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## Sequential surface chemical reaction limited growth of high quality Al<sub>2</sub>O<sub>3</sub> dielectrics

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Sequential surface reactions of trimethylaluminum and water vapor have been used to deposit  $Al_2O_3$  on Si(100) surfaces. The self-limiting nature of the surface reactions allows precise control of the thickness of the deposited layers and gives rise to films with highly conformal step coverage. High quality dielectrics have been deposited at temperatures as low as 100 °C. Resistivities of  $10^{17} \Omega$  cm, breakdown strengths of  $8 \times 10^6$  V/cm, and interface-state densities of  $10^{11}$  states/eV cm<sup>2</sup> have already been achieved and they suggest possible applications as a gate insulator or a dielectric passivation layer.

The technique of atomic layer epitaxy, first described by Suntola and Antson,<sup>1</sup> has generated much recent interest for the growth of III-V compound semiconductors.<sup>2-5</sup> The technique involves sequentially dosing a surface with appropriate chemical precursors to promote surface chemical reactions, which are by their very nature, self-limiting. In this manner, monolayer control over the crystal growth can be achieved when the surface chemical reaction terminates after a monolayer of compound has reacted with the surface. Very early in this research, however, it was pointed out that this technique was not limited to crystalline materials but could also be used to deposit amorphous materials.<sup>1</sup> Since the chemistry on an amorphous versus a crystalline substrate is likely to be similar, it was proposed that the technique could be used with equal facility on either type of surface.

In this study, a sequential surface chemical reaction to deposit  $Al_2O_3$  films is investigated. The study concentrates on low-temperature  $Al_2O_3$  dielectric deposition with the idea that future generations of Si integrated circuits will need gate insulators and passivation layers deposited at low temperatures to avoid dopant redistribution and unwanted solid-state side reactions. This sequential surface chemical reaction growth technique<sup>6</sup> is found to make excellent  $Al_2O_3$ dielectric films at temperatures as low as 100 °C and avoids plasma-related charged particle damage often encountered in other low-temperature deposition processes.

A schematic diagram of the growth apparatus is shown in Fig. 1. It consists of a diffusion-pumped stainless-steel chamber equipped with two computer-controlled pulsed nozzles and a heated substrate holder. Growths are performed at substrate temperatures between 100 and 500 °C, maintaining the chamber walls at 100 °C to minimize reactant condensation. Trimethylaluminum (TMA) and water vapor (H<sub>2</sub>O) are used as the chemical precursors to provide Al and O the growing surface. Reactions of TMA with H<sub>2</sub>O to form Al<sub>2</sub>O<sub>3</sub> and CH<sub>4</sub> are highly exothermic and occur readily with a low activation barrier. In fact, the reaction of TMA and H<sub>2</sub>O can be extremely violent under uncontrolled conditions. Under properly controlled conditions, however, this reaction is ideal for low-temperature dielectric deposition. sequence. A 20  $\Omega$  cm p-type Si(100) wafer is cleaned using repeated cycles of a sequential acidic-peroxide oxidation/HF acid oxide etch. After the final oxidation the sample is HF acid etched/passivated and loaded directly into the chamber after being blown dry with dry N2. Surfaces prepared in this manner are known to be contamination-free with all of the surface Si atoms terminated/passivated with atomic hydrogen.<sup>7,8</sup> The chamber is then evacuated and the substrate/substrate holder is raised to the growth temperature. The growth is initiated with a 6 s pressure burst of TMA and then a 20 s pump-out. The substrate is then exposed to a cycle consisting of a dose of H<sub>2</sub>O followed by a dose of TMA. The vapor pulses were varied from 0.25 to 5.0 seconds in duration with a dwell time of 4 to 10 s to reevacuate the chamber between each pulse. The room-temperature vapor pressures of  $H_2O$  and TMA are similar ( ~ 30 and 10 Torr, respectively), making the pressure rises during the vapor pulses comparable. Most of the experiments were performed employing pulses of 0.5 s duration, for which the chamber pressure rises to  $\sim 10$  mTorr. The chamber pressure is found to fall to  $\sim 10^{-5}$  Torr for a 5 s evacuation before the next pulse arrives.

