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ABSTRACT

Silica (SiO_2) film was deposited on the surface of soda lime silicate glass by immersing it in hydrofluosilicic acid (H_2SiF_6) solution supersaturated with silica gel at low temperature. The composition and the structure of these films were evaluated using ESCA, IRRS, fluoric acid etching test, and sodium leaching test, and they were compared with those of various silica films prepared by other methods. The results showed that these films made at low temperature had a dense structure and a great alkali barrier effect. By heat-treatment, the structure of this film became denser, getting close to that of fused silica. It was also found that the degree of supersaturation and the solution temperature had a great influence on the deposition rate.

Currently, soda lime silicate glass is widely used for the transparent electrode of flat panel displays such as liquid crystal display (LCD) and electroluminescent display (ELD).

In these cases, it is necessary to coat the glass substrate with silica film following transparent electroconductive film deposition (1). The purpose of the silica film is to prevent the alkali ion migration from the glass surface into transparent electroconductive film, which reduces the device lifetime.

Methods employed for making silica film, the vacuum method such as vacuum evaporation and sputtering, and the pyrolytic method such as dipping and chemical vapor deposition typically have been used up to now. However those methods have some disadvantages in actual use. The vacuum methods require expensive equipment, and the application to large areas of glass is difficult. Pyrolytic methods need high temperature exceeding 500°C to make silica film and this sometimes leads to glass deformation.

Considering these problems of conventional methods in silica film deposition, we found a new process named liquid phase deposition (LPD). In this LPD process a uniform and dense silica film can be deposited on a glass surface by immersing it in hydrofluosilicic acid (H_2SiF_6) supersaturated with silica (SiO_2) at room temperature. Furthermore, the process is simple to operate and the equipment required is very inexpensive.

In this paper, the coating conditions that influence the LPD process and the film properties are reported comparing them with those of various silica films prepared by other methods.

Experimental Techniques

Liquid phase deposition process.—The LPD process is indicated by Fig. 1. Industrial grade hydrofluosilicic acid (4 mol/l) was diluted with distilled water to make a 2 mol/l solution. Then 30g of silica gel was added to 1 liter (l) of this solution at the temperature of 35°C, and the solution was stirred for 16h at the same temperature. After stirring, the solution was filtered in order to remove undissolved silica. Thus the treatment solution saturated with silica was obtained.

Before immersing the glass, boric acid was added to the treatment solution. The quantity of added boric acid was 0.01-0.05 mol/l of treatment solution.

Boric acid reacts with fluoric acid in the treatment solution and makes the solution supersaturated with silica. Any other reagents that react with fluoric acid, for example NaOH or NH_4OH, can make the same solution condition. The mechanism of the reaction is discussed in the Results and Discussion section of this paper.

Then, the cleaned glass was immersed in this solution for a few hours at various temperatures. During the immersion silica deposition occurred preferentially on the glass surface and proceeded steadily with time. After being taken out of the solution, the glass was cleaned and dried. Some samples were heat-treated at different temperatures.

Preparation of other silica films.—Various silica films were prepared by vacuum evaporation (VE), dipping method (DIP), and chemical vapor deposition (CVD). Preparation conditions for them were derived from Ref. (2-4).

Characterization of SiO_2 film.—The compositional depth profile of the film was analyzed by ESCA(PHI-550). Si—O bond structure was evaluated by infrared reflection spectroscopy (IRRS) (5) using a Hitachi EPI-G2 IR spectrometer.

In addition the acid etching test (6, 7) was performed for the evaluation of the film density by use of the etchant comprising of 24 ml of HF [46 weight percent (w/o)], 11 ml of HNO_3 (60 w/o), and 900 ml of water at the temperature of 22°C.

For the evaluation of the barrier effect of SiO_2 film to prevent sodium migration from the glass surface, a sodium leaching test was carried out. In this test, SiO_2 coated glass 30 × 30 mm in size was prepared and immersed in 100 ml of water at 100°C for 24h. Then the sodium quantity in this water was analyzed by flame analysis. Sodium barrier effect of SiO_2 film was evaluated by comparing how much sodium was leached into the water.

