

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

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Silicon dioxide thin films were prepared by a low-temperature atmospheric-pressure chemical vapor deposition method. The raw materials were tetrakis(dimethylamino)silane and ozone in oxygen gas. At a substrate temperature above 40 °C, the thin films were obtained with a high deposition rate.

Silicon dioxide (SiO_2) thin films are widely used in the semiconductor industry for passivation and masking layers. High-quality SiO_2 layers have been traditionally prepared by the thermal oxidation of silicon. An alternative is to deposit SiO_2 by chemical vapor deposition (CVD) methods.^{1,2} Various CVD methods have been proposed; for example, silane-based CVD, and tetraethoxysilane (TEOS)-based CVD. Recently, the CVD method using TEOS and ozone has attracted much attention because of the possibility of lowering the process temperature.^{3,4}

In this letter, tetrakis(dimethylamino)silane ($\text{Si}[\text{N}(\text{CH}_3)_2]_4$) and ozone in oxygen gas are proposed as source materials for obtaining SiO_2 films by the CVD method. The deposition conditions, the structure, and hardness of the deposited film will be described in comparison with those for the CVD without mixing ozone and for TEOS/ozone CVD.

Figure 1 shows the schematics of the experimental apparatus and reactors. Tetrakis(dimethylamino)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 40 °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^3/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^3/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. Depositions were made at atmospheric pressure. For the CVD without mixing ozone, only oxygen gas was mixed in the same flow condition as that with mixing ozone. For comparison, the TEOS/ozone CVD was made under the same deposition conditions of this study. (The SiO_2 films could be obtained at substrate temperatures above 200 °C.)

Borosilicate glass plates and silicon (100) single-crystal wafers were used as substrates. In the reactor, the substrate was set horizontally.

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_3 , and H_2O (HF: HNO_3 : H_2O = 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^3/min was 463 ppm.

In the CVD with mixing ozone, transparent SiO_2 films were obtained at substrate temperatures above 40 °C. The lower limit of the substrate temperature is much lower than that for the CVD without mixing ozone, where the

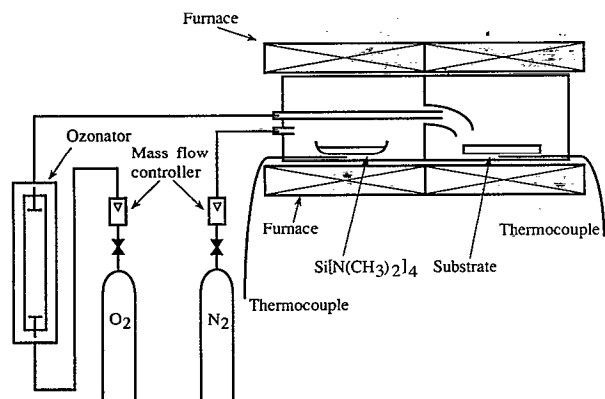


FIG. 1. Schematic representations of experimental equipment and reactors.

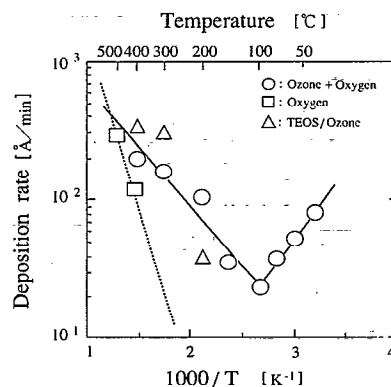


FIG. 2. Arrhenius plots of deposition rates.

