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Preparation of Silicon Oxide Thin Film using Hydrofluorosilicic Acid

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규불화수소산을 이용한 실리콘 산화물 필름 제조에 관한 연구

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초 록 전형적인 금속산화물 형태의 필름은 광학적, 전기적 성질을 가지고 있어 많은 연구 분야에서 무기기능성 물질로서 널리 이용되고 있다. 현재 공정온도가 낮은 액상 증착법(LPD)은 다른 기술들과 달리 진공상태가 불필요하다는 점과 낮은 비용, 높은 생산성, 낮은 공정온도(< 50℃) 등의 장점으로 많이 연구되고 있다.

Silica 분말을 40wt% 규불화수소산에 첨가시켜 silica로 포화된 규불화수소산 용액을 생성시키고, 붕산용액을 연속적으로 첨가하여 과포화된 규불화수소산 용액을 제조하였다. 이렇게 형성된 과포화 용액에 기질물질인 slide glass를 침지시켜 silicon oxide 필름을 형성시켰다. LPD silicon oxide 필름은 붕산용액의 농도와 첨가된 H_2O양에 의해 두께가 두꺼워짐을 알 수 있었고, Raman Spectroscopy로 silicon이 담금 용액내에서 SiF_6^{2-} 형태로 존재하는 것을 알 수 있었다.

Abstract Typical metal oxide thin films having optical and electrical properties are widely used as inorganic functional materials. Liquid phase deposition(LPD) method, a new low temperature process, has been developed for the several advantages of no vacuum system, low cost, high throughput, and low processing temperature(< 50℃).

Silica powder was added to 40 wt% hydrofluoro-silicic acid(H_2SiF_6) to obtain an immersing solution of silica-saturated hydrofluorosilicic acid solution. Boric acid solution was continuously added in the range from 0 to 0.05M to prepare supersaturated hydrofluorosilicic acid solution. LPD SiO_2 film was formed with the variation of added amount of H_2O.

The SiO_2 thin film could be prepared from hydrofluorosilicic acid by LPD method. The thickness of LPD SiO_2 film was influenced by the boric acid concentration and added amount of H_2O. Silicon in thin film existed as SiF_6^{2-} by Raman spectrum.

Keywords : Liquid phase deposition(LPD) method, Silicon oxide(SiO_2) film, Hydrofluorosilicic acid(H_2SiF_6), Boric acid (H_3BO_3).

1. Introduction

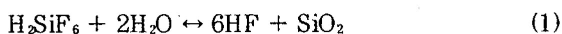
Silicon oxide is the most widely used insulator in the fabrication of semiconductor devices such as, gate insulator of metal-oxide-semiconductor (MOS) devices, the mask in the very large scale integrated (VLSI) circuit process, and the isolation layer between conductive lines. This material can be grown by many techniques including thermal oxidation, chemical vapor deposition (CVD), sputtering, E-gun evaporation, and spin-oil glass.[1~3] However all these techniques need either a vacuum system or high processing temperature. Recently, a new low temperature process, liquid phase deposition (LPD) has been developed for the several advantages of no vacuum system, low cost, high throughput, and low processing temperature (< 50℃).[2~6]

This technique was first used to form a metal oxide thin film on glass substrate to prevent the out-diffusion of alkali ions which may degrade the performance of the top liquid crystal displays (LCDs).[2,6] It was found that oxide could be deposited selectively on the substrate surface with this technique as long as the growth parameters are adjusted properly.[2,7]

T. Homma et al.[3] reported that LPD SiO_2 could be deposited only on the regions covered with hydroxyl (OH) group. Jenq-Shiuh Chou et al.[2,4] used silicic acid (SiO_2 : xH_2O) instead of silica powder to saturate hydrofluorosilicic acid at 30℃, and reported that the thick

LPD SiO_2 film was formed in the presence of native oxide on the substrate surface. Juichi Ino[5] reported that the LPD SiO_2 film adding organic dye was improved in the physical-chemical stability and coloring effect. But, the effects of different added amount of H_2O on the deposition process and the physicochemical properties of LPD SiO_2 were not clarified. Furthermore, the behavior of fluorine incorporated in the LPD SiO_2 film and the mechanism of the method are still unknown.[8~10]

