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Low pressure chemical vapor deposition of oxide from SiH_4/O_2 : Chemistry and effects on electrical properties

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The low pressure chemical vapor deposition (CVD) process of SiO₂ from SiH₄ and O₂ has been analyzed. For deposition at pressures ranging from 10^{-3} to 3 Torr, with no carrier gas, the process is dominated by fast gas-phase reactions. *In situ* analytical techniques, such as mass spectrometry and high-resolution electron energy loss spectroscopy, indicate that hydroxyl groups are reaction products and are imbedded into the growing oxide at temperatures from 300 to 600 °C. Presence of these groups is detrimental to the electrical properties of metal-oxide-semiconductor (MOS) structures, e.g., by causing low-field breakdown and by increasing the interface state density. Low-pressure (SiH₄/O₂) oxides are thus principally not well suited for gate-oxide applications because of their underlying chemistry.

Silicon technology drives towards processing of highly controlled doping profiles with characteristic dimensions of the order of $\leq 0.1 \ \mu$ m. To maintain such profiles throughout the device fabrication process, high-temperature treatments have to be minimized. To replace thermal oxidation wherever possible is particularly important as oxidation enhanced diffusion unacceptably broadens the profiles of such ubiquitous dopants as boron. Often, plasma-enhanced chemical vapor deposition (PECVD) oxides are used in place of thermal oxides for critical applications, e.g., for SiGe-based devices. In this letter we explore the potential of a thermal CVD process: SiH₄/O₂ LPCVD to form SiO₂, known also as the low-temperature oxides (LTO) process.¹

In order to evaluate the potential of the LTO process, we want to establish a clear correlation between reaction chemistry and resulting oxide electrical characteristics. To establish this correlation requires a basic understanding of the underlying chemistry of the reaction. Using an integrated processing system, reaction products are analyzed using *in situ* monitoring, and product incorporation into the growing oxide film is verified with *in situ* surface analytical techniques. Electrical properties are measured after *ex situ* metallization, and trends in those properties are compared to reaction product incorporation into the film.

The growth experiments were carried out in a multichamber ultra-high vacuum (UHV) system² that integrates wafer precleaning, film growth, and surface analytical capabilities. Gas-phase reaction products were characterized using a differentially pumped mass spectrometer. Samples used were 3.25 in. diam Si(100) wafers, B-doped (1–2 Ω cm) for x-ray photoelectron spectroscopy (XPS) and high resolution electron energy loss spectroscopy (HREELS), or double-side-polished As-doped $(3 \times 10^{18} \text{ cm}^{-3})$ wafers for thermal desorption spectrometry (TDS). RCA cleaned³ wafers were loaded into a glove-box purged with ultrapure nitrogen (10 ppb purity) and the RCA oxide was etched with a HF gas-phase process. After cleaning, the samples were first loaded through a load-lock into a UHV sample-transfer chamber and then into the reactor. SiH_4/O_2 oxide CVD growth was carried

out in a lamp-heated quartz-wall rapid thermal UHV-CVD reactor described previously.^{4,5} Total pressure during growth was measured with a baratron gauge and controlled in the pressure range from 10^{-3} to 3 Torr using flow controllers. Pure O₂/SiH₄ mixtures with mixing ratios varying from 1.5:1 to 40:1 were used, with no carrier gas. Wafer temperature was controlled with an infrared pyrometer in the temperature range from 300 to 850 °C.

The incorporation of reaction products into the growing oxide film was verified with *in situ* surface analytical techniques such as HREELS, as well as *ex situ* with Fourier transform infrared spectroscopy (FTIR). Film morphology was analyzed in some cases with scanning electron microscopy (SEM). Film thickness and optical constants of the oxide films were determined with a stylus-based technique and ellipsometry. Stoichiometry of the oxide was measured using Rutherford backscattering spectrometry (RBS). Electrical evaluation was carried out on MOS structures with $\simeq 400$ Å thick films that were metallized *ex situ* with Al and, in some cases, were subsequently forming gas annealed (9:1 N₂:H₂ at 430 °C for 30 min).

