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# Open air deposition of $SiO_2$ film from a cold plasma torch of tetramethoxysilane-$H_2$-Ar system

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A rf plasma beam was generated in the stream of atmospheric pressure argon to be exhausted from a cylindrical nozzle into air. The temperature measurements indicate a nonequilibrium low temperature nature of this plasma. By using this cold plasma torch, films were deposited on the substrates placed in air at growth rates higher than 100 Å/s by feeding tetramethoxysilane into the plasma. Fourier transform infrared spectroscopy and x-ray photoelectron spectroscopy revealed that the films were essentially $SiO_2$ and their structures and properties could be improved by admixing hydrogen in the plasma. The $SiO_2$ films deposited at a rate of 120 Å/s from $Si(OCH_3)_4$-$H_2$-Ar plasma had surfaces as smooth and hard as Corning 7059 glass.

High rate deposition of silicon-based ceramic thin films at low temperatures attracts much interest for its application to such purposes as electronic devices and protective coatings. The fabrication of silica films, in particular, has been extensively studied because of its significance in microelectronics. Thermal oxidation of silicon and high frequency plasma chemical vapor deposition (CVD) have been frequently used to make $SiO_2$ films.[1–4] Problems that remain to be solved include improvements of film growth rate and quality, as well as the decrease of deposition temperature. Glow discharge plasma is widely used for film deposition, etching,[5] surface cleaning,[6] and modification.[7] These plasma processes are usually carried out in chambers at pressures less than a few Torr, since conventionally used reactors cannot sustain homogeneous glow discharge plasma at higher pressures. Kanazawa *et al.* reported that an apparent glow discharge plasma was successfully generated in a glass chamber in which were placed condenser-type stainless steel electrodes with tungsten needles planted on the cathode and the grounded anode covered with a plate of dielectric material[8] in the atmospheric pressure helium. We employed such a plasma to the low temperature chemical vapor deposition of oxide films in view of the availability of high oxygen pressure and oxygen excitation desired for incorporating sufficient oxygen in the films.[9]

We further developed a microbeam plasma generator composed of a needle cathode and outer cylindrical anode covered with quartz tubing.[10] The plasma was generated by rf excitation of flowing helium at one atmosphere. By mixing helium with carbon tetrafluoride and methane, the beam plasma was verified to be applicable for high rate silicon etching[10] and carbon film deposition,[11] respectively. When helium was substituted for by argon, stable plasma was difficult to generate. By using a high dielectric constant insulating tubing, argon plasma was generated homogeneously as the helium plasma.[12] Based on our recent characterization of this plasma by a single probe method, optical emission spectroscopy, and the direct temperature measurement using a thermocouple, the electron temperature $T_e$ and gas temperature $T_g$ were evaluated to be 1.2 eV and 450 °C, respectively, for the Ar plasma generated in the torchtype apparatus using alumina as the dielectric material and by applying 40 W rf power.[12] Therefore, we designated this beam plasma generator as a "cold plasma torch."

The present letter reports on the application of an atmospheric pressure cold plasma torch to the deposition of $SiO_2$ films by the decomposition of tetramethoxysilane (TMOS).

The experimental setup of the cold plasma torch is shown in Fig. 1. The cathode is a tungsten needle (1 mm in diameter and 20 mm long) connected to a rf (13.56 MHz) generator. The grounded anode is a stainless-steel cylinder with 5 mm inner diameter and 15 mm long. An alumina tubing (5 mm outer diameter, 14 mm long, and 0.5 mm thick) is inserted between the cathode and anode to and from a cylindrical space with its inner and outer diameters of 1 and 4 mm, respectively. A plasma gas flows into and out of this space at a typical gas flow rate of 300 sccm.

Reactive cold plasma was generated by mixing TMOS (0.2–1 sccm) carried with Ar (5–25 sccm) and $H_2$ (0–5 sccm) into the argon plasma. The plasma beam has 4 mm diameter and lengths variable from 1 to 5 mm depending on the gas flow rate and the rf power. The applied rf power was 80–100 W. TMOS stored in a constant temperature bath at 0 °C was vaporized by bubbling argon and carried into the plasma generator. The substrates were Si(100) wafer, polished $Si_3N_4$ plate, Cu plate, and Corning glass 7059.

Film thickness was measured by the stylus method. Film morphology was examined by the high resolution scanning

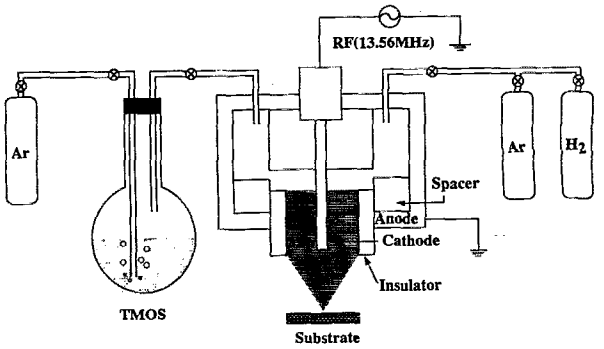


FIG. 1. Schematic diagram of cold plasma torch used for $SiO_2$ film deposition.



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TABLE I. Typical deposition conditions[a] and results of $SiO_2$ film deposition by the cold plasma torch.

| Flowrate (sccm) | | | Deposition | Carbon | Hardness |
|---|---|---|---|---|---|
| TMOS | $H_2$ | $O_2$ | rate (Å/s) | contents (at. %) | ($Kgf/mm^2$) |
| 1.0 | ··· | ··· | 1750 | ··· | |
| 0.5 | ··· | ··· | 572 | 7 | |
| 0.2 | ··· | 4.0 | 133 | 4 | |
| 0.2 | ··· | ··· | 167 | 3 | 345 |
| 0.2 | 1.0 | ··· | 133 | 2 | 627 |
| 0.2 | 3.0 | ··· | 120 | 1–2 | ··· |
| 0.2 | 5.0 | ··· | 117 | <1 | 832 |
| 0.1 | ··· | ··· | 92 | | |

[a]rf power: 90 W, Ar flowrate: 300 sccm. Substrates were not externally heated, but their surface temperature increased to about 300 °C (250 °C measured at the back surface by a thermocouple).

electron microscopy (FE-SEM) using Hitachi S4000. The bonding configuration in the films was analyzed by Fourier transform infrared spectroscopy using a Jasco FT/IR-3. The deposited film composition was determined by x-ray photoelectron spectroscopy (Mg K$\alpha$ 1254 eV) using a JEOL JPS-80.

Typical plasma conditions and film deposition results are summarized in Table I. With the increase in TMOS flow rate, the film deposition rate increased linearly. The films were deposited on various substrates such as Si(100) and Corning glass 7059 at essentially the same rates to have the same properties. When TMOS was decomposed by argon plasma without $H_2$ mixing, the deposition rate reached as high as 2000 Å/s. However, the film deposited at such a high rate had a carbon concentration higher than 5 at. % and its surface was rough and soft. The addition of $O_2$ from 1 to 5 sccm in the plasma resulted in a slight decrease in the film deposition rate without any appreciable improvement in the film properties. Then we examined the effect of $H_2$ addition to the plasma for reducing the carbon content in the film and to improve film quality, since the etching of carbon-containing films such as graphite had been reported to occur in $H_2$ plasma.[13]

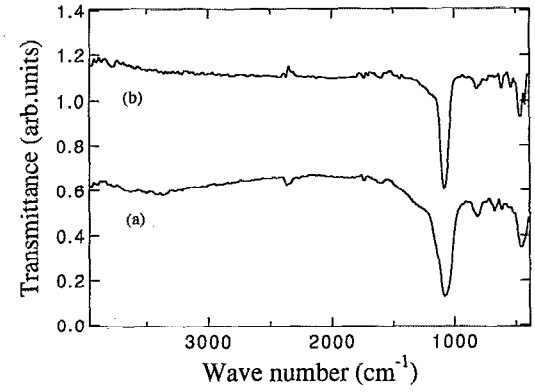


FIG. 3. FTIR spectra of $SiO_2$ film deposited at room temperature using TMOS-$H_2$ (a) and thermally oxidized silicon (b).

Figure 2 shows the film deposition rate from TMOS (0.2 sccm)-$H_2$-Ar (300 sccm) plasma as a function of $H_2$ flow rate. The increase in $H_2$ flow rate resulted in a considerable decrease in the film deposition rate. The excitation and decomposition of $H_2$ were confirmed by the presence of $H_2^+$, $H_\alpha$, and $H_\beta$ lines at 588.8, 656.3, and 486.3 nm, respectively, in the optical emission spectra of the hydrogen containing plasma. Atomic hydrogen apparently caused etching of the film surface that competes with film deposition to reduce the net deposition rate.[14] It must be noted that the deposition rate stayed at very high levels exceeding 100 Å/s even in the presence of hydrogen in the plasma. Hydrogen may also affect the decomposition mode of TMOS, since the formation of $CH_4$ was detected by gas chromatograhy of exhausting gas from a hydrogen containing plasma beam. Besides $CH_4$, the gases detected were Ar, $O_2$, $H_2$, and $N_2$ under the conditions of gas chromatography using a molecular sieve 5A column (5 mm×2 m) and He carrier at room temperature. Without $H_2$ addition, no peak corresponding to $CH_4$ was detected.

