The Fourier transform infrared (IR) spectra were obtained in transmission mode using a Magna-IR System 750 from ThermoNicolet.

XPS analysis indicated that under our process conditions La mixed with Si very efficiently to produce material with predominantly La–O–Si bonding (i.e., lanthanum "silicate"). Additional experiments have shown that the hydroxyl content of the silicate films can be controlled by predeposition substrate cleaning or postdeposition atmospheric exposure. Figure 1 shows the IR absorption spectra for two such samples. The so-called "dry" sample was prepared by deposition of 330 Å of La and subsequent anneal at 900 °C for 10 min, and kept in the dry atmosphere of a desiccator to prevent $H_2O$ absorption. Such films were fairly insensitive to $H_2O$ uptake and had not absorbed IR detectable amounts of $H_2O$ even after two weeks of atmospheric exposure. However, identically prepared samples that were deposited on insufficiently cleaned substrates exhibited a more hydrophilic nature. The so-called "wet" sample in Fig. 1 was deposited on a surface rinsed in poor quality DI water and exposed to $H_2O$ vapor at room temperature for about 40 h after preparation. Its absorption IR spectrum exhibited a broad peak around 3500 $cm^{-1}$ associated with $H_2O$/OH presence[9] in the bulk of the film.

Thin layers of amorphous silicon were deposited by plasma-enhanced chemical vapor deposition at ~150 °C using silane/helium mixtures. These were 25 and 35 Å thick for the wet and dry samples, respectively. Deposition of $a$-Si layers on $c$-Si and $SiO_2$ is known to progress through the nucleation of Si islands, which, as growth proceeds, increase in size and number and eventually coalesce to form a uniform layer. Under the conditions used in this experiment,

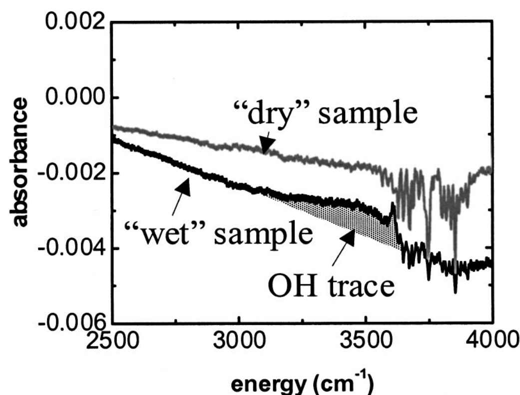


FIG. 1. IR absorption spectra for the wet and dry samples. The OH peak is clearly distinguishable in the so-called wet sample spectrum.

[a]Electronic mail: tgougou@unity.ncsu.edu

0003-6951/2002/80(23)/4419/3/$19.00  © 2002 American Institute of Physics
Downloaded 06 Jun 2002 to 152.1.53.120. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp

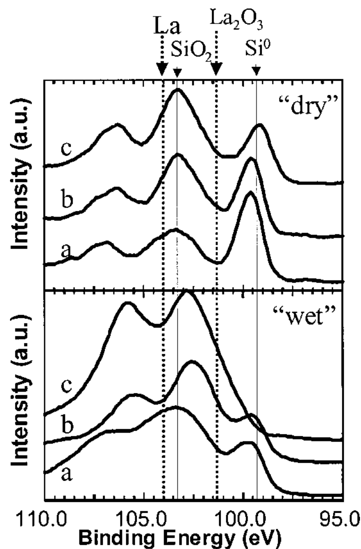


FIG. 2. Si $2p$ and La $4d$ XPS spectra for the dry and wet samples. Samples (a) are as deposited, (b) annealed at 650 °C for 30 s in Ar, and (c) annealed at 1050 °C for 10 s in Ar after deposition of the $a$-Si. For the wet sample the Si layer is completely consumed after anneal at 1050 °C.

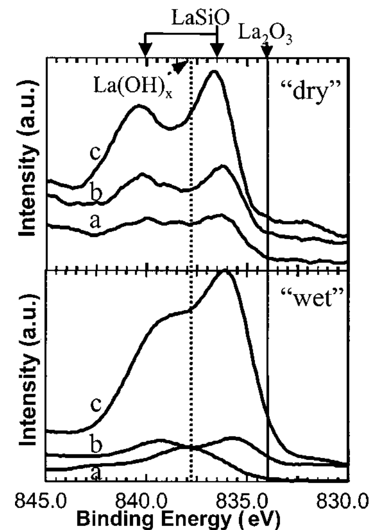


FIG. 3. La $3d$ XPS spectra for the dry and wet samples. Samples (a) are as deposited, (b) annealed at 650 °C for 30 s in Ar, and (c) annealed at 1050 °C for 10 s in Ar after deposition of the $a$-Si. For the as-deposited wet sample, the La bonding environment is different from the other samples. This is attributed to the presence of OH. Upon anneal, the OH is desorbed/replaced by Si and the XPS spectra become comparable to those for the dry sample.

atomic force microscopy analysis indicated that 25 Å of $a$-Si deposition is sufficient to achieve fully coalesced films on $c$-Si and $SiO_2$.[10] Slightly larger root mean square roughness was observed for Si deposited on the high k than for Si on $c$-Si and $SiO_2$, especially for the wet sample, which could be related to the underlying dielectric roughness or to incomplete coalescence of the silicon layer.

