Self-limiting atomic-layer deposition of Si on SiO_2 by alternate supply of Si_2H_6 and $SiCl_4$

Shin Yokoyama,[a] Kenji Ohba, and Anri Nakajima
Research Center for Nanodevices and Systems, Hiroshima University, 1-4-2 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan

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Atomic-layer deposition of Si on SiO_2 with a self-limiting growth mode was achieved at substrate temperatures between 355 and 385 °C by means of alternate supply of Si_2H_6 and $SiCl_4$ gas sources. The growth rate was saturated at 2 ML per cycle at these temperatures and for Si_2H_6 exposure time over 120 s. The smooth surface (~0.26 nm in arithmetic average roughness) was obtained under the self-limiting condition irrespective of a film thickness up to 6.5 nm. [DOI: 10.1063/1.1389508]

Atomic-layer-controlled deposition (ALD) has recently been attracting a great deal of attention as the size of the electronic devices decreases. Especially for gate insulators with a high dielectric constant such as Al_2O_3,[1] ZrO_2,[2] and HfO_2,[3] the ALD process is recognized as a practical method because of its excellent thickness uniformity, low growth temperature, and less particle generation.

Besides the dielectric films, the ALD of semiconducting Si films on SiO_2 is very useful, for example, for quantum devices, in which a small Si island with precisely controlled size is necessary to be sandwiched in the insulating films.[4] This technology will be useful for the ultra-large-scale integrated (ULSI) circuits, for example, to fabricate a precisely size-controlled floating gate memory and accurate resistors. It is also applicable to fabricate a silicon on insulator substrate having an extremely flat thin Si layer.

Although there are many reports on the atomic-layer epitaxy (ALE) of Si,[5–8] there are only a few reports concerning the ALD of Si on SiO_2.[9,10] Tanaka *et al.*[9,10] reported the ALD of Si on SiO_2 by cryogenic laser-induced deposition using Si_2H_6. They obtained a self-limiting growth mode, in which the growth rate is automatically adjusted to a monolayer per cycle, at substrate temperatures −26 to −49 °C. However, it may be difficult to obtain a high-purity Si film because the residual impurity gases in the vacuum chamber will be easily adsorbed on the cooled substrate. In this letter, we have achieved atomic-layer deposition of Si on SiO_2 with a self-limiting growth mode at more practical substrate temperatures by means of alternate supply of $SiCl_4$ and Si_2H_6. The growth rate is nearly constant (~2 ML/cycle) at temperatures between 355 and 385 °C, and a very smooth surface is obtained irrespective of the film thickness.

The time sequence for temperature and gas supply is shown in Fig. 1. The ALD system consists of a quartz chamber (volume of ~100 cm^3), a turbomolecular pump (1500 l/s), and computer-controlled halogen lamp and gas valves.[11] The substrate is OH-terminated SiO_2,[12] which was obtained by dilute HF treatment of thermally oxidized *p*-Si(100) at 1000 °C, followed by a short deionized water rinse (1 min) and spin dry. After evacuating the chamber into $<2\times10^{-7}$ Torr, $SiCl_4$ (200 Torr, at a substrate temperature $T_1=375$ °C: fixed) and Si_2H_6 (20%, He base, 200 Torr, $T_2=345–420$ °C) gases are alternately supplied. For the $SiCl_4$ exposure, we employed the same condition used in the self-limiting atomic-layer deposition of silicon nitride by alternate supply of $SiCl_4$ and NH_3,[13] because the $SiCl_4$ adsorption was reported to be saturated at ~1 ML at this condition. The typical growth cycle was 20. The film thickness was measured by the ellipsometry.

The growth rate is shown in Fig. 2 as a function of reciprocal substrate temperature at Si_2H_6 exposure. The Si growth rate for the exposure of only Si_2H_6 (the same condition except for no supply of $SiCl_4$) is also plotted in Fig. 2. For the alternate gas supply of $SiCl_4$ and Si_2H_6, the growth rate is nearly constant (~2 ML/cycle) in the temperature range between 355 and 385 °C. On the other hand, for the gas exposure of only Si_2H_6, the growth rate exponentially increases with the temperature and the activation energy of ~2.0 eV is obtained from Fig. 2, which coincides with that for the thermal dissociation of Si_2H_6 into SiH_4 and SiH_2.[14] Without the exposure of Si_2H_6, i.e., only the $SiCl_4$ exposure, the film growth did not take place. Therefore, the HCl desorption reaction of $SiCl_4$ with the surface H–Si bond, and/or HCl desorption reaction of Si_2H_6 with the surface Cl–Si bond probably cause the self-limiting growth of ~2 ML/cycle in the temperature range 355–385 °C. Namely,

