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Self-Limiting Atomic-Layer Selective Deposition of Silicon Nitride by Temperature-Controlled Method

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1. Introduction

We have been studying atomic-layer deposition (ALD) of silicon nitride[1-3]. The ALD technique will be applicable to form the quantum structures. Since the atomic-layer-controlled ultrathin silicon nitride can be deposited on Si substrate or gate oxide, this technique will also be useful for the suppression of the impurity (especially boron) diffusion into the channel region from the poly-Si gate, which is one of the big problem for the ultrasmall MOS transistors[4]. Moreover, the self-limiting ALD technique is suitable for the large-wafer process with high controllability. To make such quantum structures or the barrier layers for impurity diffusion, the selective deposition of silicon nitride with atomic scale controllability becomes a key technology.

The ALD of silicon nitride has been investigated by means of alternate supply of SiH_2Cl_2 and NH_3 dissociated by plasma[1,2] or thermal catalytic reaction on W filament[3]. For these methods, the film thickness per cycle was saturated at a half-molecular layer (M.L.)/cycle for the wide range of deposition conditions such as the substrate temperature and gas exposure time. In the thermal catalytic ALD[3], the selective deposition of silicon nitride only onto a hydrogen-terminated Si and no deposition onto SiO_2 was achieved, however, it is limited only for thin (<4 nm) film deposition. In the plasma ALD[1,2], the selective deposition was difficult due to the hydrogen atoms generated with the NH_3 plasma.

In this paper the self-limiting selective deposition of silicon nitride on Si and only slight deposition on SiO_2 have been succeeded at any growth cycles by using the temperature-controlled ALD. In this process, only thermal reaction on the substrate is employed and high- temperature treatment is involved as a key process to obtain a high selectivity. The mechanism of this selective deposition is also proposed.

2. Experimental

Figure 1(a) shows the schematic diagram of the experimental apparatus. Silicon nitride films have been deposited by alternately supplying NH_3 and $SiCl_4$ gases. The substrate tempearture is changed by the infrared lamp controlled by the computer synchronized with the gas supplying sequence. Typical temperature and gas supply sequence is shown in Fig. 1(b). The substrate temperature at the exposure of $SiCl_4$ is 375°C. After the $SiCl_4$ exposure, the temperature is raised to 900~1050°C and maintained for 60 s. This high-temperature treatment is the key process to remove the adsorbed Si atoms on the SiO_2 surface after the $SiCl_4$ exposure while the Si atoms on the Si surface is expected to stay. Then the temperature is decreased to 550°C and the NH_3 is irradiated. This sequence was repeated 40 times. The deposited film thickness was measured by ellipsometry.

3. Results and Discussions

Figure 2 shows the $SiCl_4$ exposure time dependence of the growth rate. The deposition rate saturates at ~one M.L./cycle for the $SiCl_4$ exposure time longer than 120 s, which indicates the self-limiting mechanism of the ALD growth. Figure 3 shows the selectivity of the ALD growth of the silicon nitirde on the Si and SiO_2 surfaces. When the heat-treatment temperature is 900°C, the film thickness deposited on the SiO_2 is about a half of that on the Si. However, when the heat treatment temperature is increased to 1050°C the film thickness on the SiO_2 becomes neglegibly small (below the detection limit). On the other hand, the film thickness on the Si substrate is maintained constant eventhough the heat-treatment temperature is changed. The reason of this selective deposition is considered as follows. On the SiO_2 surface the reaction, adsorbed $Si+SiO_2$->2SiO (which is easily evaporated)[5], occurs during the high-temperature treatment. The proposed growth mechanism is summarized in Fig. 4. The atomic composition of the grown film was measured by the angle-resolved x-ray photoelectron spectroscopy (XPS). The result is shown in Fig. 5. Though the atomic ratio of N/Si is slightly smaller than that of the stoichiometric film (1.33), the deposition of the silicon nitride layer on Si substrate is confirmed by XPS.