After deposition of the $a$-Si film, each wet and dry sample was divided into three parts, and each part was exposed to different thermal treatment. One was left as deposited, while the others were annealed at 650 °C for 30 s in Ar in a rapid thermal anneal (RTA) instrument. One of the samples was further annealed at 1050 °C for 10 s. Subsequently, XPS was used to probe the polySi/$LaSiO_x$ interface for each sample.

Figure 2 (top) shows typical XP spectra for the three samples originating from the dry sample while Fig. 2 (bottom) shows the corresponding spectra for the wet sample. This energy range includes contributions from the Si $2p$ and La $4d$ electrons making peak deconvolution difficult. However, the $Si^0$ peak at 99.3 eV, originating from the amorphous Si layer,[11] is readily distinguishable. Upon annealing the dry sample, the position of the $Si^0$ peak did not shift substantially, although its magnitude decreased somewhat consistently with a small amount of silicon oxidation. For the wet sample, anneal at 1050 °C resulted in the disappearance of the $Si^0$ peak, consistent with nearly complete consumption of the polysilicon layer.

A close look at the XPS data for the $LaSiO_x$ films gives insight into possible mechanisms for the observed silicon oxidation. For the spectra in the top part of Fig. 3, corresponding to the dry sample: (a) as deposited; (b) annealed at 650 °C; and (c) annealed at 1050 °C, the La $3d$ peaks shifted by about 0.5 eV to higher binding energy upon anneal, and are consistent with a mixed metal/silicon oxide (silicate) with fairly stable composition. The increase in the integrated intensity is consistent with an increase in the La concentration near the surface due to silicon or La diffusion. For the wet sample (Fig. 3, bottom) the La $3d$ spectrum shows a markedly different bonding environment for the as-deposited and annealed states. For the as-deposited film, the peaks were shifted by almost 2.5 eV to higher binding energy as compared to the dry sample, which was attributed to the presence of $La(OH)_x$. Upon anneal, the spectra have features qualitatively similar to the annealed dry sample.

In the O $1s$ XP spectra (not shown), annealing of the dry sample resulted in no significant shifts in the peak position. However, annealing the wet sample at 1050 °C resulted in significant shift ($\sim$1.5 eV to lower binding energy). It is important to note that for both samples the XPS data in Fig. 3 indicate that the dielectric did not phase separate into $La_2O_3$ and $SiO_2$ even when heated at 1050 °C for 10 s.

The IR and XPS data are consistent with the following possible explanation. Exposing $LaSiO_x$ films to significant water vapor results in OH absorption into the film bulk. When silicon is deposited on the dielectric, the incorporated OH enables reactions to proceed at the interface. Annealing the wet sample at 650 °C results in significant loss of H and OH species, producing a large number of unsatisfied bonds. Silicon atoms diffusing from the deposited silicon layer can then satisfy these bonds and be oxidized to form a mixed metal/silicon oxide. The reaction proceeds further upon anneal at 1050 °C, consistent with the distinct increase in La-related peak intensities. If the concentration of hydroxyl groups is sufficiently large and the thickness of the silicon is sufficiently thin, the oxidation reaction may completely oxidize the silicon layer (consistent with the Si $2p$ data shown for the wet sample in Fig. 2). In contrast, XPS data for the dry sample show no substantial change in the bonding structure at the interface. The small decrease in silicon thickness could be due to a reaction proceeding at a much-reduced rate. We must conclude that the presence of the OH groups substantially enhances reactivity at the interface between

Downloaded 06 Jun 2002 to 152.1.53.120. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp

polysilicon and La silicates. We are currently investigating similar effects in other high-k materials.

The authors would like to thank Scott Burnside, Tammi Schmit, and Justin Bennett for assistance with the XPS data, Rob Ashcraft and Dong Niu for assistance with the IR and RTA, and Kevin Bray for assistance with the surface roughness analysis. Financial support from SRC and NSF is gratefully acknowledged.

[1] S. I. Association, *The International Technology Roadmap for Semiconductors*, 1999 ed. (International SEMATECH, Austin, TX, 1999).
[2] G. D. Wilk, R. M. Wallace, and J. M. Anthony, J. Appl. Phys. **89**, 5243 (2001), and references therein.
[3] L. Manchanda, M. D. Morris, M. L. Green, R. B. van Dover, F. Clemens, T. W. Sorsch, P. J. Silverman, G. Wilk, B. Busch, and S. Aravamundham, Microelectron. Eng. **59**, 351 (2001).
[4] J. J. Chambers and G. N. Parsons, Appl. Phys. Lett. **77**, 2385 (2000).
[5] H. Ono and T. Katsumata, Appl. Phys. Lett. **78**, 1832 (2001).
[6] J. J. Chambers, B. W. Busch, W. H. Schulte, T. Gustafsson, E. Garfunkel, S. Wang, D. M. Maher, T. M. Klein, and G. N. Parsons, Appl. Surf. Sci. **181**, 87 (2001).
[7] P. D. Kirsch and J. G. Ekerdt, J. Vac. Sci. Technol. A **19**, 207 (2001).
[8] J. J. Chambers and G. N. Parsons, J. Appl. Phys. **90**, 918 (2001).
[9] A. Gupta and G. N. Parsons, J. Vac. Sci. Technol. B **18**, 1764 (2000).
[10] K. R. Bray and G. N. Parsons, Phys. Rev. B **65**, 035311/1 (2002).
[11] J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy* (Perkin-Elmer, Eden Prairie, MN, 1992).

Downloaded 06 Jun 2002 to 152.1.53.120. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp