Effects of Tris(tert-pentoxy)silanol Purge Time on SiO₂ Thin-Film Growth Rate in Rapid Atomic Layer Deposition

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Unusual growth per cycle (GPC) behaviors, depending on the tris(tert-pentoxy)silanol purge time, were observed in catalytic SiO₂ growth by atomic layer deposition (ALD). Short purge times led to decreases in GPC, and normal saturated GPC was observed for longer purge times, following ideal ALD behavior. When an extremely long purge time was used, a decreased growth rate was observed; loss of surface hydroxyl groups as a result of increased cross-linking was considered to be a possible cause. SiO₂ films of comparable quality to those obtained using longer purge times were obtained by increasing the Ar flow rate during purging.

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Silicon dioxide (SiO₂) is one of the most widely used materials in the semiconductor industries. Its role includes use as gate dielectrics in metal oxide semiconductor field-effect transistors, dielectric layers in capacitors in dynamic random access memories, insulating layers between metal interconnects such as Al or Cu, and moisture barriers in organic light-emitting diodes and organic thin-film transistors.¹ There are several methods for forming SiO₂ thin films, including thermal oxidation of Si, evaporation, chemical vapor deposition (CVD), plasma-enhanced CVD (PECVD), and atomic layer deposition (ALD). Among these, ALD has been highlighted as an ideal method for forming very conformal and ultrathin films in the continued scaling-down of semiconductor devices. ALD is a self-limiting technique, characterized by alternating exposure of the metal precursor and the reactant.²,³ The chemical reaction occurs only at the film surface, so extremely conformal growth of SiO₂ films is enabled on complex three-dimensional structures. However, the biggest hurdle for implementing ALD in semiconductor devices is its low growth per cycle (or per time), adding high costs for mass production.

An ALD process consists of four steps: precursor pulse, purging, reactant pulse, and purging. These four steps make one growth cycle. In general, the growth per cycle (GPC) of ALD SiO₂ ranges from 0.05 to 0.1 nm/cycle. Given that one reaction cycle of the ALD process takes 1–30 s, the growth per time corresponds to 0.1–6 nm/min. The growth per cycle (GPC) of ALD SiO₂ ranges from 0.05 to 0.1 nm/cycle. Given that one reaction cycle of the ALD process takes 1–30 s, the growth per time corresponds to 0.1–6 nm/min. The continued scaling-down of semiconductor devices. ALD is a self-limiting technique. The chemical reaction occurs only at the film surface, so extremely conformal growth of SiO₂ films is enabled on complex three-dimensional structures. However, the biggest hurdle for implementing ALD in semiconductor devices is its low growth per cycle (or per time), adding high costs for mass production.

In the conventional ALD process, the purge step following the reaction cycle is the shortest step in a complete reaction cycle. The purge step allows time for the chemical reaction to come to completion. Therefore, the purge time is critical to the ALD process. In this study, the purge step is used to further analyze the effects of the purge time on the ALD process. The purge time is varied from 1 s to 1000 s in order to study its effects on the growth rate and film thickness.

The growth rate of ALD SiO₂ films is affected by the purge time. The growth rate is defined as the rate at which the film thickness increases with time. The growth rate is usually expressed in nanometers per cycle (nm/cycle) or nanometers per minute (nm/min). The growth rate is also affected by the purge time, which is the time between the deposition of the precursor and the purge step. The purge time is usually varied from 1 s to 1000 s in order to study its effects on the growth rate and film thickness.

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SiO₂ ALD has its own unique growth mechanism, unlike that of other conventional ALD processes.

Figure 2a shows a schematic reaction flow diagram of normal rapid SiO₂ ALD, in which surface TMA acts as chemisorption sites for incoming TPS molecules. When a short TPS purge time is used, it is assumed that a large amount of water, which is one of the byproducts, will exist inside the reactor. When TMA is pulsed in the following step, some fraction of the TMA molecules will react with water in the gas phase, and be consumed. This eventually decreases the number of TMA molecules chemisorbed on the substrate and decreases the GPC. Even if TMA is chemisorbed on an OH-terminated surface, the remaining water molecules can oxidize Al. If this occurs, OH-terminated Al cannot catalyze chemisorption of the incoming silanol molecules, as depicted in Figure 2b. This is also supported in part by the following experiment. When only TPS was injected into an Al₂O₃ sample, there was no indication of SiO₂ growth on this Al₂O₃ surface. This result suggests that fully hydroxylated Al and/or Al–O–Al surfaces may not effectively catalyze the insertion of TPS.

