

# Silicon dioxide thin films prepared by chemical vapor deposition from tetrakis(diethylamino)silane and ozone

Toshiro Maruyama and Satoshi Ohtani

Department of Chemical Engineering, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

(Received 3 February 1994; accepted for publication 23 March 1994)

Silicon dioxide thin films were prepared by a low-temperature atmospheric-pressure chemical vapor deposition method. The raw materials were tetrakis(diethylamino)silane and ozone in oxygen gas. The amorphous films were obtained at a substrate temperature above 200 °C. The films were superior in chemical stability and hardness to the films which were prepared from tetraethoxysilane and ozone.

Recently, the atmospheric-pressure chemical vapor deposition (CVD) method using tetraethoxysilane (TEOS) and ozone has attracted much attention because it gives better quality SiO<sub>2</sub> films at low deposition temperatures (350–400 °C).<sup>1,2</sup> In the meantime, the authors<sup>3</sup> proposed tetrakis(dimethylamino)silane {Si[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>} and ozone in oxygen gas as source materials. This system showed a characteristic low deposition temperature (≥40 °C), but the hardness of the deposited film is lower than that for TEOS-ozone system.

In this letter, tetrakis(diethylamino)silane {Si[N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>} and ozone in oxygen gas are proposed as source materials for obtaining SiO<sub>2</sub> films by the atmospheric-pressure CVD method. The deposition conditions, the structure, and hardness of the deposited film will be described in comparison with those for the CVDs from Si[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>-ozone<sup>3</sup> and TEOS-ozone system.

Figure 1 shows the schematics of the experimental apparatus and reactors. Tetrakis(diethylamino)silane (Shin-Etsu Chemical Co., Ltd.) was used as the silicon source. It is a liquid at room temperature. It was heated at a temperature of 60 °C, and the vapor was carried into the reactor with nitrogen gas as a carrier. The flow rate of the carrier gas was 300 cm<sup>3</sup>/min. The ozone was generated in an ozonator which converts a fraction of the incoming oxygen gas. The flow rate of oxygen gas was 100 cm<sup>3</sup>/min. A 6-W low-pressure mercury lamp (wavelength 184.9 nm) was used as the ozonator. The ozone and oxygen gas were mixed with the vapor

of silicon source in the entrance nozzle. Silicon (100) single-crystal wafers were used as substrates. In the reactor, the substrate was set horizontally. Depositions were made at atmospheric pressure. For comparison, the depositions from TEOS-ozone and Si[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>-ozone system were conducted in the same reactor under the same experimental conditions except the source temperature (40 °C).

The composition of the film was measured by x-ray photoelectron spectroscopy. The infrared spectra were obtained by means of a Fourier transform infrared spectrometer (Shimadzu FTIR-4300). The samples were prepared by depositing films on silicon single-crystal substrates. The dynamic hardness of the film was measured with an ultramicrodynamic hardness meter (Shimadzu DUH-200). The etch rate was obtained by dipping the film into the P-etching solutions which consisted of HF, HNO<sub>3</sub>, and H<sub>2</sub>O (HF:HNO<sub>3</sub>:H<sub>2</sub>O=3:2:69 in weight). Ozone concentration was measured by means of a multipurpose recording spectrophotometer. The absorbance at 253.7 nm showed that the ozone concentration for oxygen gas flow rate of 100 cm<sup>3</sup>/min was 463 ppm.

Transparent amorphous films were obtained at substrate temperatures above 200 °C. X-ray photoelectron spectroscopy showed that the films were near-stoichiometric SiO<sub>2</sub> without containing nitrogen. The films showed smooth surface morphologies, and the particle generations were very

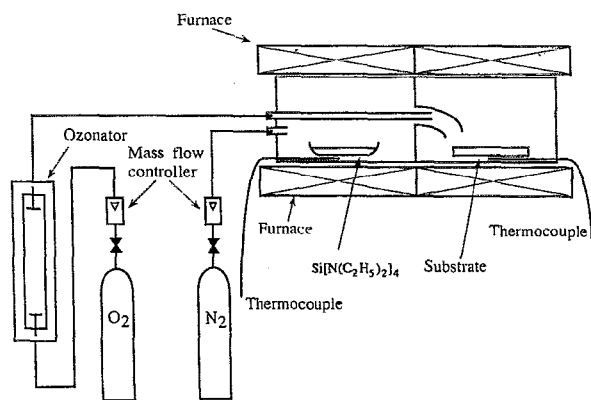


FIG. 1. Schematic representations of experimental equipment and reactors.

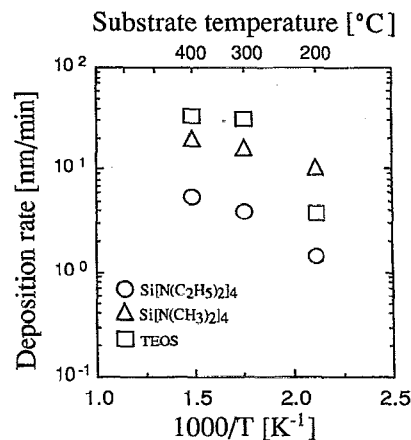


FIG. 2. Arrhenius plots of deposition rates.