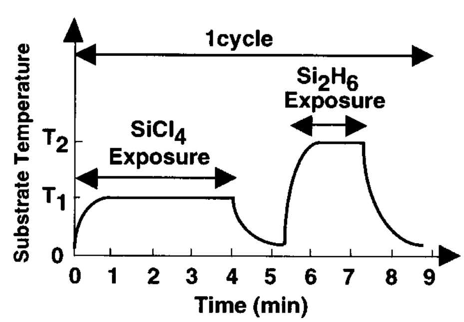

FIG. 1. Typical time sequence of gas supply and substrate temperature control. T_1 and T_2 indicate the substrate temperature during $SiCl_4$ exposure and Si_2H_6 exposure, respectively. The substrate temperature was computer-controlled synchronized with the gas supply. The vacuum evacuation time between $SiCl_4$ and Si_2H_6 exposures is 90 s. The pressure in the chamber just before each gas supply is $\sim2\times10^{-4}$ Torr.

[a]Electronic mail: yokoyama@sxsys.hiroshima-u.ac.jp

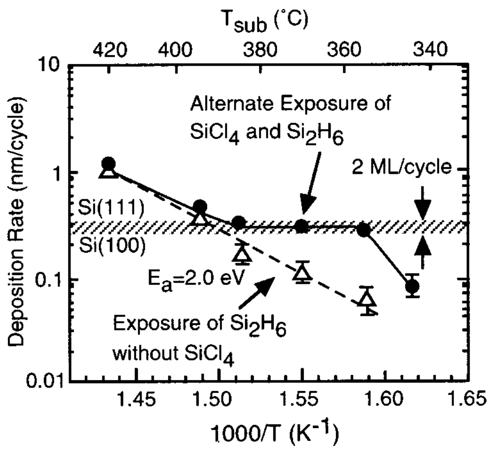

FIG. 2. Growth rate of Si as a function of substrate temperature at Si_2H_6 exposure. The $SiCl_4$ and Si_2H_6 exposures times are 4 and 2 min, respectively. Two monolayer thicknesses of 0.27 nm for Si(100) and 0.31 nm for Si(111) are indicated in the figure.

each HCl desorption reaction automatically stops when 1 ML of Si covers the surface. Here, the Cl- and/or H-terminated surface acts as a surfactant to operate the self-limiting mechanism.[15] While at higher temperatures (>400 °C) the dissociation of Si_2H_6 becomes predominant and the growth rate increases independent on the $SiCl_4$ exposure.

The deposition rate for the $SiCl_4/Si_2H_6$ alternate supply at a substrate temperature of 355 °C (at Si_2H_6 exposure) is shown in Fig. 3 as a function of Si_2H_6 exposure time. The deposition rate saturates at a roughly 2 ML/cycle for the Si_2H_6 exposure time longer than 120 s.

Here, we discuss the reason for the success in the self-limiting growth in our method. In order to obtain the self-limiting growth mode, an alternate supply of chloride and hydride gas sources has been usually employed for the ALD or ALE.[5,8,16–18] Gates *et al.*[5] reported an ALE of Si using Si_2Cl_6 and Si_2H_6, however, the self-limiting growth mode was not achieved. The essential reason for our success in the self-limiting growth for the $SiCl_4/Si_2H_6$ system is probably an employment of a relatively low substrate temperature (355–385 °C) at Si_2H_6 exposure. While in the Si_2Cl_6/Si_2H_6 case,[5] the substrate temperature was relatively high (465 °C), which may cause continuous Si deposition through thermal dissociation of Si_2H_6 at the substrate surface. In compensation for using the low substrate temperature, we employed a high gas pressure of 200 Torr in order to gain the growth rate. While in the Si_2Cl_6/Si_2H_6 case,[5] a low Si_2H_6 gas pressure of 2×10^{-3} Torr was sufficiently enough to obtain a practically large growth rate because of the high substrate temperature. On the other hand, concerning the $SiCl_4$ exposure condition, the monolayer adsorption of $SiCl_4$ on the OH-terminated SiO_2 surface[18] and on the NH-terminated silicon nitride surface[13] has been indirectly proven, respectively, from the ALD of SiO_2 using a $SiCl_4/H_2O$ system[18] and from the ALD of silicon nitride using a $SiCl_4/NH_3$ system.[13] In these cases, a relatively high gas pressure of 1–10 Torr (Ref. 18) or 200 Torr (Ref. 13) and a relatively low temperature [427 °C (Ref. 18) or 375 °C (Ref. 13)] conditions were used. Therefore, we have employed the same $SiCl_4$ exposure condition as the $SiCl_4/NH_3$ system.[13] It is speculated from the rate saturation of the ~2 ML/cycle in Figs. 2 and 3 that the $SiCl_4$ adsorption is also saturated at ~1 ML on the SiH-terminated surface at the condition used.

