# Effects of annealing on the electrical and interfacial properties of amorphous lanthanum scandate high-$K$ films prepared by molecular beam deposition

J. M. J. Lopes, U. Littmark, M. Roeckerath, St. Lenk, J. Schubert, S. Mantl, and A. Besmehn

Citation: Journal of Applied Physics **101**, 104109 (2007);
View online: https://doi.org/10.1063/1.2735396
View Table of Contents: http://aip.scitation.org/toc/jap/101/10
Published by the American Institute of Physics

# Effects of annealing on the electrical and interfacial properties of amorphous lanthanum scandate high-$\kappa$ films prepared by molecular beam deposition

J. M. J. Lopes,[a] U. Littmark, M. Roeckerath, St. Lenk, J. Schubert, and S. Mantl
*Institute for Bio- and Nanosystems (IBN1-IT) and Center of Nanoelectronic Systems for Information Technology, Research Center Jülich, D-52425 Jülich, Germany*

A. Besmehn
*Central Division of Analytical Chemistry (ZCH), Research Center Jülich, D-52425 Jülich, Germany*

(Received 2 February 2007; accepted 21 March 2007; published online 24 May 2007)

Amorphous $LaScO_3$ thin films were grown on (100) Si by molecular beam deposition and the effects of postdeposition thermal treatments on the film properties were studied after anneals in $O_2$ or inert Ar atmosphere at 400 or 650 °C. Rutherford backscattering spectrometry, transmission electron microscopy, x-ray diffraction, and x-ray photoelectron spectroscopy (XPS) were employed to investigate the samples. Capacitance-voltage and current-voltage measurements allowed their electrical characterization. Postdeposition annealing in $O_2$ reduces hysteresis, flatband voltage, and also leakage current density. In contrast, films treated in Ar ambient revealed a different behavior. The observations were associated with the interface evolution as studied by XPS, which verify that an $O_2$ atmosphere favors the formation of a $SiO_2$-rich interface between the film and the Si substrate, while a La-Sc-silicate-like compound predominates in this region after treating the samples in Ar. Additionally, postdeposition annealing results in an improvement of the dielectric constant up to 33, which is higher than that previously determined for $LaScO_3$ or other amorphous alternative high-$\kappa$ oxide films deposited by various techniques. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2735396]

## I. INTRODUCTION

The aggressive scaling of metal-oxide-semiconductor field effect transistors (MOSFETs) has led to an extensive research for materials that could replace the ultrathin (<1 nm) $SiO_2$-based films as a gate dielectric. According to the *International Technology Roadmap for Semiconductors*,[1] the implementation of a gate material with a dielectric constant $\kappa$ higher than 20 has to be realized in the near future in order to meet the requirements of low leakage and high performance.

Among several candidates, ternary rare-earth oxides are emerging with promising properties for such high-$\kappa$ applications. Results on amorphous thin films of scandates ($LaScO_3$, $DyScO_3$, $GdScO_3$) (Refs. 2–5) grown by different deposition techniques, have shown that this class of materials offers $\kappa$ values higher than 20, as well as large optical band gaps (>5 eV) and band offsets (2–2.5 eV) to silicon. Concerning the thermal stability of the amorphous phase after annealings at high temperatures, required for complementary MOS processing, x-ray diffraction studies show that $LaScO_3$ films start to crystallize at 800 °C,[2,6] while $DyScO_3$ and $GdScO_3$ films remain amorphous even after treatments at 1000 °C.[2,3] These crystallization onset temperatures are significantly higher than that observed for pure $HfO_2$ films (~500 °C),[7] and comparable to those observed for Hf-based dielectrics films such as $HfSiO_x$ and $HfAlO_x$, which retain their structure up to temperatures close to 1000 °C but have limited $\kappa$ values of less than 20.[8]

In addition to the structural stability of the high-$\kappa$ film, possible changes at the interface to silicon under thermal treatments are crucial. The growth of an interface with a lower-$\kappa$ value will lead to the reduction of the total capacitance in the MOS stack and may also result in intolerable leakage current densities, both unacceptable effects for future transistor applications. In this contribution, we investigated the effects of postdeposition anneals on the electrical and interfacial properties of amorphous $LaScO_3$ films on Si deposited by molecular beam deposition (MBD). Our study shows that the chemical composition of the interface depends on the annealing conditions and results in different capacitance and leakage current characteristics. Interestingly, an enhancement of the $\kappa$ value is also observed after thermal treatment of the $LaScO_3$ films.