Figure 1 shows a calculated difference mass-spectrum $[(SiH_4 + O_2)-SiH_4-O_2]$, for the LTO reaction. The individual mass spectra were taken *in situ* at $\simeq 10^{-3}$ Torr. The figure indicates the consumption (dashed line) and creation (solid line) of species during the reaction. SiH₄ and O₂ are consumed, as seen in the region around 16 and 28–33 atomic mass units (amu) which represent a typical mass spectrometer cracking pattern for SiH₄ and O₂. Reaction products are also readily identified as H₂O (16–18 amu) and SiOH_x-type molecules (45–48 amu).⁶ In addition, H₂ is also created during the reaction (not shown in the figure).⁷

At low pressures and temperature, the dominant reaction product is hydrogen (not shown in the figure), with only a small contribution due to H₂O and other species with hydroxyl groups ($\leq 10\%$). The amount of H₂O created during the reaction increases significantly with total pressure and wafer temperature. This indicates that different reaction channels contribute to the variety of reaction

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FIG. 1. Difference mass-spectrum indicating the consumption (dashed line) and creation (solid line) of species during the SiH₄/O₂ reaction. Plotted is the difference between the mass spectrum for the gas mixture (SiH₄ + O₂) *minus* two spectra for the pure gases at equivalent total pressure (10^{-3} Torr). Typical species are indicated: water (18 atomic mass units-amu), Si (28-SiH₄ cracked in the mass spectrometer), SiH₄ or O₂ (32), and SiOH (45).

products observed. In fact, especially at elevated pressure, the SiH_4/O_2 reaction details are expected to be extremely complicated. However, for the sake of the argument to be made in this letter, it is only important to notice that under all conditions analyzed here, we always observed the creation of gas-phase H₂O and hydroxyl-group containing species in non-negligible amounts.

Oxide deposition rates for an O_2/SiH_4 mixing ratio of 15 are shown in Fig. 2. The deposition rates exhibit a very steep total pressure dependence of the order of P_{tot}^4 , giving further support to the notion of very complicated reaction pathways. In the high-pressure/high-deposition-rate range of the figure dust (i.e., SiOH_x particles) deposition occurs on the wafer and in the reactor (known as snow formation). The high reaction order, the formation of dust particles, and the observation of gas-phase reaction products at low wafer temperatures all indicate that the SiH₄/O₂ reaction occurs predominantly in the gas phase under the conditions studied.⁸

The deposition regime studied here approaches the pressure regime in which SiH₄/O₂ mixtures undergo spontaneous, explosive reaction.⁹ That reaction, although possibly initiated at a surface, is another clear indication for the predominantly gas-phase nature of the reaction. This is in contrast to atmospheric deposition conditions, where a surface limited growth is postulated.^{10,11} Although our experiments cannot unambiguously rule out a minor contribution of surface-limited film growth, we assume that growth is dominated by gas-phase reactions. Film growth under low-pressure LTO conditions is thus based on the deposition of precursor molecules such as the SiOH_x-species detected in the gas phase.



FIG. 2. Oxide deposition rates as a function of the total pressure in the reaction during SiH₄/O₂ reaction (no carrier gas). Wafer temperature was varied from $\simeq 200$ to 850 °C; the lines are least-square fits through the data at a given temperature. The dashed line indicates the region above which strong gas-phase nucleation creates dust deposits in the reactor.

