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Atomic layer controlled growth of SiO_2 films using binary reaction sequence chemistry

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SiO_2 thin films were deposited with atomic layer control using binary reaction sequence chemistry. The SiO_2 growth was accomplished by separating the binary reaction $SiCl_4+2H_2O\rightarrow SiO_2+4HCl$ into two half-reactions. Successive application of the half-reactions in an ABAB... sequence produced SiO_2 deposition at temperatures between 600 and 800 K and reactant pressures of 1–10 Torr. The SiO_2 growth was monitored using ellipsometry versus substrate temperature and reactant exposure time. The maximum SiO_2 deposition per AB cycle was 1.1 Å/AB cycle at 600 K. The surface topography measured using atomic force microscopy was extremely flat with a roughness nearly identical to the initial substrate. © *1997 American Institute of Physics.*
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The miniaturization of semiconductor microelectronic devices to the nanoscale limit requires atomic layer controlled deposition techniques. Nanoscale device fabrication will require exquisite control over many film properties such as thickness, morphology, crystallinity, and electrical characteristics. Lower deposition temperatures must also be realized because nanoscale structures are very sensitive to interlayer and dopant diffusion. Many of these new requirements may be achieved by atomic layer control of growth using binary reaction sequence chemistry.[1–3]

SiO_2 continues to be one of the most important and widely used materials in the microelectronics industry. Oxide gate thicknesses $\leqslant$50 Å will be employed in future devices. Higher density dynamic random access memory (DRAM) must deposit conformal SiO_2 films on very high aspect ratio trenches.[4] Larger flat panel displays will require uniform SiO_2 film deposition over extremely large substrates.[5] Very thin SiO_2 films may also be employed in nanolaminate structures to tailor the mechanical, electrical, and optical properties of materials.[6]

Self-limiting surface reactions applied in a binary reaction sequence can lead to atomic layer controlled growth.[1–3,7–9] This technique is known as atomic layer epitaxy (ALE) or atomic layer processing (ALP) and was first demonstrated by Suntola and co-workers for the deposition of ZnS films.[2] Much recent research has been devoted to developing atomic layer controlled growth techniques for the growth of various oxides and SiO_2.[7–11]

A binary reaction sequence for the deposition of SiO_2 is (7):

$$(A)\ SiOH^*+SiCl_4\rightarrow SiOSiCl_3^*+HCl,$$

$$(B)\ SiCl^*+H_2O\rightarrow SiOH^*+HCl,$$

where the surface species are indicated by the asterisks. Each half-reaction involves the reaction between a gas phase precursor and a surface functional group (i.e., SiOH* or SiCl*). The surface reaction continues until all of the initial surface functional groups have been replaced by the new functional group. Once the surface has achieved the new functionality, no further reaction can occur because the remaining precursor has no reactivity towards the newly deposited surface species.

If each half-reaction is self-limiting, application of the binary reaction sequence in an ABAB... fashion should produce layer-by-layer controlled growth. The principal advantage of the ABAB... binary reaction sequence approach is that the reaction kinetics should not affect the SiO_2 deposition. Provided that the surface reactions are allowed to reach completion everywhere on the substrate, small changes in the surface temperature, reactant pressure and exposure times will not change the film growth per AB cycle.

In this letter, SiO_2 thin films were grown using binary reaction sequence chemistry and evaluated using *in situ* spectroscopic ellipsometry and *ex situ* atomic force microscopy. The experiments were performed in an apparatus that has been described elsewhere.[8] In brief, the apparatus consists of a sample load lock chamber, a central deposition chamber and a high vacuum chamber for surface analysis. The central deposition chamber has a base pressure of 1×10^{-7} Torr. A recent addition to the deposition chamber is an *in situ* spectroscopic ellipsometer (J.A. Woolam Co. M-44) that simultaneously collects ellipsometric data at 44 visible wavelengths.

The ellipsometer is mounted on ports positioned at 50° with respect to the surface normal. The ports are equipped with gate valves to protect the birefringent-free windows from deposition during film growth. The best sensitivity for the spectroscopic ellipsometer is achieved at the Brewster angle of 76° for the Si(100) substrate. To increase the sensitivity, these ellipsometric measurements at 50° were conducted on thin Al_2O_3 films with ~300 Å thicknesses grown on Si(100). The Al_2O_3 films were deposited on Si(100) with excellent conformality and precise thickness control using binary reaction sequence chemistry (8).