## II. EXPERIMENTAL PROCEDURE

Amorphous $LaScO_3$ thin films were deposited by MBD using a conventional molecular-beam epitaxy chamber with a controlled admission of oxygen for growth of oxides. RCA cleaned *p*-type (100) Si wafers were used as substrates. Prior to the $LaScO_3$ deposition, the wafers were HF-dipped to remove the chemical oxide. The films were deposited at room temperature (RT) to minimize the formation of an interfacial layer during the growth. Lanthanum and scandium were codeposited from individual effusion cells in an $O_2$ back-

[a]Electronic mail: j.m.lopes@fz-juelich.de

 

ground atmosphere of $\sim 1 \times 10^{-6}$ mbar, which allows oxidation of the evaporated lanthanum and scandium atoms. The temperatures in the effusion cells were chosen to yield a deposition rate of 0.1 Å/s of $LaScO_3$ on the Si substrate. Layers with thicknesses varying from 3 to 56 nm were grown, as measured by x-ray reflectometry (XRR). Postdeposition thermal treatments were performed in Ar or $O_2$ atmosphere at 400 or 650 °C for 10 min. The samples were structurally investigated by means of Rutherford backscattering spectrometry (RBS), transmission electron microscopy (TEM), and x-ray diffraction (XRD). X-ray photoelectron spectroscopy (XPS) analysis of the thinnest films using a monochromatic Al $K_\alpha$ x-ray source allowed the investigation of the $LaScO_3$/Si interfacial region.

For the electrical characterization of the films, 70 nm thick Pt top contacts with an area of $245 \times 245$ $\mu m^2$ were deposited by electron beam evaporation through a shadow mask. Ohmic backside contacts were made by MBD deposition of 150 nm Al, followed by a forming gas anneal (90% $N_2$+10% $H_2$) at 450 °C for 10 min to improve the Al contact to silicon. Capacitance-voltage (*C-V*) and current-voltage (*I-V*) curves were measured using an impedance analyzer (HP 4192A) and a semiconductor parameter analyzer (HP 4155B), respectively.

## III. RESULTS AND DISCUSSION

The composition of as-deposited and annealed $LaScO_3$ films was analyzed by RBS and the film thicknesses further measured with XRR. Whereas RBS in principle determines a film thickness as the atomic coverage per unit area, the XRR analysis delivers a genuine physical thickness. The RBS results show a stoichiometry with a Sc:La ratio equal to $1 \pm 0.2$ independent of the thermal treatment. On the contrary, the oxygen content decreases with annealing temperature from $2 \pm 0.2$ oxygen atoms per metal atom for as-deposited layers to $1.5 \pm 0.1$ after applying high-temperature annealing. The latter number is consistent with the nominal crystalline value for $LaScO_3$. No significant influence of the annealing gas on this behavior was noticed. The gradual leakage of oxygen from the film during high-temperature thermal treatment naturally also shows up in the total film coverage as measured by RBS: as-deposited layers have a 20 at % oxygen over coverage as compared to annealed films.

Combining the RBS coverage with the XRR thicknesses, the atomic number density (atoms/$cm^3$) on the films can be calculated. Interestingly, this value does not change significantly after annealing, in spite of the oxygen loss. The absolute result is $6.1 \pm 0.4 \times 10^{22}$ atoms/$cm^3$, corresponding to $81 \pm 5$% of the nominal crystalline $LaScO_3$ density value. Regarding the microstructure, XRD patterns as well as TEM images reveal that the $LaScO_3$ films remain amorphous after the thermal treatments.