Results and Discussion

The coating conditions.—The dependence of SiO_2 deposition rate on added boric acid quantity is indicated in Fig. 2. As the boric acid quantity was increased, the deposition rate increased linearly. Figure 3 shows the temperature dependence of the deposition rate. It is found in this figure that the deposition rate increased in proportion to the increase of the treating temperature.

These results may be due to the existence of two equilibria processes in the treatment solution. The one process is in the hydrofluosilicic acid (H_2SiF_6) as shown in equilibrium [1] (8)

$$H_2SiF_6 + 2H_2O \rightleftarrows 6HF + SiO_2 \qquad [1]$$

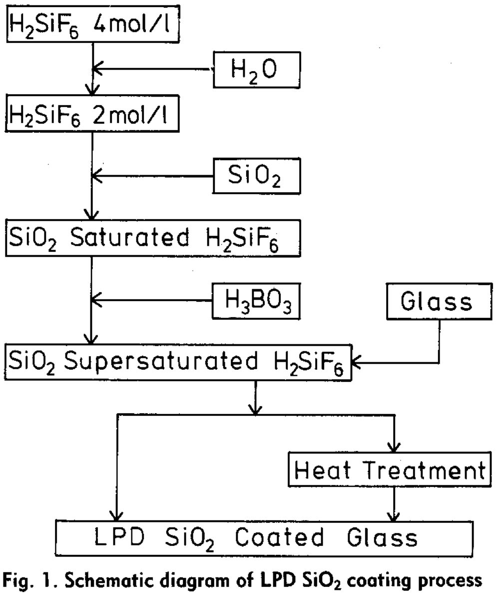

Fig. 1. Schematic diagram of LPD SiO_2 coating process

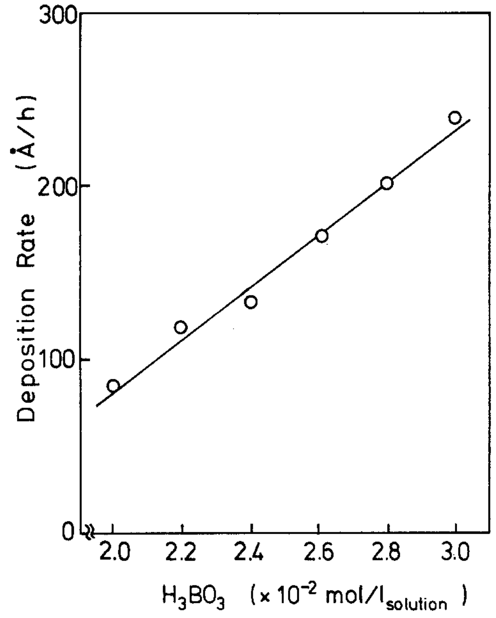

Fig. 2. Dependence of deposition rate on added H_3BO_3 quantity at 35°C.

In this equilibrium, the addition of SiO_2 leads the shift from right to left. Therefore the treatment solution comprising hydrofluosilicic acid saturated with silica may include hydrofluoric acid which was minimized in equilibrium [1].

However this equilibrium may be changed by the addition of boric acid to the treatment solution. Normally boric acid easily reacts with hydrofluoric acid as shown by equilibrium [2]

$$H_3BO_3 + 4HF \rightleftarrows BF_4^- + H_3O^+ + 2H_2O \qquad [2]$$

Accordingly, the addition of boric acid to the treatment solution leads to the consumption of the minimized hydrofluoric acid and brings about the transient state supersaturated with SiO_2 in equilibrium [1].

Such supersaturation of SiO_2 shifts the equilibrium process [1] from left to right following silica deposition mainly on the glass surface. The effect of boric acid on the SiO_2 deposition rate as seen in Fig. 2 is considered to be due to the change of SiO_2 supersaturation in equilibrium [1].

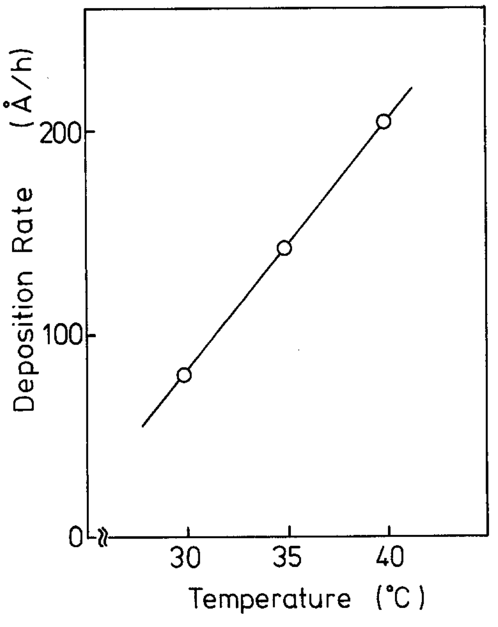

Fig. 3. Temperature dependence of deposition rate. 2.4 × 10^{-2} mol/l solution H_3BO_3 was added.

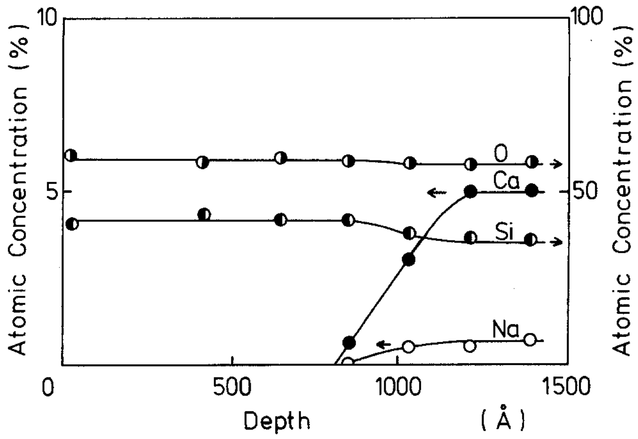

Fig. 4. Depth profile of LPD SiO_2 coated glass with a thickness of 930Å in as deposited state.

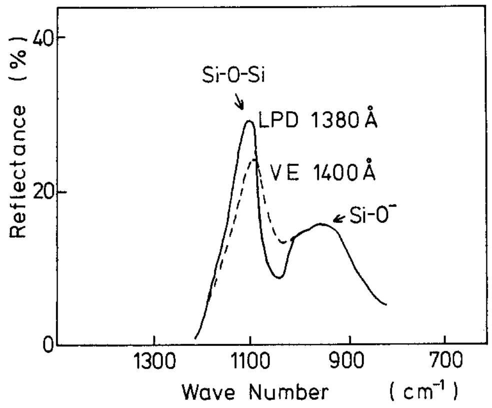

Fig. 5. IRRS comparison between LPD SiO_2 coated glass and vacuum evaporated SiO_2 coated glass.

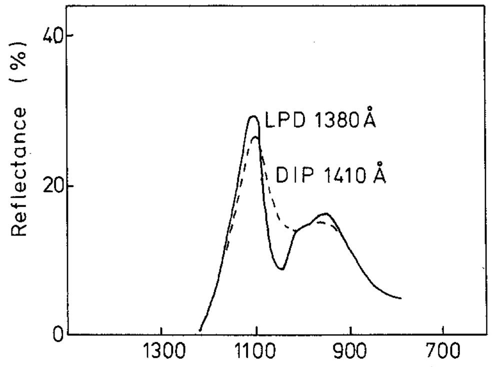

Fig. 6. IRRS comparison between LPD SiO_2 coated glass and dipping SiO_2 coated glass.

