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Effects of post-deposition annealing in O\textsubscript{2} on the electrical characteristics of LaAlO\textsubscript{3} films on Si

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LaAlO\textsubscript{3} films were deposited on p-type Si(100) by sputtering from a LaAlO\textsubscript{3} target. \(C \times V\) characteristics were determined in nonannealed and O\textsubscript{2}-annealed capacitors having LaAlO\textsubscript{3} films as dielectric and RuO\textsubscript{2} as top electrode. Thermal annealing in O\textsubscript{2} atmosphere reduced flat band voltage to acceptable values for advanced Si-based devices. \(^{16}\text{O} \rightarrow ^{18}\text{O}\) isotopic substitution was characterized by Rutherford backscattering spectrometry and nuclear resonant reaction profiling. Chemical analysis of the films was accomplished by x-ray photoelectron spectroscopy. The electrical improvements observed after thermal annealing in O\textsubscript{2} were attributed to the incorporation of oxygen from the gas phase, possibly healing oxygen vacancies in the films and providing mobile oxygen to the interface. © 2005 American Institute of Physics. [DOI: 10.1063/1.1989447]

In order to meet the required power consumption and reliability constrains, several materials holding a dielectric constant higher than that of SiO\textsubscript{2} (\(\kappa = 3.9\)) have been proposed as replacement for silicon oxide/oxinitride for gate dielectrics in ultralarge scale integration (ULSI) metal-oxide-semiconductor field effect transistor (MOSFET) device technology.\textsuperscript{1-3}

Lanthanum oxide (La\textsubscript{2}O\textsubscript{3}) has been considered as a potential high-\(\kappa\) dielectric due to its high dielectric constant (\(\kappa = 30\)) as compared to SiO\textsubscript{2} and wide band gap (\(\sim 5\) eV).\textsuperscript{1,4} However, during thermal annealing of La\textsubscript{2}O\textsubscript{3} films on Si, most of the stability requirements are not fulfilled.\textsuperscript{5-7} As an alternative, lanthanum aluminate (LaAlO\textsubscript{3}) is expected to be more thermodynamically stable in contact with Si and may eventually meet thermal processing requirements, since the addition of Al raises the crystallization temperature and chemical stability of most high-\(\kappa\) materials studied so far.\textsuperscript{5,8-10} Since the LaAlO\textsubscript{3} bulk dielectric constant and band gap (\(\kappa_{\text{bulk}} = 20-25\), band gap = 5.6 eV) do not differ significantly from that of La\textsubscript{2}O\textsubscript{3},\textsuperscript{11} this material constitutes indeed a potential alternative for high-\(\kappa\) dielectric application. Although scarce, experimental investigation of LaAlO\textsubscript{3} films on Si has shown that, analogous to many other high-\(\kappa\) dielectrics on Si, post-deposition annealing (PDA) performed at various different temperatures is crucial to produce a gate stack with electrical characteristics within ULSI design specifications.\textsuperscript{11}

This letter reports on the effects of PDA in O\textsubscript{2} atmosphere on the electrical, physicochemical and atomic transport characteristics of LaAlO\textsubscript{3} films deposited on Si. Lanthanum aluminate films 5–40 nm thick, as determined by x-ray reflectometry, were sputter deposited from a LaAlO\textsubscript{3} ceramic target in a 5 × 10\textsuperscript{-2} mbar Ar plasma excited by a 13.56 MHz radio frequency, on HF last p-type Si(100) wafers etched in a buffered (20%) HF solution for \(\sim 30\) s. The distance between the substrate and target was fixed at 9 cm and the plasma power at 1 W/cm\textsuperscript{2}. The gas flow rate in the deposition chamber was set to 150 sccm. As it is shown below, within experimental uncertainties the as-deposited LaAlO\textsubscript{3} films had a La/Al ratio equal to 1. \textit{Ex situ} thermal annealing was performed in a Joule-effect heated furnace at 450 or 600 °C, for 30 min in 200 mbar of O\textsubscript{2}. The used O\textsubscript{2} gas was enriched to 97% in the \(^{18}\text{O}\) isotope, allowing to distinguish oxygen atoms previously existent in the films (mostly \(^{16}\text{O}\)) from those incorporated from the annealing atmosphere (\(^{18}\text{O}\)). Metal-oxide-semiconductor (MOS) capacitors were prepared by depositing on the as-deposited LaAlO\textsubscript{3} films conducting RuO\textsubscript{2} electrodes through a shadow mask by reactive sputtering of a Ru target in Ar/O\textsubscript{2} atmosphere. RuO\textsubscript{2} was chosen as the top electrode because a flat band voltage of nearly zero is expected for ideal RuO\textsubscript{2}/LaAlO\textsubscript{3}/p-Si capacitors.\textsuperscript{12} The electrodes top areas were 0.36 mm\textsuperscript{2}. An InGa backside contact was deposited in order to improve electrical contact.