Figure 1 shows the *C-V* and *I-V* measurements for a ~4.5 nm thick $LaScO_3$ film on *p*-Si, as deposited at RT as well as for the films postannealed in Ar and $O_2$ at 650 °C for 10 min. Corresponding results for films annealed at 400 °C are not shown since they reveal a similar trend regarding the *C-V* and *I-V* characteristics. The *C-V* curves shown in Fig. 1(a) were recorded under forward and reverse bias sweeps at a frequency of 100 kHz and a hold time of 3 s for each measuring point. For the as-deposited film, a curve with large hysteresis (~235 mV), large negative flatband voltage of −0.75 V, and without saturation in the accumulation regime (up to −2.5 V) is measured. Postdeposition annealing improves the *C-V* behavior, with the best results obtained in $O_2$ atmosphere. In this case, a curve almost free of hysteresis (<25 mV) and with a flatband voltage of −0.1 V is observed. The negative flatband voltage and the hysteresis are due to oxide charges and interface traps, probably related to the existence of oxygen vacancies in the oxide and at the interface to Si.[9,10] Consequently, the $O_2$ annealing is more effective in the suppression of such deficiencies in comparison to the annealing in an inert Ar atmosphere. In addition to these effects, a reduction of the capacitance in the accumulation regime is also observed, which is related to the growth of a lower-$\kappa$ interfacial layer after annealing in Ar or $O_2$. Regarding frequency dispersion, *C-V* curves measured at frequencies between 10 and 500 kHz (not shown) on as-deposited as well as on annealed (Ar or $O_2$) films show only a limited variation of ~2% in the accumulation capacitance. At higher frequency (1 MHz), the dispersion is around 20% and 10% for the nonannealed and annealed films, respectively. Similar dispersion levels were also observed for other rare earth oxides ($GdScO_3$ and $DyScO_3$) grown by different techniques.[2,11] However, in contrast to results of Ref. 11, an inversion capacitance was not observed for *C-V* curves measured between 10 kHz and 1 MHz.

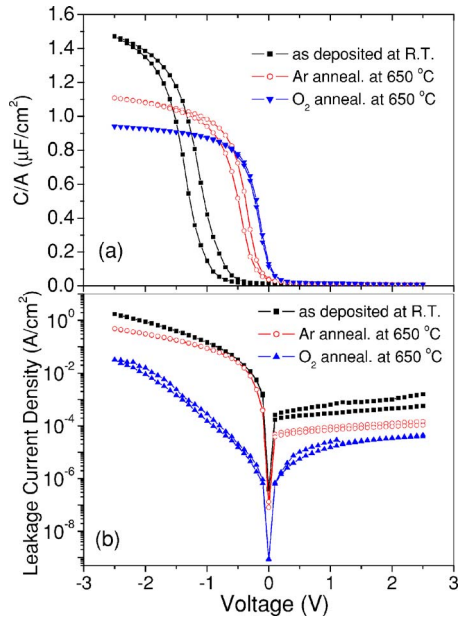


FIG. 1. (Color online) *C-V* curves at 100 kHz (a) and *I-V* curves (b), for Pt/$LaScO_3$/*p*-Si capacitor stacks fabricated with as-deposited, and annealed (Ar or $O_2$ ambient at 650 °C) $LaScO_3$/*p*-Si samples.

Figure 1(b) shows leakage current measurements. A hold time of 20 s was chosen for each measuring point in order to wait for all relaxation processes to decline. It can be seen that the leakage current density of the as-deposited film is high (0.15 A/$cm^2$ at −1 V) and does not decrease after treatment

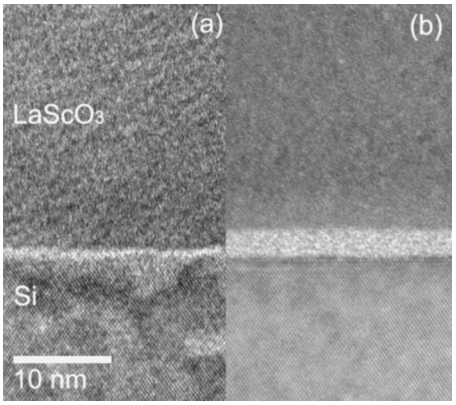


FIG. 2. Cross-sectional TEM images of ~25 nm thick $LaScO_3$ films on Si: as-deposited films (a), and (b) $O_2$-annealed films at 650 °C.

in an Ar ambient. In contrast, $O_2$ annealing reduces the leakage current density three orders of magnitude to $2 \times 10^{-4}$ A/cm$^2$ at the same voltage.