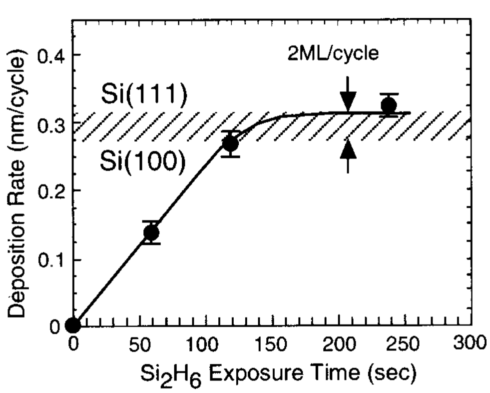

FIG. 3. Deposition rate of Si vs Si_2H_6 exposure time at a substrate temperature of 355 °C. The $SiCl_4$ exposure time is fixed at 4 min.

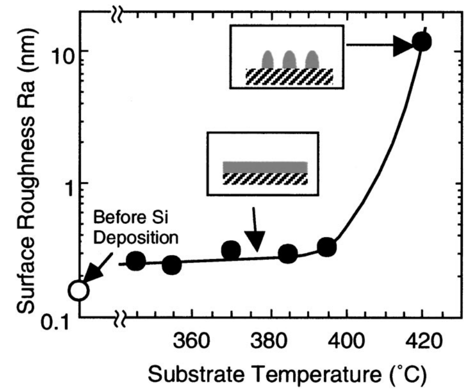

FIG. 4. Surface roughness vs substrate temperature at Si_2H_6 exposure. The growth cycle is 20. The $SiCl_4$ and Si_2H_6 exposure times are 4 and 2 min, respectively.

Figure 4 shows the surface roughness measured by atomic-force microscopy as a function of substrate temperature at Si_2H_6 exposure. Below 395 °C the surface is smooth (~0.26 nm in arithmetic average roughness: R_a), while it becomes rough at temperatures over 395 °C, possibly due to Si nucleation.[5] Figure 4 indicates the growth mode change from the layer by layer (Frank–Van der Merwe[15]) mode to island growth (Volmer–Weber[19] or Stranski–Krastanov[20]) mode at high temperatures. The surface roughness is also

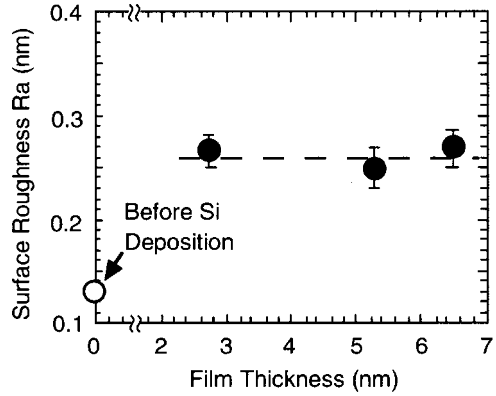

FIG. 5. Surface roughness vs film thickness. The substrate temperature at Si_2H_6 exposure is fixed at 355 °C. The gas exposure times are the same as in Fig. 4. It was confirmed that the film thickness was proportional to the growth cycle.

plotted as a function of the film thickness in Fig. 5. It is recognized that the surface is maintained smooth up to a film thickness of 6.5 nm as far as the self-limiting condition is employed.

In conclusion, we have demonstrated the self-limiting growth of Si on SiO_2 at practical growth temperatures 355–385 °C using chloride/hydride gas sources. A smooth surface was obtained under the self-limiting growth condition. The epitaxial Si growth with the self-limiting mechanism would be expected under this growth condition. This technique will help in the realization of sophisticated ULSI and quantum devices.

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