4. Conclusions

The self-limiting atomic-layer selective deposition of silicon nitride was succeeded by using the temperature-controlled method, which uses NH_3 and $SiCl_4$ source gases. The self-limiting growth (1 M.L./cycle) mechanism was confirmed for the $SiCl_4$ exposure time. The growth selectivity (on Si/on SiO_2) of over 20 was obtained by employing the high-temperature (1050°C) heat treatment after $SiCl_4$ exposure.

This technology leads to the possibility of realizing the well-controlled quantum effect devices and will contribute to the fabrication of the highly reliable MOS transistors.

References

1) H. Goto et al.: Appl. Phys. Lett. 68, No. 23, p. 3257 (1996).
2) S. Yokoyama et al.: Applied Surface Science 112, p. 75(1997).
3) S. Yokoyama et al.: Applied Surface Science (1998) in press.
4) C.T. Liu et al.: 1996 Symposium on VLSI Technology Digest of Technical Papers p. 18(1996).
5) R.C. Henderson: J. Electrochem. Soc. 119, p. 772(1972).

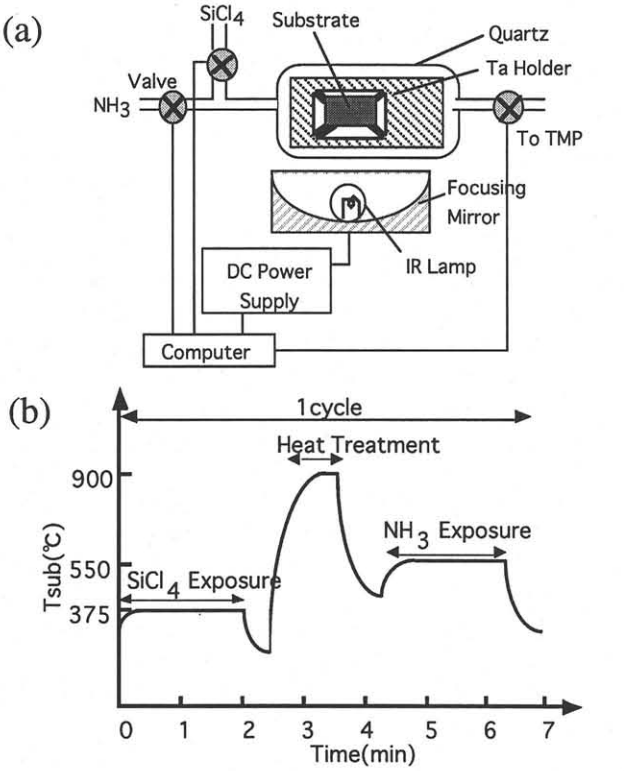

Fig. 1 (a) Experimental apparatus and (b) typical gas supply and temperature sequence. $SiCl_4$ gas is used in this study to achieve a deposition rate of one M.L./cycle. In the previous study[1-3] a half M.L./cycle was obtained using SiH_2Cl_2. The low growth rate for the SiH_2Cl_2 is considered to be due to the large steric hindrance effect of SiH_2Cl_2 molecule[2].

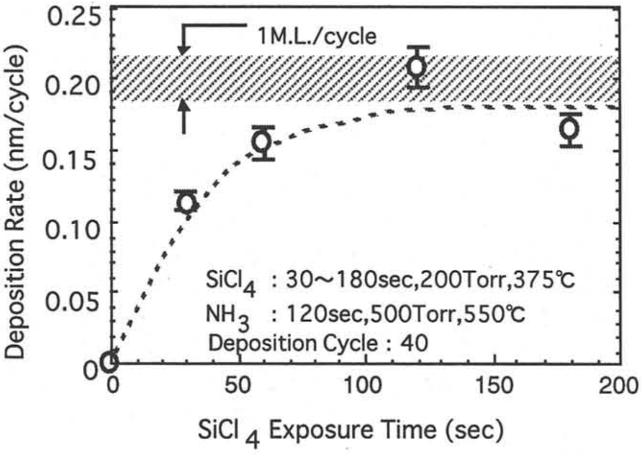

Fig. 2 $SiCl_4$ exposure time dependence of deposition rate. The refractive index measured by ellipsomery was ~1.8, while the refractive index of the stoichiometric Si_3N_4 is ~2.0. The deposition rate saturates at ~one M.L./cycle for the $SiCl_4$ exposure time longer than 120s.