TEM observations confirm the formation of an interfacial layer after postdeposition annealing. Figure 2 displays this behavior for a ~25 nm thick $LaScO_3$ film. While the as-deposited film [Fig. 2(a)] is almost free of an interfacial layer (<1 nm), annealing at 650 °C in $O_2$ leads to the growth of an interface about 3 nm thick [Fig. 2(b)]. Interestingly, a similar evolution was observed for the Ar annealed samples, implying that the interface thickness does not depend significantly on the annealing atmosphere. Associating these results with the electrical properties [see Fig. 1(b)] indicates that the leakage current density is not simply related to the thickness of the interfacial layer seen by TEM, but rather related to the specific chemical composition developed during each thermal treatment.

Therefore, we employed detailed XPS investigations to elucidate the change of the interfacial composition due to thermal treatments in Ar or $O_2$ at 400 and 650 °C as shown in Fig. 3. Si 2*s* detailed spectra were obtained using a pass energy of 11.75 eV and a step size of 0.05 eV. Because of the interference of the La 4*d* with the Si 2*p* regions, it was not possible to measure the Si 2*p* region. The spectra were corrected for charging by shifting the metallic Si-Si peak from the substrate material to 150.7 eV. After subtraction of a Shirley background, Gauss-Lorentzian peaks were fitted to the spectra. The dashed lines found in the figure indicate three binding energies as obtained from reference samples (see Ref. 12): Si-Si (right), La-Sc-silicate (middle), and $SiO_2$ (left). Figure 3(a) shows the Si 2*s* region of the as-deposited $LaScO_3$ film. Two peaks are obvious for this sample. The low binding energy Si 2*s* peak corresponds to Si from the substrate. The left-hand peak has a higher binding energy (+1.9 eV) compared to the Si-Si peak, and is clearly lower than the $SiO_2$ reference value. In addition, this peak is slightly shifted to a lower binding energy compared to the reference silicate peak, corresponding to the bonding between the $LaScO_3$ and the Si substrate. In summary, no interfacial $SiO_2$ compound is found for this sample.

After annealing in Ar at 400 °C [Fig. 3(b)], two other peaks appear apart from the Si-Si bond. The peak located in the middle is more pronounced than that observed for the as-deposited sample and is related to La-Sc-silicate formation, although with less oxygen than the reference sample. The fittings also reveal the appearance of a peak close to the $SiO_2$ region that can be attributed to nonstoichiometric $SiO_x$ formed at the interface concomitantly with the silicate. After annealing at 650 °C [Fig. 3(c)], the intensity of both peaks increases in comparison to the 400 °C case, consistent with the growth of a thicker interfacial layer by annealing at the higher temperature. Importantly, it can be seen that in this case the La-Sc-silicate compound predominates at the interface. The peaks are also slightly shifted to higher binding energies, which may be related to a temperature-driven oxygen diffusion from the $LaScO_3$ matrix to the interfacial region.