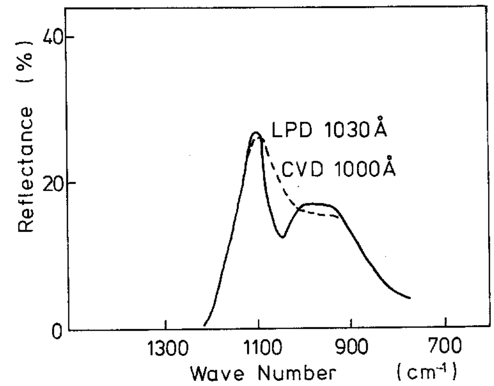

Fig. 7. IRRS comparison between LPD SiO_2 coated glass and CVD SiO_2 coated glass.

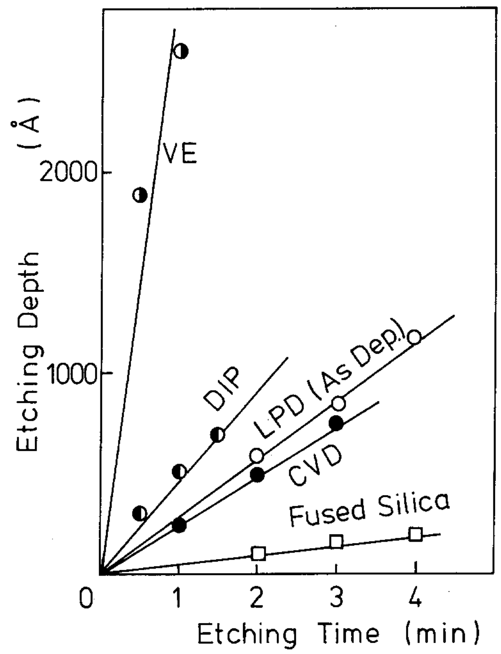

Fig. 8. Etch rate of various SiO_2 films

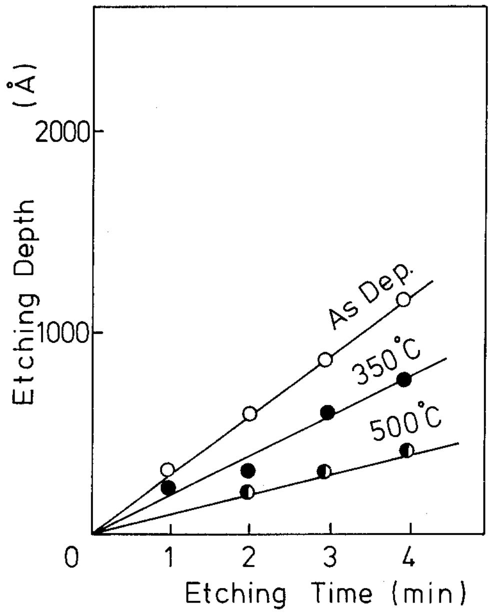

Fig. 9. Etch rate of heat-treated LPD SiO_2 films

As for the effect of the treatment temperature on SiO_2 deposition rate seen in Fig. 3, the solubility of SiO_2 in H_2SiF_6 solution should be discussed.

SiO_2 becomes more and more soluble in the H_2SiF_6 solution at lower temperature. In other words, the equilibrium [1] moves to the left at lower temperature, but if the H_2SiF_6 solution saturated with SiO_2 at 35°C is warmed to more than 35°C, there occurs the transient state supersaturated with SiO_2 in the H_2SiF_6 solution just as after the addition of boric acid. For this reason the SiO_2 deposition rate is enhanced at higher treatment temperature as seen in Fig. 3.

Characterization of LPD film.—Figure 4 is the compositional depth profile of the deposited layer with a thickness of 930Å analyzed by ESCA. The elements detected in overall depth equivalent to the thickness of deposited layer were only silicon [Si] and oxygen [O], and its ratio of atomic concentration was almost 2.0 in terms of [O]/[Si]. Furthermore none of the other elements such as sodium and calcium were detected in the same depth. From these results the deposited layer was found to be SiO_2 film.