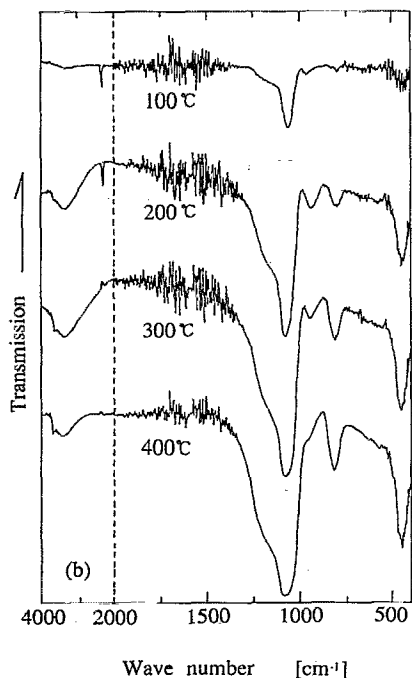
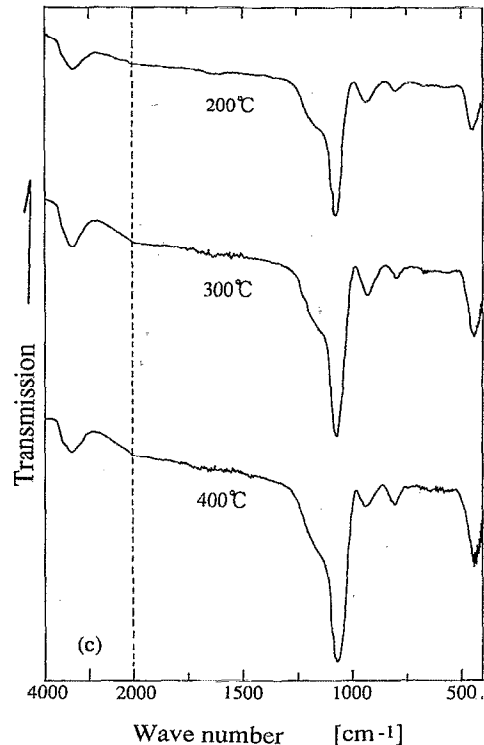
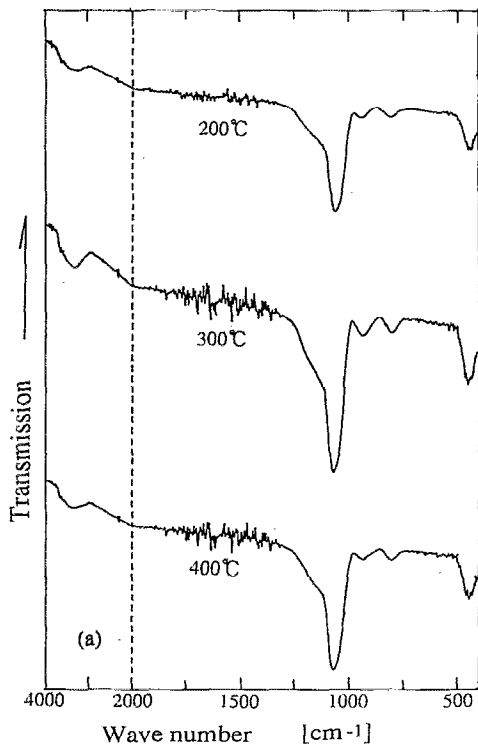


FIG. 3. IR transmission spectra of SiO<sub>2</sub> films prepared from (a) Si[N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>-ozone, (b) Si[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>-ozone, and (c) TEOS-ozone system.

low. When ozone is not contained in oxygen gas, no film was obtained under the experimental condition of this study (at substrate temperatures below 400 °C).

Figure 2 shows the Arrhenius plots of deposition rates. Also shown in this figure are the deposition rates of SiO<sub>2</sub> films prepared from Si[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>-ozone and TEOS-ozone system.<sup>5</sup> The deposition rate for Si[N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>-ozone system is lower than the latter.