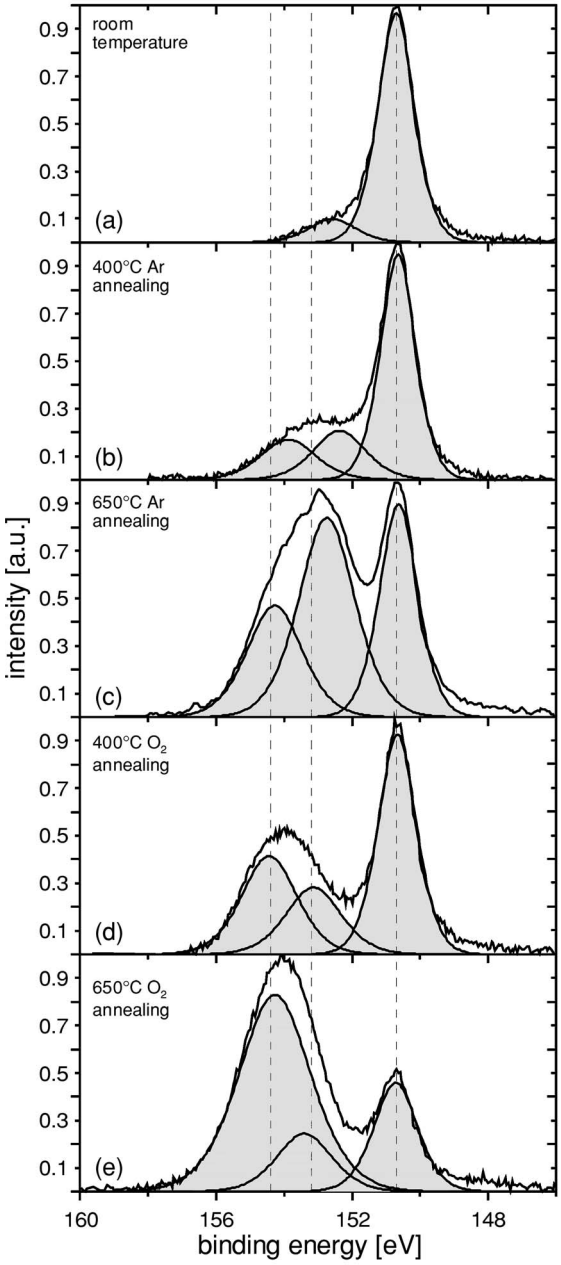


FIG. 3. Si 2*s* XPS spectra for as-deposited $LaScO_3$ films on Si (a), Ar-annealed [400 °C (b) and 650 °C (c)], and $O_2$-annealed [400 °C (d) and 650 °C (e)]. The dashed lines found in the figure indicate three binding energies as obtained from reference samples (see Ref. 12): Si-Si (right), La-Sc-silicate (middle), and $SiO_2$ (left).

The formation of oxygen-richer compounds occurs after $O_2$ annealing as displayed in Figs. 3(d) and 3(e). The peak positions show good agreement with the reference values for La-Sc-silicate and $SiO_2$, respectively. However, in contrast to the Ar annealing, the $SiO_2$ peaks show higher intensities for both annealing temperatures (400 °C and 650 °C). These results indicate that the $O_2$ atmosphere supplies oxygen atoms that diffuse through the film during the annealing, reaching the interfacial region and favoring the growth of stoichiometric $SiO_2$ instead of a silicate. Thus, we can infer from the comparison between these data and the *C-V* and *I-V* characteristics (see Fig. 1) that such a $SiO_2$-rich interface most probably yields to a lower defect charge density and larger band offsets than the $SiO_2$-free interface of the as-deposited film, as well as the silicate-like one observed after Ar annealing. Here, it is important to remark that the forming gas annealing, further used to improve the Al backside contact, does not result in any significant alteration in the compositional characteristics of the interface, and therefore, the correlation between XPS and electrical results is justified.

An improvement in the $\kappa$ value of the $LaScO_3$ films was also observed after thermal treatment. Figure 4 shows the capacitance equivalent thickness (CET) of the $LaScO_3$ films, as-deposited [Fig. 4(a)], postannealed in Ar or $O_2$ at 400 °C [Fig. 4(b)], and at 650 °C [Fig. 4(c)]. The CET values were calculated from the capacitance in the accumulation regime at −2 V for *C-V* curves measured at 100 kHz, and plotted as a function of the physical thickness determined by XRR measurements. In contrast to the equivalent oxide thickness (EOT), the CET does not take quantum-mechanical effects into account. The CETs were calculated using $\kappa=3.9$ for a pure $SiO_2$ interface. From the slope of the linear fit, it is possible to deduce the dielectric constant ($\kappa$) of the films excluding the contribution of a lower-$\kappa$ interfacial layer. While the as-deposited films have a $\kappa$ value of about 17 [Fig. 4(a)], the films postannealed at 400 °C and 650 °C yield $\kappa \sim 26$ and 30–33, respectively [Figs. 4(b) and 4(c)]. These latter values are higher than those previously determined for other amorphous alternative high-$\kappa$ oxide films (e.g., $HfO_2$) exhibiting $\kappa=22-23$.[2–4,13] The low dielectric constant deduced for the nonannealed films may be related to its higher oxygen content as compared to the annealed samples. In agreement with TEM observations, the intersection between the CET axis and the linear fit indicates the existence of an interfacial layer between the high-$\kappa$ film and the Si substrate. However, as a result of their different chemical compositions, we can expect slightly different $\kappa$ values for the interfacial layer of the Ar and $O_2$ annealed $LaScO_3$/Si samples.