The Fourier transform infrared spectrum of the film deposition from TMOS (0.2 sccm) and $H_2$ (5 sccm) on a Si(100) substrate are shown in Fig. 3(a), together with the

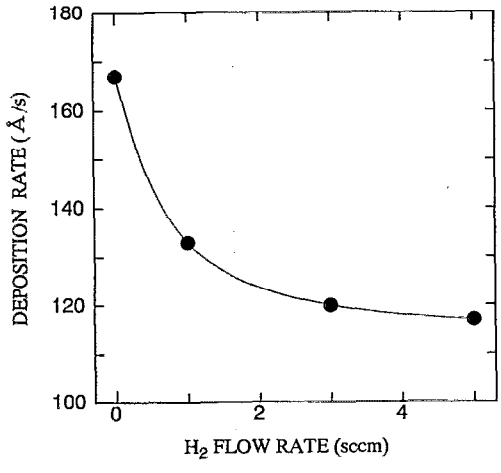


FIG. 2. Descending deposition rate of $SiO_2$ film as a function of $H_2$ flow rate (rf 90 W, TMOS 0.2 sccm).

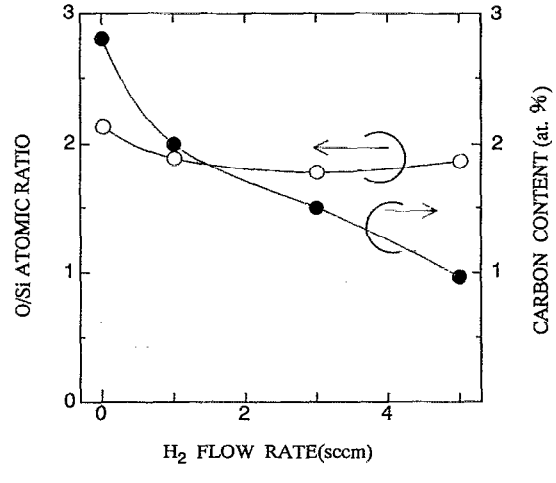


FIG. 4. O/Si atomic ratio (○) and carbon atomic percents (●) as a function of $H_2$ flow rate (rf 90 W, TMOS 0.2 sccm).

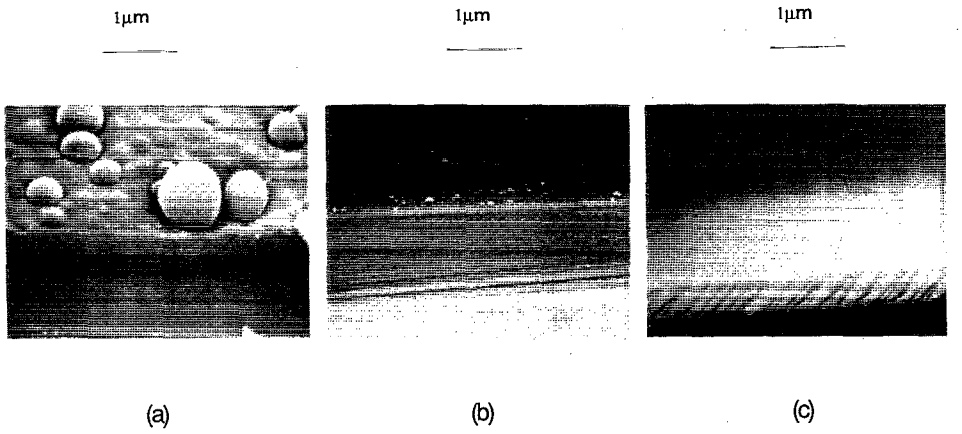


FIG. 5. Cross-sectional SEM photograph of $SiO_2$ film (a) 0 sccm, (b) 1 sccm, (c) 5 sccm of $H_2$ flow rate, respectively (rf 90 W, TMOS 0.2 sccm) $H_2$.

spectrum of thermally oxidized $SiO_2$ [Fig. 3(b)]. Both spectra are analogues to each other and have three characteristic absorption bands at 1080, 800, and 480 $cm^{-1}$ which are assignable to Si-O-Si stretching. Si-O-Si bending, and Si-O-Si rocking modes, respectively.[15] The deposited $SiO_2$ film shows weak and broad absorption(s) in the range between 3200 and 3600 $cm^{-1}$. The absorption is presumed to result from water which was adsorbed to or contaminated in the film. In some of the films deposited under the same conditions, we also observed a weak absorption around 950 $cm^{-1}$ which can be assigned to OH. By annealing the films at 500 °C for 1h, the absorptions in these ranges disappeared. No clear Si-H (2300–2100 $cm^{-1}$ stretching) and $CH_3$ (2975–2945 $cm^{-1}$) absorption bands were observed. The half-width and wave number of the $SiO_2$ stretching bands near 1080 $cm^{-1}$ were reported to be strongly dependent on the bonding environment, oxygen stoichiometry, and the density and porosity of film.[16] The film spectrum had the absorption centered at 1080 $cm^{-1}$ with a full width at half-maximum (FWHM) of 80 $cm^{-1}$. This FWHM value is only slightly larger than the value (70 $cm^{-1}$) observed in the spectrum for thermally oxidized silicon.