Figures 5, 6, and 7 show IRRS spectra compared to the LPD SiO_2 film with SiO_2 films prepared by other methods in the order of the silica network. The intensive peaks around 1100 and 950 cm^{-1} are due to the stretching vibration of Si—O—Si bond and Si—O bond with nonbridging oxygen, respectively. Generally nonbridging oxygen gives rise to a polarized state in the SiO_2 film which leads to chemical instability.

From Fig. 5-7, it was found that the LPD SiO_2 film was richer in Si—O—Si bond compared with the other SiO_2 films. This implies that the LPD SiO_2 film has a more orderly silica network and consequently more chemical stability.

Figure 8 shows the results of the etching test using different SiO_2 films. The etch rate of LPD film is even lower in the as deposited state than it is in that of other SiO_2 films prepared by vacuum evaporation (VE) at 150°C and by dipping method (DIP) at 500°C. That is very close to the etch rate of CVD SiO_2 film prepared at 400°C. Such a low etch rate of LPD SiO_2 film may be derived from its superior chemical stability.

Table I. Results of Na leaching test

Sample	Leached Na ($\mu g/cm^2$)
Soda lime silicate glass	1.71
DIP SiO_2 1200Å	0.42
LPD SiO_2 1000Å (as deposited)	0.24
LPD SiO_2 1000Å (heat-treated at 500°C)	0.07

Furthermore LPD SiO_2 films become denser through heat-treatment as demonstrated in a lower etch rate in Fig. 9. Comparing Fig. 8 with Fig. 9, it is likely that LPD SiO_2 film approaches that of the fused silica in etch rate through heat-treatment.

Table I shows the sodium leaching test results comparing the effect of preventing sodium migration from the glass surface among soda lime silicate glass and the same glass coated with SiO_2 film. It is obvious in this table that SiO_2 film is greatly effective as an alkali barrier. Above all, it is noteworthy that LPD SiO_2 film, especially after heat-treatment, is superior to DIP SiO_2 film. Such an alkali barrier effect of the LPD SiO_2 film may be due to the orderly Si—O bond deduced from the fact in IRRS and the dense structure from the etch rate.

Even now when liquid crystal display (LCD) is in wide use, there is still the problem that the alkali ion migration from the front glass substrate into the liquid crystal layer reduces the device lifetime. LPD SiO_2 film is a very effective solution to this problem.

Conclusions

The liquid phase deposition (LPD) process was studied in order to form a uniform silica film on a glass surface at low temperature. The following can be concluded.

1. The deposition rate in this process is influenced by the solution temperature and the quantity of added boric acid, in other words, by the degree of supersaturation.
2. The LPD silica film prepared at low temperature has a dense structure and good chemical stability.
3. By heat-treatment the LPD silica film structure becomes denser getting close to that of fused silica.
4. The LPD silica film has a great alkali barrier effect.

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Etching of Tungsten and Tungsten Silicide Films by Chlorine Atoms

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ABSTRACT

Thin films of tungsten and tungsten silicide were etched both within and downstream from a Cl_2 plasma discharge at 200 mtorr pressure and temperatures below 150°C. When samples were positioned downstream from the discharge, etching proceeded solely by chemical reaction of the film with chlorine atoms. Without a discharge, molecular chlorine did not etch tungsten or tungsten silicide. Downstream and in-plasma tungsten etch rates were approximately equal at 110°C, but the chlorine atom etch rate dropped more rapidly than the in-plasma etch rate as temperature decreased. The chemical reaction between chlorine atoms and the tungsten film was proportional to the gas phase Cl atom mole fraction. A pretreatment consisting of either a dilute hydrofluoric acid dip or a short plasma etch cycle was necessary for atom etching of tungsten silicide films. The etch rates of tungsten silicide in Cl_2 plasmas were approximately an order of magnitude higher and less temperature sensitive than those in the downstream (atom) configuration.