Figures 3(a)–3(c) show infrared absorption spectra of

films deposited at some different substrate temperatures. The spectra are similar to each other; i.e., absorption peaks at about 1080, 800, and 460 cm<sup>-1</sup> represent Si-O-Si asymmetric-bond-stretching vibration, network Si-O-Si symmetric-bond-stretching vibration and network Si-O-Si bond-bending vibration. A trace of the Si—OH bond (absorption peak 3300 cm<sup>-1</sup>) can be identified. The peak around 950 cm<sup>-1</sup> is due to Si—OH bonds containing nonbridging oxygen atoms. Generally nonbridging oxygen gives rise to a

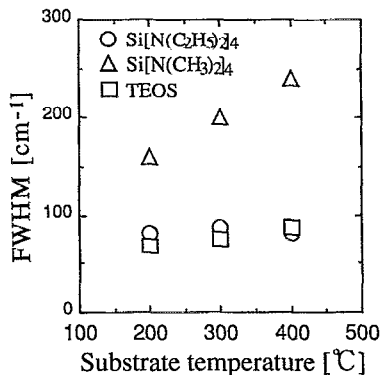


FIG. 4. Full width at half-maximum of the 1080  $\text{cm}^{-1}$  absorption peaks of IR transmission spectra as a function of substrate temperature.

polarized state in the  $\text{SiO}_2$  film which leads to chemical instability.<sup>4</sup>

Figure 4 shows the full width at half-maximum (FWHM) of the 1080  $\text{cm}^{-1}$  absorption peaks of infrared transmission spectra as a function of substrate temperature. The value of FWHM is nearly equal to that for TEOS-ozone system, and is much smaller than that for  $\text{Si}[(\text{CH}_3)_2\text{N}]_4$ -ozone system. Thus, the development of the Si-O-Si skeleton in the film prepared from  $\text{Si}[(\text{C}_2\text{H}_5)_2\text{N}]_4$ -ozone system is similar to that prepared from TEOS-ozone system.

Figure 5 shows the etch rate of the film dipped into the P-etching solution. With increasing substrate temperature, the etch rate decreases exponentially. It is nearly equal to the

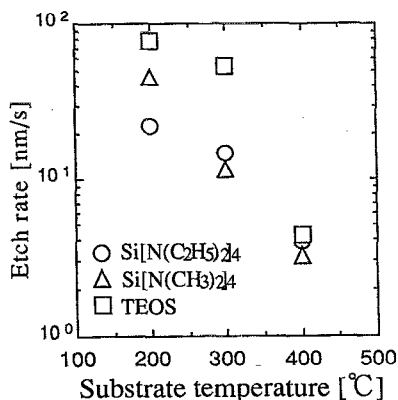


FIG. 5. Etch rate of  $\text{SiO}_2$  film as a function of substrate temperature.

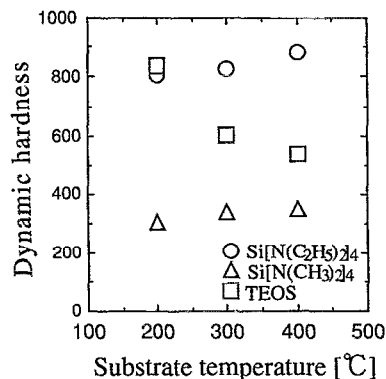


FIG. 6. Dynamic hardness of  $\text{SiO}_2$  film as a function of substrate temperature.

corresponding value for  $\text{Si}[(\text{CH}_3)_2\text{N}]_4$ -ozone system and smaller than that for TEOS-ozone system. The difference in etch rate is attributable to the difference in content of non-bridging oxygen in the film. As can be seen in FTIR spectra, the peaks around 950  $\text{cm}^{-1}$  for both  $\text{Si}[(\text{C}_2\text{H}_5)_2\text{N}]_4$ -ozone and  $\text{Si}[(\text{CH}_3)_2\text{N}]_4$ -ozone systems<sup>3</sup> are smaller than that for TEOS-ozone system.

Figure 6 shows the dynamic hardness of the film as a function of substrate temperature. It is nearly independent of the substrate temperature, being consistent with the results for  $\text{Si}[(\text{CH}_3)_2\text{N}]_4$ -ozone system. The film is harder than those for  $\text{Si}[(\text{CH}_3)_2\text{N}]_4$ -ozone and TEOS-ozone systems.

In conclusion, silicon dioxide thin films were prepared by a low-temperature atmospheric-pressure chemical vapor deposition method. The raw materials were tetrakis(diethylamino)silane and ozone in oxygen gas. The amorphous films were obtained at a substrate temperature above 200  $^{\circ}\text{C}$ . The films were superior in chemical stability and hardness to the films which were prepared from tetraethoxysilane and ozone.

This work was supported by the Ookura Foundation.

<sup>1</sup>Y. Ikeda, Y. Numasawa, and M. Sakamoto, *NEC Res. Develop.* **94**, 1 (1989).

<sup>2</sup>K. Kotani, M. Matsuura, A. Fujii, H. Genjou, and S. Nagao, *IEDM Tech. Dig.*, 1989, p. 669.

<sup>3</sup>T. Maruyama and T. Shirai, *Appl. Phys. Lett.* **63**, 611 (1993).

<sup>4</sup>H. Nagayama, H. Honda and H. Kawahara, *J. Electrochem. Soc.* **135**, 2013 (1988).