The compositional analyses of the films were carried out by x-ray photoelectron spectroscopy (XPS). The film composition was evaluated from the integrated XPS peak area of Si $2p$, O $1s$, and C $1s$. The XPS of films deposited from TMOS (0.2 sccm) and $H_2$ (0–5 sccm) on Si substrates are shown in Fig. 4. The XPS showed the carbon contamination of as much as 5 at. % in the film prepared from hydrogen free plasma. By mixing 5 sccm $H_2$ in the plasma, the carbon content was reduced below 1 at. %, whereas the O/Si ratio was scarcely affected and stayed about 2.0. Thus, essentially stoichiometric and carbon free $SiO_2$ films could be obtained from the hydrogen mixed plasma of the TMOS-Ar system.

Figure 5 shows a cross-sectional scanning electron microscope (SEM) image of $SiO_2$ films deposited on Si substrates at various $H_2$ flow rates. The surface morphology was remarkably improved by the mixing of $H_2$. Spherical structures about 0.5–0.8 $\mu$m in diameter are observed on the film surface deposited from the plasma without mixing $H_2$. With the increase of $H_2$ flow rates, the diameter of spherical structure decreased and disappeared. The film made by mixing 5 sccm $H_2$ at a rate of 120 Å/s was very smooth, homogeneous, and as hard as Corning glass 7059. The hardnesses measured by a SHIMADZU DHU-50 were 832, 2716, 1500, and 773 $Kgf/mm^2$ for the film, polished $Si_3N_4$ plate, Si(100) wafer, and Corning glass 7059, respectively.

In conclusion, $SiO_2$ films could be deposited on various substrates exposed to air at rates exceeding 100 Å/s by the plasma decomposition of mixtures of $Si(OCH_3)_4$ and $H_2$ using a cold plasma torch of our original design. The characterization of films by IR, XPS, and SEM revealed that the mixing of hydrogen was quite effective to reduce the carbon contamination and improve the film quality.

Further experiments to evaluate the step coverage are in progress using trenched Si(100) substrates.

[1] K. Fujino, Y. Nishimoto, N. Tokumasu, and K. Maeda, J. Electrochem. Soc. **137** 2883 (1990).
[2] K. Kawasaki, Y. Yoshida, and Y. Murayama, Jpn. J. Appl. Phys. **30**, 1803 (1991).
[3] I. T. Emesh, G. D'Asti, J. S. Mercier, and P. Leung, J. Electrochem. Soc. **136**, 3404 (1989).
[4] P. Pan, L. A. Nesbit, R. W. Douse, and R. T. Gleason, J. Electrochem. Soc. **132**, 2012 (1985).
[5] J. C. Arnold and H. H. Sawin, J. Appl. Phys. **70**, 5314 (1991).
[6] E. Taglauer, Appl. Phys. A **51**, 238 (1990).
[7] C. Morant, J. M. Sanz, and L. Galan, Phys. Rev. B **45**, 1391 (1992).
[8] S. Kanazawa, M. Kogoma, T. Moriwaki, and S. Okazaki, J. Phys. D: Appl. Phys. **21**, 838 (1988).
[9] H. Koinuma, K. Fukuda, M. Kogoma, S. Okazaki, T. Hashimoto, M. Kawasaki, and M. Yoshimoto, Proceedings of the International Symposium on Plasma Chemistry, Pugnochiuso, Italy **3**, 1521 (unpublished), Vol. 3, p. 1521.
[10] H. Koinuma, H. Ohkubo, T. Hashimoto, K. Inomata, T. Shiraishi, A. Miyanaga, and S. Hayashi, Appl. Phys. Lett. **60**, 816 (1992).
[11] K. A. Chaudhary, S. Yamada, K. Inomata, A. Takano, M. Yoshimoto, and H. Koinuma, Rep. Res. Lab. of Eng. Mat., Tokyo Institute of Technology (unpublished), Vol. 17, p. 163.
[12] K. A. Chaudhary, K. Inomata, T. Shiraish, G. J. Collins, and H. Koinuma (unpublished).
[13] H. Yasuda, and T. Hsu, Surf. Sci. **76**, 232 (1978).
[14] T. A. Brooks, D. W. Hess, J. Appl. Phys. **64**, 841 (1988).
[15] W. A. Pliskin, J. Vac. Sci. Techol. **14**, 1064 (1977).
[16] W. A. Pliskin and H. S. Lehman, J. Electrochem. Soc. **112**, 1013 (1965).