Figure 1(a) shows the high frequency (1 MHz) \(C \times V\) characteristics of MOS capacitors built up with 5 and 40 nm thick, as-deposited LaAlO\textsubscript{3} dielectrics film on Si, as well as of capacitors made with LaAlO\textsubscript{3} films annealed in O\textsubscript{2} in the above described conditions. The simulated curve was calculated assuming 5.0 eV as the RuO\textsubscript{2} work function. Figure 1(a) shows that the flat band voltage shift measured for the capacitor bearing an as-deposited LaAlO\textsubscript{3} film displays a high, negative flat band voltage, as reported previously,\textsuperscript{5,11} indicating a high oxide charge density (>10\textsuperscript{13} cm\textsuperscript{-2}). The strong flat band voltage shift reduction after thermal annealing in O\textsubscript{2} suggests that the oxide charges are possibly related to oxygen deficiencies in the LaAlO\textsubscript{3} matrix.\textsuperscript{11} The hysteresis in the \(C \times V\) curves indicate the presence of interfacial electronic traps and/or mobile charge in the oxide. Annealing the 5 nm MOS capacitors in O\textsubscript{2} leads to a reduction of the capacitance at accumulation regime, possibly by growing a lower-\(\kappa\) interfacial layer. This lower-\(\kappa\) interfacial layer has a...
smaller influence on the capacitance at accumulation of the thicker 40 nm dielectric film as compared to the much thinner 5 nm thick dielectric. As a result, differences in the capacitance at accumulation are barely observed in the \(C \times V\) curves for capacitors made up with 40 nm thick LaAlO\(_3\) films. Figure 1(b) shows the capacitance equivalent to SiO\(_2\) thickness \(t_{eq}\) versus LaAlO\(_3\) thickness \(t_{LAO}\) for MOS capacitors after annealing in O\(_2\) atmosphere at 600 °C. From the slope of the linear fit to the data in Fig. 1(b) it is possible to calculate the dielectric constant of the deposited LaAlO\(_3\) films, excluding the effects of the lower-\(\kappa\) interfacial layer. The calculated dielectric constant was approximately 14, which is substantially lower than the dielectric constant of the bulk material. This may be attributed to the lower density of the LaAlO\(_3\) amorphous phase (5.5 g/cm\(^3\) for this work) as compared to its crystalline phase (6.5 g/cm\(^3\)). Assuming that the molecular polarizability (\(\alpha\)) is the same for both LaAlO\(_3\) crystalline and amorphous phases and considering the Clausius Mossotti equation, \(\kappa = \frac{4\pi n^2}{(\kappa + 2)}\), where \(n\) is the refractive index, \(\kappa\) is the dielectric constant, and \(\alpha\) is the molecular polarizability, a smaller increase of the molecular volume \(\Delta V\) compared to the atomic volume \(\Delta V_{atom}\) leads to a much larger reduction of the dielectric constant.

As-deposited and \(18\)O\(_2\)-annealed LaAlO\(_3\) films on Si. Typical errors in the areal densities are 3% for La, 10% for Al, and 5% for \(^{16}\)O and \(^{18}\)O. These densities are given in Table I. It also shows that thermal annealing in \(^{18}\)O\(_2\) promotes exchange of \(^{16}\)O atoms previously in the bulk material. This may be attributed to the lower density of the LaAlO\(_3\) amorphous phase (5.5 g/cm\(^3\) for this work) as compared to its crystalline phase (6.5 g/cm\(^3\)). Assuming that the molecular polarizability (\(\alpha\)) is the same for both LaAlO\(_3\) crystalline and amorphous phases and considering the Clausius Mossotti equation, \(\kappa = \frac{4\pi n^2}{(\kappa + 2)}\), a small increase of the molecular volume \(\Delta V_{mol}\), or in other words, a lower mass density effectively leads to a much larger reduction of the dielectric constant.

Extrapolating the \(t_{eq}\) versus \(t_{LAO}\) curve to \(t_{LAO} = 0\) gives a thickness of the lower-\(\kappa\) interfacial layer of about 4 nm. However, for the thicker LaAlO\(_3\) films the intermediate layer may be thinner than 4 nm.

La, \(^{16}\)O, and \(^{18}\)O areal densities of as-deposited and \(^{18}\)O\(_2\)-annealed, 13 nm thick LaAlO\(_3\) films were determined by Rutherford backscattering spectroscopy (RBS) of incident 1 MeV He\(^+\) ions parallel to the (100) axis of the underlying Si substrate (channeled RBS), detected in grazing direction. A typical channeled-RBS spectrum for an \(^{18}\)O\(_2\)-annealed sample is shown in Fig. 2(a). Since the Al signal overlaps the Si signal, the Al areal densities were independently determined by nuclear reaction analysis using the \(^{27}\)Al(\(p\), \(\gamma\))\(^{28}\)Si nuclear reaction at 992 keV. All areal densities are given in Table I. It also shows that thermal annealing in \(^{18}\)O\(_2\) promotes exchange of \(^{18}\)O atoms previously in the bulk material. Within experimental uncertainties, no net oxygen incorporation is observed after \(^{18}\)O\(_2\)-annealing at 450 °C of the 13 nm LaAlO\(_3\)/Si sample, while 600 °C annealing promotes both \(^{16}\)O–\(^{18}\)O exchange and net oxygen incorporation. In addition, no metal losses are observed.