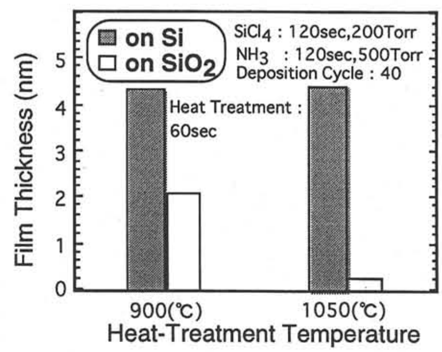

Fig. 3 Growth selectivity of ALD silicon nitride on Si and SiO_2 surfaces at different heat-treatment temperatures. By using high-temperature treatment at 1050°C for 60s, the selectivity of over 20 is achieved.

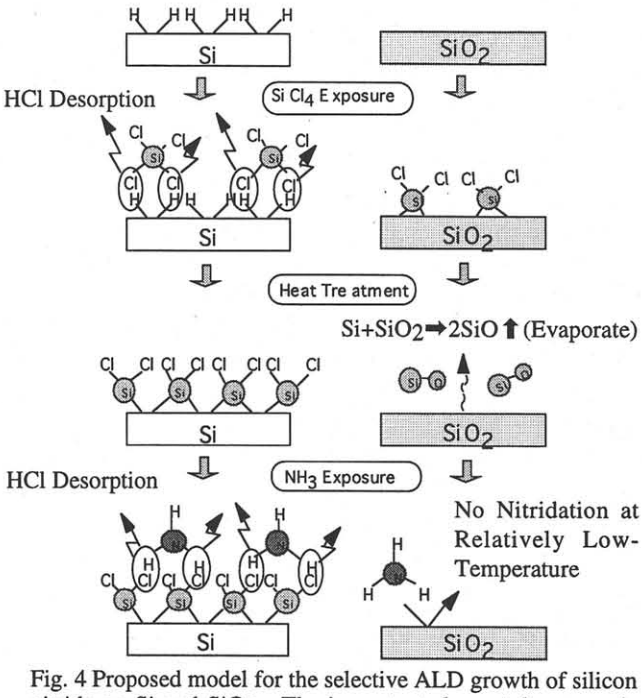

Fig. 4 Proposed model for the selective ALD growth of silicon nitride on Si and SiO_2. The important elemental process is the HCl geneartion reaction between $SiCl_4$ and NH_3 molecules. On SiO_2 surface the reaction, adsorbed Si+SiO_2 ->2SiO↑, at high temperatures leads to no depositon of silicon nitride on SiO_2.

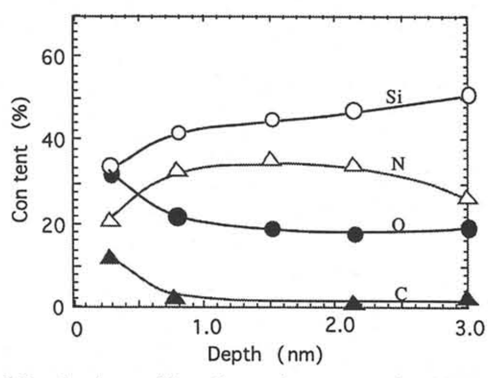

Fig. 5 In depth profile of atomic content in ALD silicon nitride. The atomic concentration ratio of N/Si is about 0.8, while that of the stoichiometric film is 1.33. The film contains about 20% of oxygen, which may originate from the residual gases (oxygen and H_2O) in the vacuum chamber and/or from the impurities in the source gases.