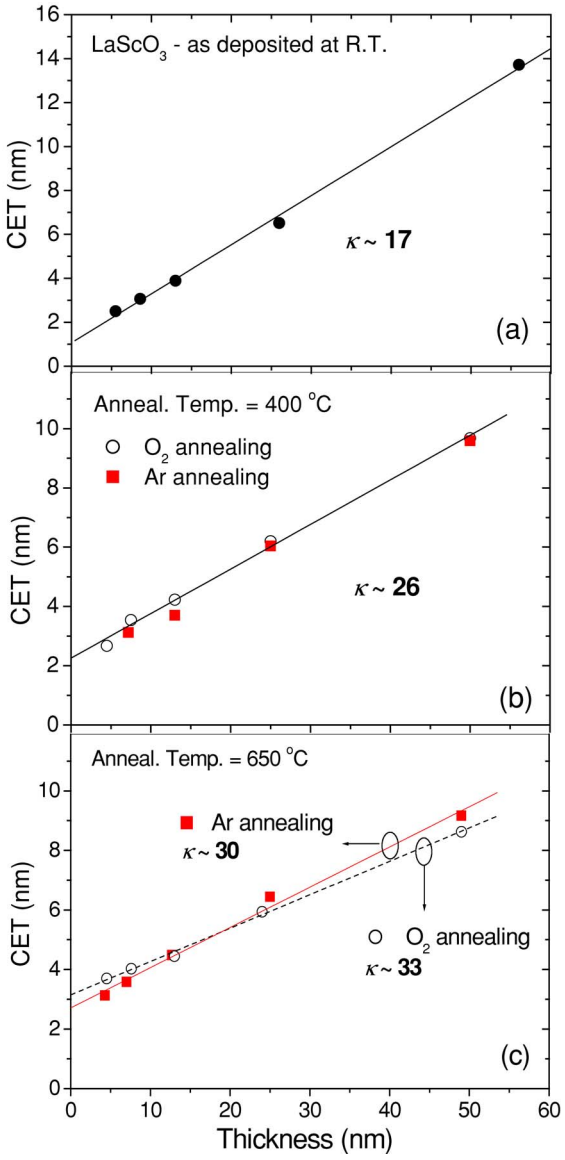


FIG. 4. (Color online) CET plotted as a function of the XRR film thickness for $LaScO_3$ films on Si: as-deposited films (a), Ar-, and $O_2$-annealed films at 400 °C (b), Ar-, and $O_2$-annealed films at 650 °C (c). The CETs were calculated using $\kappa=3.9$ assuming a pure $SiO_2$ interface.

## IV. SUMMARY

In summary, we have shown that proper postdeposition thermal treatments improve the *C-V* and *I-V* properties of amorphous $LaScO_3$ films deposited on Si(100) by MBD. In particular, $O_2$ annealing reduces hysteresis, flatband voltage, and also leakage current density. Such improvements could not be observed after Ar treatment at the same temperatures. Regarding frequency dispersion, *C-V* measurements at frequencies between 10 and 500 kHz show only a limited variation of ~2% in the accumulation capacitance for as-deposited and annealed (Ar or $O_2$) films. At 1 MHz, this value yielded to 20% and 10% for the nonannealed and annealed films, respectively. Inversion capacitance was not observed between 10 kHz and 1 MHz. XPS analysis provided evidence for the formation of La-Sc-silicate as the predominant compound at the interface after treating the films in Ar, while $O_2$ atmosphere induces the formation of interfacial $SiO_2$. Most strikingly it was observed that postdeposition annealing enhances the $\kappa$-value up to 33, surpassing clearly $\kappa$-values previously determined for $LaScO_3$ or other amorphous alternative high-$\kappa$ oxide films deposited by different techniques.[2–4] The improvement may be related to a readjustment of the oxygen content and structure in the amorphous matrix after thermal treatment, but further investigations are needed for clarification. The use of controlled postdeposition thermal treatments may also be most useful for tailoring and