Deposited oxides have been analyzed in situ with HREELS and ex situ with FTIR and RBS. The oxides were found to be stoichiometric SiO₂. However, all deposited oxides analyzed contain significant amounts of hydroxyl groups (OH species).¹² At low deposition temperature ($\simeq 300$ °C), LTO films were seen to exhibit even imbedded molecular water. The presence of hydroxyl groups or water in the oxide matrix causes the oxide density to be low compared to thermal oxides, giving rise, e.g., to high etch rates in buffered HF.¹² Clear shifts in oxide phonon frequencies towards lower energy, as evidenced by HREELS and FTIR, indicate a softening of the oxide matrix. Similar results have been published recently for PECVD oxides.¹³ The amount of imbedded hydroxyl groups has been evaluated using TDS. The desorption spectra from 200 Å thick oxides show a broad maximum in the water desorption rate between 450 and 700 °C. This is consistent with Fig. 3, which shows that significant amounts of H₂O are released from the oxide, even when deposited at temperatures approaching 600 °C.

The concentrations of hydroxyl groups in the oxide also strongly depend on the oxide deposition rate. Highest concentrations were found for the fastest depositions. We postulate then that the gas-phase hydroxyl-group-containing precursor molecules contribute to the oxide deposition process. Hydroxyl-group removal then occurs from the surface and is thus limited by the wafer temperature and hampered by high deposition rates which bury such groups in the oxide.

Electrical measurements performed after metallization show that low-temperature oxides (\leq 450 °C) exhibit high leakage currents, low-field breakdown, and strong carrier trapping in the oxide. Interface state densities were high, as



FIG. 3. Water content of 200 Å thick LTO films as determined by thermal desorption spectrometry (TDS). The temperature on the horizontal axis indicates the oxide deposition temperature. The curve shows the integrated amount of molecular water (18 amu) desorbing in the temperature range from 300 to 750 $^{\circ}$ C.

could be judged from the C-V plots, but impossible to determine accurately because of the superimposed leakage currents. After forming gas anneal the current-voltage characteristics have improved sufficiently to permit a more



FIG. 4. Electrical evaluation of Al-gate MOS capacitors fabricated on 400 Å LTO films deposited on RCA-cleaned Si(100) surfaces. The figure plots (bottom) current voltage curves and (top) high-frequency/ quasistatic capacitance-voltage curves for several characteristic samples: LTO grown at 355 °C and 575 °C for the C/V plot, and 355, 380, 450, and 575 °C for the I/V plot. All samples were forming gas annealed before the measurement.

detailed analysis. The quality of the current-voltage characteristics, the oxide breakdown field, the interface state density, and oxide fixed charge show a clear improvement for oxides deposited at higher temperatures, as seen in Fig. 4. Oxides deposited at temperatures above 450 °C have properties comparable to those of good PECVD oxides, such as a breakdown field of $\simeq 10-12$ MV/cm, and midgap interface state densities of $\simeq 2-3 \times 10^{10}$ cm⁻² eV⁻¹. However, the fixed charge in these oxides is still significantly higher than in thermal oxides $(3-6\times 10^{11}$ cm⁻²). The correlation of deposition temperature with the quality of the electrical parameters, and the effectiveness of the forming gas anneal demonstrate clearly the impact of hydroxyl-groups on the electrical parameters of the oxide.

We have demonstrated in this letter that the low-pressure SiH_4/O_2 reaction is predominantly a fast gas-phase reaction with reaction products that contain hydroxyl groups. Incorporation of such groups into the oxide was demonstrated to lead to low-quality electrical properties. The low-pressure, low-temperature thermal CVD reaction of SiH₄ and O₂ is thus *fundamentally* not well suited for gate-oxide applications because of its underlying chemistry, which leads to incorporation of hydroxyl species in the film. This limitation may be overcome in PECVD processes, where selective excitation of certain species allows to change/choose reaction pathways to a certain degree.¹⁴ However, also thermal LTO films can be improved if the restriction of low-temperature processing is lifted. Postoxidation in a rapid thermal oxidation step will eliminate most bulk hydroxyl-groups and grow a new, thermal gateoxide/silicon interface. Lastly, LTO quality is sensitive to surface preparation prior to deposition, because the oxide is deposited, not grown into the substrate like a thermal oxide or, to a certain degree, a PECVD oxide.¹⁵

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