Figure 3. Film thicknesses of SiO₂ for one deposition cycle while varying the TPS purge time from 10 to 120 s. Almost identical film thicknesses are obtained.

To check whether the remaining water molecules in the reactor affect the next-injected TMA, the following experiments were conducted. Only one cycle of deposition was conducted, and the final TPS purge time was varied from 10 to 120 s. Figure 3 indicates that the deposited film thicknesses were almost identical (±1.5 nm difference), irrespective of the TPS purge time. From a combination of these results with those for regime 1 in Figure 1, it is concluded that certain molecules that are not sufficiently purged out after the TPS pulse step hinder the next reaction. It is believed that water molecules play a role in decreasing the growth rate, and water is one of the byproducts of the cross-linking of siloxane polymers. In this regard, regime 2 in Figure 1 appears to be the optimum condition in terms of the TPS purge time. It is understood that long purge times of 120–400 s lead to complete removal of interfering species generated during the cross-linking reaction, resulting in production of thick SiO₂ films.

Purge times longer than 400 s led to a decrease in the obtained film thickness, as shown in Figure 1 (regimes 3 and 4). A consequence of extremely long purge times is believed to be a decrease in the number of surface hydroxyl groups, which act as surface chemisorption sites for incoming TMA. As discussed above, using only one deposition cycle gave SiO₂ films of the same thickness. Extremely long purge times result in a reduction in the number of surface hydroxyl groups by increasing cross-linking, and this decreases the amount of chemisorbed TMA. Less TMA chemisorption reduces the efficient insertion and cross-linking of silanols.

To effectively purge out byproducts generated during cross-linking reactions, while decreasing the overall process time, several methods were considered. Increasing the growth temperature promotes efficient removal of the byproducts, but it also increases the cross-linking reaction, leading to too-fast termination of SiO₂ growth. One simple way of increasing the purge efficiency is to add more Ar gas. The effect of increasing the Ar flow rate during TPS purging on the growth rate was determined as follows. The purge time was fixed at 10 s, and additional Ar flows of 50, 100, and 150 sccm were used, resulting in total Ar flow rates of 230, 280, and 330 sccm. Figure 4a shows
the final thicknesses of the grown SiO₂ films. The final thickness of the SiO₂ film with normal Ar purging (180 sccm) is also included for comparison. Increasing the Ar flow rate did not deteriorate the thickness uniformity within the film (±2%). As the flow rate increases, a monotonic increase in the growth rate is obtained. This suggests that a higher growth rate can be obtained with a shorter purge time by using more efficient purge conditions. The quality of the grown films was checked by comparing their WERs in 1% HF solution. SiO₂ films grown by a thermal method and PECVD were included as control films. Figure 4b shows a plot of the calculated WER with purge time for each film; the figure shows that the WER decreases with increasing TPS purge time, indicating that a denser film is formed. As discussed earlier, a short purge time may decrease the density of TMA chemisorbed on the OH-terminated surface. This leads to less efficient cross-linking of siloxane polymers, and the final film has a less dense structure. In contrast, a longer purge is sufficient for the formation of a densely cross-linked SiO₂ structure, so a lower WER is expected. The WER of the SiO₂ film with the longest purge time, 1300 s, is lower than that of the SiO₂ film grown by PECVD, although it is still somewhat higher than that of the thermally grown film. Even the film grown at the shortest purge time, 10 s, has a WER comparable to that of the SiO₂ film grown by PECVD. As more Ar is added during purging, a gradual decrease in WER is observed. The WER of the film grown with the aid of an additional 150 sccm Ar flow is 5.4 Å/s, which is comparable to that of the SiO₂ film grown with the normal TPS purge time of 1000 s. Our results also suggest that optimization of the gas flow and chamber design should be carried out in parallel with process parameter optimization. By enhancing the efficiency of the removal of byproducts generated during cross-linking reactions, high-quality SiO₂ films can be obtained with increased GPCs and growth per time, making rapid/catalytic SiO₂ ALD more compatible with the mass-production scale.

The effects of the TPS purge time on the GPC of rapid SiO₂ ALD were investigated. A short TPS purge time led to a decrease in the GPC of SiO₂; this may be the result of consumption of TMA by reaction with water molecules remaining in the reaction chamber during insufficient purging. When a longer purge time is used, a decrease in GPC was observed, and this was attributed to the loss of surface hydroxyl groups, which act as chemisorption sites for TMA. Increasing the flow rate of Ar during the purge step enabled the formation of high-quality SiO₂ films in considerably shorter purge times.

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References