The Si(100) substrates were rinsed with methanol and blown free of particles before loading into the deposition chamber. The Si(100) surface was then cleaned using an anneal at 875 K for 1 min. This anneal was followed by a H_2O plasma exposure at room temperature to hydroxylate the surface and remove surface carbon. Immediately following the cleaning procedure, the substrate temperature was

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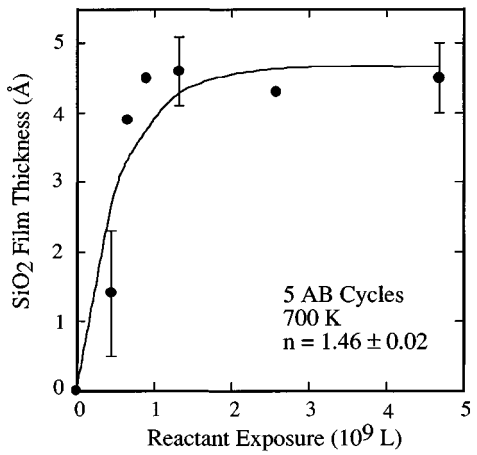

FIG. 1. Ellipsometric measurements of SiO_2 film thickness deposited on thin Al_2O_3 films on Si(100) at 700 K after 5 AB cycles for various total reactant exposures.

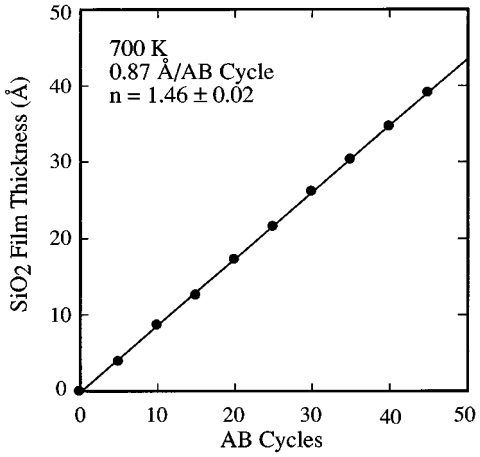

FIG. 2. Ellipsometric measurements of SiO_2 film thickness deposited on thin Al_2O_3 films on Si(100) at 700 K vs number of AB reaction cycles.

ramped to the desired reaction temperature for film growth. Earlier work on SiO_2 deposition revealed that temperatures $\geqslant$600 K are needed for the two half-reactions to reach completion.[7]

Once a half-reaction has reached completion, additional reactant exposure should produce no additional growth. Fig. 1 demonstrates the self-limiting nature of the half-reactions at 700 K. The SiO_2 film thickness was measured using the *in situ* ellipsometer after 5 AB cycles for various total H_2O and $SiCl_4$ reactant exposures. The $SiCl_4$ exposures were equal to the H_2O exposures. A typical AB cycle occurred with the following sequence: Dose $SiCl_4$ (1–10 Torr)/Evacuate $(1\times10^{-4}$Torr)/Dose H_2O(1–10 Torr)/Evacuate $(1\times10^{-4}$ Torr).

For total H_2O and $SiCl_4$ exposures $<2x10^9$ L after 5 AB cycles, Fig. 1 shows that the SiO_2 film thickness is dependent on the total reactant exposure. This behavior reveals that the surface half-reactions have not reached completion. In contrast, both half-reactions have saturated for reactant exposures $>2\times10^9$ L after 5 AB cycles and additional reactant exposure results in no additional growth. The error bars represent the 90% confidence limits and the solid line is intended only to guide the eye.