As can be seen in Fig. 2, the thickness of the  $Al_2O_3$  deposited, as determined by ellipsometry, is proportional to the number of vapor pulses to which the sample is subjected. Approximately 1 Å of oxide is grown during each cycle resulting in extremely precise thickness control, albeit at a rel-



A typical deposition is performed using the following

FIG. 1. Schematic diagram of Al<sub>2</sub>O<sub>3</sub> deposition apparatus.

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FIG. 2.  $Al_2O_3$  film thickness vs the number of vapor exposure cycles for a 450 °C substrate temperature using 0.5 s vapor pulses and a 9 s pump-out time.

atively low growth rate (3-6 Å/min). A plot of film thickness versus H<sub>2</sub>O pulse duration for a fixed number of cycles (200) is shown in Fig. 3. As expected for a self-terminating surface-controlled reaction, the thickness saturates at longer pulse durations. Similar behavior is observed varying the TMA pulse duration. Also expected for a surface-controlled reaction, the deposited films are highly conformal to surface topography on the wafer. In fact, films of uniform thickness are also deposited on the underside of the wafer, highlighting that films grow wherever the vapors reach. The preceding results were for a substrate temperature of 450 °C. It should be noted, however, that the growth properties described above are found to be independent of the substrate temperature, emphasizing the low activation barrier for this chemical reaction.

The overall mechanism of deposition is extremely simple to understand. Infrared spectroscopic studies have shown that surface O--H groups react with TMA at room temperature, bonding the Al to the O freeing  $CH_4$  into the



FIG. 3. Al<sub>2</sub>O<sub>3</sub> film thickness vs the  $H_2O$  vapor pulse duration for a 0.5 s trimethylaluminum vapor pulse duration at a substrate temperature of 450 °C.

gas phase.<sup>9,10</sup> This leaves a methylated Al atom behind, free to react with H<sub>2</sub>O during the next vapor pulse, again freeing CH<sub>4</sub> into the gas phase, but this time leaving Al-O-H groups on the surface. As the process is repeated,  $Al_2O_3$  is formed as the surface reaction proceeds. Consistent with this interpretation, the films are found to be stoichiometric by Rutherford backscattering (RBS) and free of carbon contamination to better than 0.5% by x-ray photoelectron spectroscopy (XPS). A detailed understanding of growth process, however, requires that one explain the anomalously low growth rate. As can be seen in Fig. 3, the growth rate saturates at  $\sim 1.1$  Å per cycle. The separation of hexagonally close-packed planes of oxygen in sapphire is 2.17 Å. Thus it appears that approximately half a monolayer of Al<sub>2</sub>O<sub>3</sub> is grown per cycle. This result is not understood at the present time.

The films produced have refractive indices between 1.65 and 1.70, indicating that a relatively dense phase of  $Al_2O_2$  is being produced. Transmission electron diffraction (TEM) shows these films to be amorphous, with an upper limit of 10-15 Å crystallite sizes, if they exist at all. The best Al<sub>2</sub>O<sub>3</sub>/Si interfaces were formed at 450 °C. The capacitance versus voltage (CV) curves for evaporated Al dots (10 mil diameter) on such a deposit are shown in Fig. 4. The oxide capacitance (i.e., the capacitance in strong accumulation) gives a dielectric constant of 7 for this film, rather low for what one would expect for good  $Al_2O_3$  ( $\epsilon = 9.8$ ). Given the high refractive index of this film, however, the low dielectric constant may be an artifact of fluctuations in the size of the evaporated Al dots (shadow mask proximity effects). As can be calculated from comparison of the quasi-static and high-frequency CV curves, a relatively low interface-state density of  $\sim 10^{11}$  states/eV cm<sup>2</sup> at midgap is found for this deposit. The fiatband voltage (-0.2 V) is, however, somewhat higher than what one would expect for an Al contact at this doping level (ideally -0.8 V), and corresponds to a negative interface charge of  $\sim 6 \times 10^{11}$  charges/cm<sup>2</sup>. Hysteresis in the CV curves (0.05-0.25 V) is also non-negligible



FIG. 4. Capacitance vs voltage (CV) curves for an Al<sub>2</sub>O<sub>3</sub> sample grown at 450 °C using 0.5 s duration vapor pulses. Solid curve: high-frequency CV (100 kHz). Broken curve: low-frequency CV (quasi-static CV using the linear ramp method).