improving the interface and electrical properties of other rare earth oxide films (e.g., $GdScO_3$, $DyScO_3$, $LaLuO_3$),[3,4,14] which allow for a higher thermal budget in CMOS processing. Currently, studies are in progress aiming at the synthesis of high-$\kappa$ $LaScO_3$ with an ultrathin interfacial layer.

## ACKNOWLEDGMENTS

One of the authors (J.M.J.L.) acknowledges the Alexander von Humboldt Foundation for a research fellowship.

[1] *International Technology Roadmap for Semiconductors: 2005* (Semiconductor Industry Association, San Jose, CA, 2005).
[2] C. Zhao, T. Witters, B. Brijs, H. Bender, O. Richard, M. Caymax, T. Heeg, J. Schubert, V. V. Afanas'ev, A. Stesmans, and D. G. Schlom, Appl. Phys. Lett. **86**, 132903 (2005).
[3] M. Wagner, T. Heeg, J. Schubert, St. Lenk, S. Mantl, C. Zhao, M. Caymax, and S. De Gent, Appl. Phys. Lett. **88**, 172901 (2006).
[4] K. H. Kim, D. B. Farmer, J. S. M. Lehn, P. V. Rao, and R. G. Gordon, Appl. Phys. Lett. **89**, 133512 (2006).
[5] V. V. Afanas'ev, A. Stesmans, C. Zhao, M. Caymax, T. Heeg, J. Schubert, Y. Jia, D. G. Schlom, and G. Lucovsky, Appl. Phys. Lett. **85**, 5917 (2004).
[6] L. F. Edge, D. G. Schlom, S. Rivillon, Y. J. Chabal, M. P. Agustin, S. Stemmer, T. Lee, M. J. Kim, H. S. Craft, J.-P. Maria, M. E. Hawley, B. Holländer, J. Schubert, and K. Eisenbeiser, Appl. Phys. Lett. **89**, 062902 (2006).
[7] K. Hyoungsub, P. C. McIntyre, and K. C. Saraswat, Appl. Phys. Lett. **82**, 106 (2003).
[8] J. Robertson, Rep. Prog. Phys. **69**, 327 (2006), and references cited therein.
[9] L. Miotti, K. P. Bastos, C. Driemeier, V. Edon, M. C. Hugon, B. Agius, and I. J. R. Baumvol, Appl. Phys. Lett. **87**, 022901 (2005).
[10] B.-E. Park and H. Ishiwara, Appl. Phys. Lett. **82**, 1197 (2003).
[11] S. Van Elshocht, P. Lehnen, B. Seitzinger, A. Abrutis, C. Adelman, B. Brijs, M. Caymax, T. Conard, S. De Gendt, A. Franquet, C. Lohe, M. Lukosious, A. Moussa, O. Richard, P. Williams, T. Witters, P. Zimmerman, and M. Heyns, J. Electrochem. Soc. **153**, F219 (2006).
[12] Reference samples: 4 nm thick $SiO_2$ thermally grown on Si; 50 nm La-Sc-silicate layer grown on Si by MBD (the composition is La:Sc:Si:O=1:1:1:5, as determined by RBS).
[13] Y.-S. Lin, R. Puthenkovilakam, and J. P. Chang, Appl. Phys. Lett. **81**, 2041 (2002).
[14] J. M. J. Lopes, M. Roeckerath, T. Heeg, E. Rije, J. Schubert, S. Mantl, V.V. Afanas'ev, S. Shanuilia, A. Stesmans, Y. Jia, and D. G. Schlom, Appl. Phys. Lett. **89**, 222902 (2006).