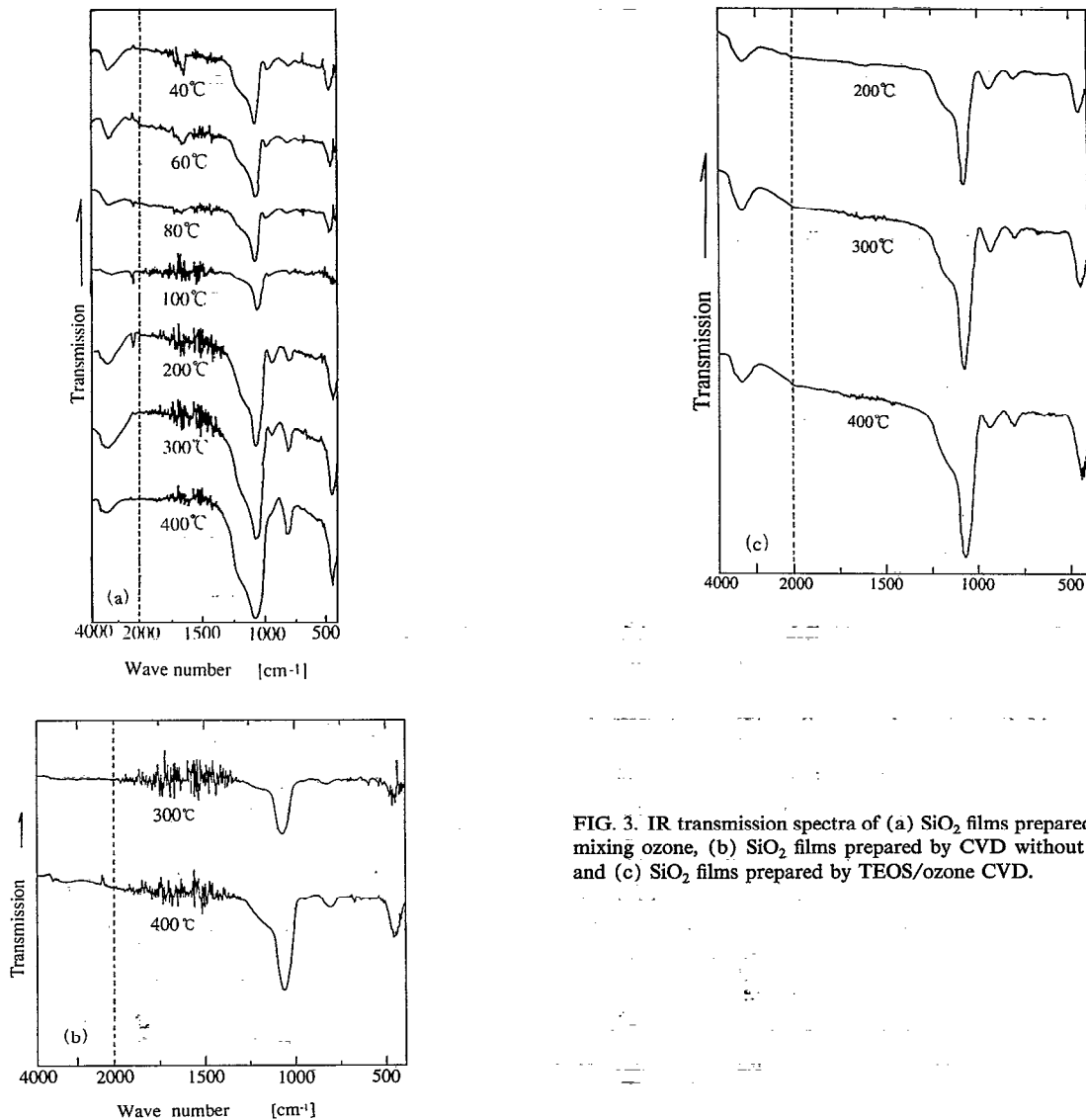


FIG. 3. IR transmission spectra of (a) SiO₂ films prepared by CVD with mixing ozone, (b) SiO₂ films prepared by CVD without mixing ozone, and (c) SiO₂ films prepared by TEOS/ozone CVD.

SiO₂ films could be grown at a temperature above 300 °C. The films prepared by the CVDs with and without mixing ozone showed smooth surface morphologies, and the particle generations were very low.

Figure 2 shows the Arrhenius plots of deposition rates. The deposition rate for CVD with mixing ozone is higher than that for the CVD without mixing ozone. For the CVD with mixing ozone, however, the deposition rate decreases with increasing substrate temperature in a temperature range 40–100 °C. This is probably because the adsorption of tetrakis(dimethylamino)silane on the substrate is dominating.

Figures 3(a)–3(c) show infrared absorption spectra of films deposited at some different substrate temperatures. Concerning the results for CVD with mixing ozone [Fig. 3(a)] and for TEOS/ozone CVD [Fig. 3(c)], the spectra are similar to each other; i.e., absorption peaks at about 1080, 800, and 460 cm⁻¹ 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 peaks at about 950 and 3300 cm⁻¹) can be

identified. Concerning the results for CVD without mixing ozone [Fig. 3(b)], however, the Si-OH peak remains essentially nonexistent.

Figure 4 shows the dynamic hardness of the film as a function of substrate temperature. It is nearly independent of the substrate temperature at a temperature above 200 °C, being consistent with the results of infrared absorp-

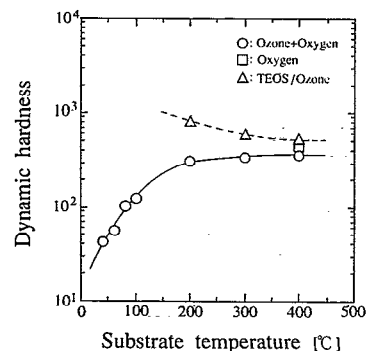


FIG. 4. Dynamic hardness of SiO₂ film.

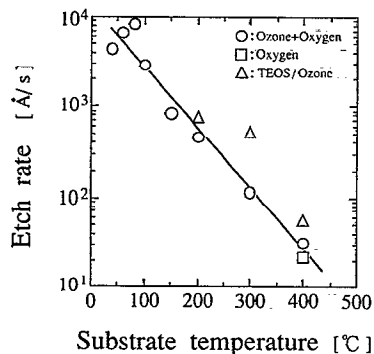


FIG. 5. Etch rate of SiO_2 film.

tion spectra. The corresponding values for TEOS/ozone CVD are a little larger.

Figure 5 shows the etch rate of the film dipped into the *P*-etching solution. With increasing substrate temperature,

the etch rate decreases exponentially. At a substrate temperature above 200 °C it is nearly equal to the corresponding value for TEOS/ozone CVD. Being consistent with the results of the dynamic hardness, the films prepared at temperatures below 100 °C prove to be of poorer quality.

In conclusion, silicon dioxide thin films were prepared by a low-temperature atmospheric-pressure chemical vapor deposition method. The raw materials were tetrakis(dimethylamino)silane and ozone in oxygen gas. At a substrate temperature above 40 °C, the thin films were obtained with a high deposition rate.

¹T. Maruyama and J. Shionoya, *Jpn. J. Appl. Phys.* **28**, L2253 (1989).

²T. Maruyama and T. Tago, *Thin Solid Films* (to be published).

³Y. Ikeda, Y. Numasawa, and M. Sakamoto, *NEC Res. Develop.* **94**, 1 (1989).

⁴K. Kotani, M. Matsuura, A. Fujii, H. Genjou, and S. Nagao, *IEDM Tech. Dig.* 669 (1989).