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FIG. 5. Current vs applied field curve for an  $Al_2O_3$  sample grown at 450 °C using 0.5 s duration vapor pulses.

and needs further investigation. The leakage current for this 400-Å-thick film, however, is excellent, as seen in Fig. 5, where a line representing a resistivity of  $\sim 10^{17} \Omega$  cm has been drawn for comparison. Field-assisted tunneling in accumulation begins at  $\sim 2$  MV/cm, while it begins at  $\sim 1$  MV/cm in inversion. This asymmetry is a clear indication that states within the Al<sub>2</sub>O<sub>3</sub> band gap participate in the tunneling process. Given the direction of the asymmetry, these states must be located closer to the Si conduction-band minimum than the valence-band maximum (i.e., the upper portion of the Al<sub>2</sub>O<sub>3</sub> band gap). Catastrophic breakdown fields in accumulation are quite good [ $\sim (6-8) \times 10^{\circ}$  V/cm]; however, field strengths in inversion are expected to be lower since field-assisted tunneling begins earlier.

In summary, sequential surface chemical reactions of TMA and  $H_2O$  are found to deposit high quality  $Al_2O_3$  with

extremely precise thickness control. Resistivities of  $10^{17}$   $\Omega$  cm, breakdown strengths of  $8 \times 10^6$  V/cm, and interface state densities of  $10^{11}$  states/eV cm<sup>2</sup> have already been achieved and suggest that this dielectric might be useful as a low-temperature gate insulator or passivation layer on Si. The highly conformal nature of these films makes them particularly well suited to applications with severe topographies. The object of future research will be to reduce the number of defect states in the deposited Al<sub>2</sub>O<sub>3</sub> to raise the point at which field-assisted tunneling occurs (for comparison, field-assisted tunneling for thermally grown SiO<sub>2</sub> begins at ~5 MV/cm).

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- T. Suntola and M. J. Antson, U.S. Patent No. 4 058 430 (1977); M. Pessa,
- H. Mäkelä, and T. Suntola, Appl. Phys. Lett. 38, 131 (1981).
- <sup>2</sup>J. Nishizawa, H. Abe, and T. Kurabayashi, J. Electrochem. Soc. **132**, 1197 (1985).
- <sup>3</sup>S. M. Bedair, M. A. Tischler, T. Katsuyama, and N. A. El-Masry, Appl. Phys. Lett. 47, 51 (1985).
- <sup>4</sup>A. Doi, Y. Aoyagi, and S. Namba, Appl. Phys. Lett. 49, 785 (1989).
- <sup>5</sup>K. Mori, M. Yoshida, A. Usui, and H. Terao, Appl. Phys. Lett. **52**, 27 (1988).

<sup>6</sup>Atomic layer epitaxy is somewhat of a misnomer for this technique as it is difficult to imagine layer-by-layer growth of an amorphous material.

<sup>7</sup>E. Yablonovitch, D. L. Allara, C. C. Chang, T. Gmitter, and T. B. Bright, Phys. Rev. Lett. **57**, 249 (1986).

<sup>8</sup> V. A. Burrows, Y. J. Chabal, G. S. Higashi, K. Raghavachari, and S. B. Christman, Appl. Phys. Lett. 53, 998 (1988).

<sup>4</sup>D. J. C. Yates, G. W. Dembinski, W. R. Kroll, and J. J. Elliott, J. Phys. Chem. 73, 911 (1969).

<sup>10</sup>G. S. Higashi and L. J. Rothberg, J. Vac. Sci. Technol. B 3, 1460 (1985).

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