The patterning of tungsten and tungsten silicide for microelectronic circuits has been accomplished by a variety of halogen-based dry processing etching techniques (1-8). Publications on the patterning of these materials using chlorine have only summarized the effects that the process parameters have on the anisotropy, etch rate, and selectivity (5). The limited results suggest that the etch rate of tungsten is related to the concentration of chlorine atoms, Cl, produced by either laser irradiation (8) or gas-phase electron impact dissociation (5) of molecular chlorine, Cl_2. However, the etching process was controlled empirically and thus is not based on a fundamental understanding of the etching mechanism.

Control of thin film etching processes during microelectronic device manufacture is often difficult. In large part, the difficulties arise from the complexity of RF glow discharges, coupled with plasma-film interactions. One method of simplifying the etch chemistry of these processes is to utilize an upstream discharge to generate reactive atoms for etching. Since ion, electron, and photon bombardment are absent in this configuration, the pure atom etch chemistry can be studied. Comparison of downstream etching with in-plasma or discharge etching then generates insight into the role of the plasma. Furthermore, such investigations yield fundamental information concerning atom reactions with materials. In this paper we present results on the chlorine atom etching (downstream or flowing afterglow reactor configuration) and Cl_2 discharge etching of tungsten and tungsten silicide thin films.

Experimental

The reactor used for plasma etching (in the discharge) has been described in an earlier publication (5). The flow reactor was modified for atom etching by connecting a discharge and flow tube upstream from the etching reactor. A schematic of the system can be found in Ref. (9).

An upstream RF discharge was used to dissociate Cl_2 molecules into Cl atoms, which then passed through a flow tube into the reactor where they reacted chemically with tungsten or tungsten silicide samples without the influence of the discharge. Power was supplied by a Tegal Corporation 300W RF generator and matching network to the upstream discharge via two 1.0 cm wide copper bands that were placed around the 3.8 cm diam quartz discharge tube. Spacing between the bands was 1.0 cm. A metal box enclosed the discharge area to ensure RF shielding and to facilitate forced air cooling of the tube. The 3.8 cm diam Pyrex flow tube contained two 90° bends to prevent light from the upstream discharge from reaching the reactor and thus the photomultiplier tube. The flow tube was coated with Halocarbon Corporation 1200 wax to minimize recombination of Cl atoms. The tubes and reactor were connected using MDC Corporation glass to metal Kwik-Flange adapters.

Samples were placed inside the 2.6 liter Pyrex reactor chamber on a temperature controlled 2.5 cm diam anodized aluminum rod that served as the lower electrode for plasma etching experiments. Rod temperature was varied from 25° to 150°C using heating tape and an Omega Engineering Incorporated Model 650/660 controller. In order to reduce the surface area for atom recombination and thus increase the atom concentration at the sample surface, the upper electrode was removed during tungsten atom etching experiments.

Molecular and atomic chlorine traveled approximately 60 cm from the discharge section to the sample location. The chlorine flow rate was controlled by a needle valve and measured with a rotameter. Vacuum was provided by a liquid nitrogen cold trap and a Busch Corporation Lotos corrosion resistant mechanical pump. The pressure in the reactor (200 mtorr) was established by a throttling valve at the exit from the reactor and was monitored by a capacitance manometer.

The gas phase chlorine atom concentration at the position of the sample was measured by titration with nitrosyl chloride (10-13). The NOCl titrant (Matheson) entered the reactor approximately 7 cm upstream from the sample location through a manifold to disperse gas evenly throughout the flow cross section. Flow rate was regulated by a needle valve and measured with a Tylan FM 360 mass flowmeter. Monel and Teflon were the materials used for the NOCl delivery system. A Hamamatsu R1928 photomultiplier tube with a Melles Griot 03FIV008 filter was used to monitor the 550 nm emission (chemiluminescence) resulting from the recombination reaction of chlorine atoms (9, 13, 14) at the position of the sample.

Tungsten films were prepared by sputter deposition and had a thickness of 100 nm and resistivity of 500 μΩ-cm.

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