Oxygen incorporation and interfacial layer formation during annealing were further inspected, by determining the \(^{18}\)O profiles in 13 nm LaAlO\(_3\)/Si samples. The \(^{18}\)O profiles were determined by narrow resonance nuclear reaction profiling (NRP) using the narrow (F\(=\)100 eV) resonance at 151 keV in the cross section curve of the \(^{18}\)O(\(p\), \(\alpha\))\(^{15}\)N nuclear reaction. Figure 2(b) shows the excitation curves of the \(^{18}\)O(\(p\), \(\alpha\))\(^{15}\)N nuclear reaction near the excitation at 151 keV.
keV for as-deposited and $^{18}$O$_2$-annealed LaAlO$_3$/Si samples. The corresponding $^{18}$O profiles are shown in the inset. Since the natural abundance of $^{18}$O is 0.2%, if the excitation curve for the as-deposited sample is multiplied by a factor of 500, the oxygen profile extracted from this enhanced excitation curve represents the total ($^{16}$O + $^{18}$O) oxygen profile in the as-deposited sample, thus indicating the energy position corresponding to oxygen at the original interface. The $^{18}$O profile for the 13 nm LaAlO$_3$/Si sample annealed at 450 °C reveals that oxygen from the gas phase was mainly incorporated in near surface and bulk regions, barely reaching the LaAlO$_3$/Si interface. On the other hand, during annealing at 600 °C the propagating $^{18}$O front reaches slightly beyond the original LaAlO$_3$/Si interface. If these findings are considered together with the data in Table I, one can say that during annealing at 450 °C most $^{18}$O is incorporated in the LaAlO$_3$ film in exchange for $^{16}$O previously existing in the oxide, while during annealing at 600 °C, $^{18}$O is partly incorporated in exchange for $^{16}$O and partly to form an $^{18}$O-containing interfacial layer. This enhanced oxygen incorporation in the interfacial region promoted by the annealing at 600 °C heals interfacial electronic traps, bringing as a result an enhancement in the reduction of the hysteresis and flat band voltage shift for the sample annealed at 600 °C as compared to the one annealed at 450 °C [see Fig. 1(a)].

Figure 3(a) shows the Al 2p and La 3d$^{5/2}$ photoelectron regions from the as-deposited and 13 nm thick LaAlO$_3$ films on Si, excited by a Mg Kα (1253.6 eV) x-ray source and measured at 30° take-off angle. The binding energy was referenced assigning to the C 1s component from adventitious carbon 284.6 eV. Since the samples were 13 nm thick, the interface and substrate regions do not contribute significantly to the x-ray photoelectron spectra (XPS). One notices from Fig. 3(a) that both thermal annealings shifted the Al 2p component toward lower binding energy, closer to the expected binding energy of Al 2p electrons in LaAlO$_3$. The small binding energy difference (less than 0.2 eV) of the Al 2p component for samples annealed at 450 and 600 °C may be attributed to uncertainties intrinsic to the charge referencing method. The La 3d$^{5/2}$ photoelectrons display two components, one at lower binding energy assigned to LaAlO$_3$ and a strong satellite component at higher binding energy. The latter can be assigned to photoemission followed by charge transfer from the valence band to the La 4f level which is characteristic of oxidized lanthanum species, such as La in LaAlO$_3$ or in La–(OH) which is probably formed in the surface region of the sample during air exposure. Thermal annealing at 450 °C in $^{18}$O$_2$ reduced the FWHM of both La 3d$^{5/2}$ components from typically 3.2 to 2.9 eV, while annealing at 600 °C promoted a further reduction of the FWHM to 2.7 eV. The FWHM reductions suggest reduction of the number of La configurations in the films, most probably because thermal annealing in oxygen atmosphere led to stoichiometry completion of the as-deposited, O-deficient LaAlO$_3$ compound film. Furthermore, it suggests also a reduction of differential charging after annealing.

In summary, postdeposition annealing of LaAlO$_3$ films on Si in O$_2$ atmosphere, at temperatures up to 600 °C, strongly reduces flat band voltage shift and C × V hysteresis of MOS capacitors. These improvements were associated with the reduction of oxide charge and interfacial density of electronic traps, owing to oxygen incorporation from the gas phase. Improvements brought about by 600 °C annealing as compared to 450 °C annealing can be a consequence of the fact that at 600 °C the propagating oxygen front reaches the interface, providing mobile oxygen to reduce oxygen deficiency in this particularly sensitive region.

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