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

Toshiro Maruyama and Toshimasa Shirai
Department of Chemical Engineering, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

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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 (SiO₂) thin films are widely used in the semiconductor industry for passivation and masking layers. High-quality SiO₂ layers have been traditionally prepared by the thermal oxidation of silicon. An alternative is to deposit SiO₂ by chemical vapor deposition (CVD) methods. 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.

In this letter, tetrakis(dimethylamino)silane (Si[N(CH₃)₂]₄) and ozone in oxygen gas are proposed as source materials for obtaining SiO₂ 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 cm³/min. The ozone was generated in an ozonator, which converts a fraction of the incoming oxygen gas. The 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 cm³/min was 463 ppm.

In the CVD with mixing ozone, transparent SiO₂ 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...
SiO$_2$ 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-
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.

FIG. 5. Etch rate of SiO₂ film.

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.

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