Figure 2 shows the *in situ* ellipsometric measurements of SiO_2 film thickness versus number of AB cycles at 700 K. The growth rate at 700 K was 0.87 Å/AB cycle and the refractive index was $n=1.46\pm0.02$. This refractive index was confirmed using additional *ex situ* ellipsometric measurements at various angles of incidence. The linear growth rate indicates that the number of reactive surface sites remains constant. The constant growth rate per AB cycle also argues that the SiO_2 film is growing conformally with no roughening. Using the refractive index of $n=1.46$, the growth rates at 600 K and 800 K were 1.1 Å/AB cycle and 0.75 Å/AB cycle, respectively. The decrease in the growth rate versus temperature correlates with the thermal stability of the SiOH* surface functional groups.[12]

The surface topography of the SiO_2 films was studied using an atomic force microscope (AFM) in tapping mode (Digital Instruments-Nanoscope III). The SiO_2 films were grown directly on Si(100) for these AFM experiments. Figure 3 shows the surface topography after 75 AB cycles at 700 K using exposures sufficient for both half-reactions to reach completion. Analysis of these AFM images yielded a surface roughness of ±3 Å (RMS). In comparison, the roughness of a cleaned Si(100) wafer was ±2 Å(RMS). The SiO_2 surface roughness also exhibits nearly the same power spectral density versus spatial wavelength as the Si(100) wafer. This near equivalence confirms that the SiO_2 films are growing conformally on Si(100).

A model for SiO_2 film growth was developed that assumes that the maximum number of Si atoms and SiO_2 units that can be deposited per AB cycle is equal to the number of SiOH* hydroxyl groups.[7] The SiOH* coverage at 700 K is $\sim2\times10^{14}$ OH units/cm^2.[12] The SiO_2 monolayer coverage can be derived using the measured refractive index of $n=1.46$ for the SiO_2 films. This refractive index is consistent with a density of 2.21 g/cm^3 or a number density of $\rho=2.2\times10^{22}$ SiO_2 units/cm^3. The thickness of a SiO_2 monolayer can then be calculated as $\rho^{-1/3}=3.5$ Å. Likewise, $\rho^{2/3}$ represents an SiO_2 monolayer coverage of 7.9×10^{14} SiO_2 units/cm^2.

Based on the thickness and coverage of a SiO_2 mono-

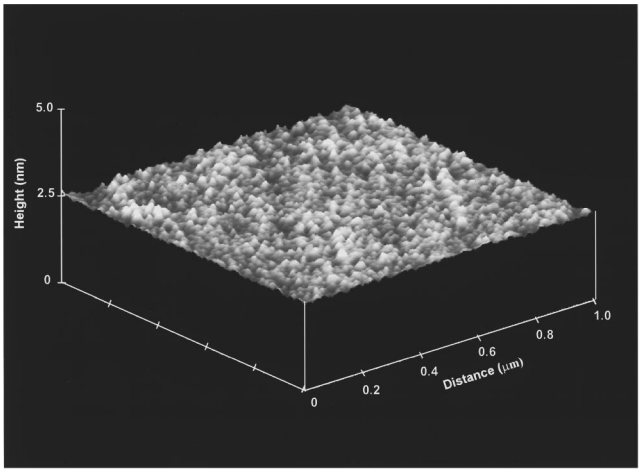

FIG. 3. Atomic force microscope image of a SiO_2 film deposited directly on Si(100) at 700 K after 75 AB cycles. The horizontal full scale is 1 μm. The vertical full scale is 5 nm and the light-to-dark range is 10 Å.

layer, the deposition of 2×10^{14} SiO_2 units/cm^2 per AB cycle is consistent with a thickness of ~0.9 Å/ AB cycle. This predicted SiO_2 deposition compares favorably with the measured SiO_2 growth of 0.87 Å/ AB cycle at 700 K. The SiO_2 growth per AB cycle at 600 K and 800 K were predicted to be 1.17 Å/AB cycle and 0.74 Å/AB cycle, respectively. The agreement between the predicted and measured growth rates argues that the SiO_2 film density is independent of growth temperature and consistent with a refractive index of n=1.46. In addition, the agreement indicates that SiO_2 film growth by binary reaction sequence chemistry is occurring via the SiOH* surface functional groups.

In conclusion, SiO_2 films were deposited with atomic layer control using binary reaction sequence chemistry. The SiO_2 growth per AB cycle was extremely linear and AFM measurements revealed an exceptionally flat SiO_2 film with a surface roughness similar to the initial Si(100) substrate. The temperature dependent SiO_2 growth per AB cycle was proportional to the SiOH* coverage as expected for the binary reaction sequence chemistry.

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