The basic chemical mechanism of SiO_2 deposition were represented by the following two equilibrium reactions[2,4~7]:



$$H_2SiF_6 + 2H_2O \leftrightarrow 6HF + SiO_2 \quad (1)$$

$$H_3BO_3 + 4HF \leftrightarrow BF_4^- + H_3O^+ + 2H_2O \quad (2)$$

In this equilibrium, the addition of silica powder leads the shift from right. Therefore the treatment solution comprising hydrofluorosilicic acid saturated with silica may include hydrofluoric acid which was minimized in reaction (1). However this equilibrium may be changed by adding boric acid to the treatment solution. Normally Boric acid easily reacts with hydrofluoric acid, as shown in reaction (2). Thereby, the consuming of hydrofluoric acid brings the reaction (1) to the transient state supersaturated with SiO_2. This supersaturated SiO_2 enhances reaction (1) from left to right followed by silica deposition on the substrates.

In this study, the preparation of LPD SiO_2 film with hydrofluorosilicic acid (H_2SiF_6) was investigated to decide two parameters of initiator concentration and added amount of H_2O affecting to film properties, and to propose the models of film formation mechanisms.

2. Experimental

The preparation of LPD SiO_2 film was carried out in a system equipped with a PE vessel, a water bath, a dispenser of aqueous boric acid (H_3BO_3) solution, a magnetic stirrer, and a heater. A schematic diagram of the processes for preparing LPD SiO_2 film is shown in Figure 1. The 35g of amorphous silica powder (99.99%, ca. 0.45㎛ in diameter) was added to 1 liter of 40wt% of hydrofluorosilicic acid (H_2SiF_6) to prepare the silica saturated immersing solution without refining. Undissolved silica powder was removed by 0.45㎛ fine Teflon filter. To supersaturate this solution, the aqueous boric acid solution was continuously added into magnetically stirring beacker at 500 rpm in the range from 0 to 0.05M without refining. The reaction temperature was controlled at 30±2℃. Pure water was obtained from the purification of distilled water by Milli Q (Millipore Corp., Belford, MA) apparatus.

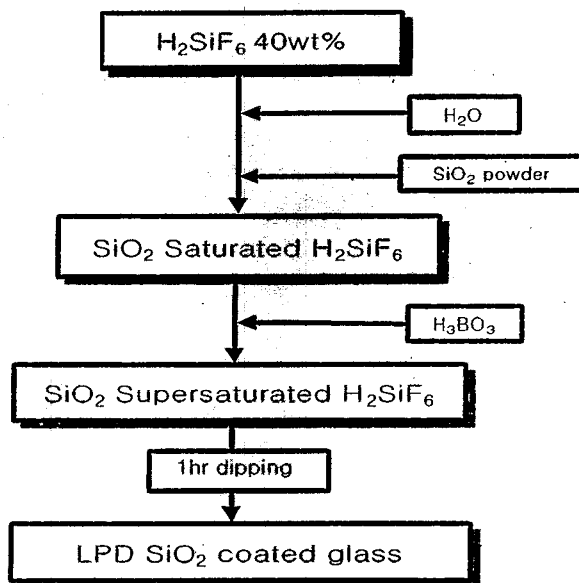


Fig. 1. Schematic diagram of the process for LPD SiO_2 deposition.

The slide glass was used as a substrate after cleaning with H_2O_2 + HCl (1 : 1) solution and acetone to remove the organic materials. The formed LPD SiO_2 film was rinsed with distilled-water and dried in room temperature (25±2℃) and atmosphere.

Chemical structure was analyzed by Fourier Transform Infrared spectroscopy (FT-IR). The Raman spectroscopy was used for investigation of reaction mechanism. The thickness of formed LPD SiO_2 film was measured by ellipsometer. And the formation condition of LPD SiO_2 film was analyzed by the SEM photograph.

3. Results and discussion

Figure 2 shows the FT-IR spectra of LPD SiO_2 films with the immersion time. (a)-(d) are the spectrum of LPD SiO_2 films for 1hr, 3hr, 5hr, and 15hr, respectively. This absorption band was similar to that found in the spectra of thermal oxide.[8] The thickness of LPD SiO_2 film was estimated from the peak intensity of FT-IR at $1090cm^{-1}$ which was attributed to Si-O-Si stretching.[10] From the relationship between the thickness or intensity of LPD SiO_2 film and immersion time, the peak intensity of Si-O-Si band ($1090cm^{-1}$) was decreased with the increasing of immersion time. The optimum immersion time was seem to be 1hr in this work, because of the high Si-O-Si band ($1090cm^{-1}$) intensity.

Figure 3 shows the thickness of LPD SiO_2 film as a function of boric acid concentrations. The thickness of

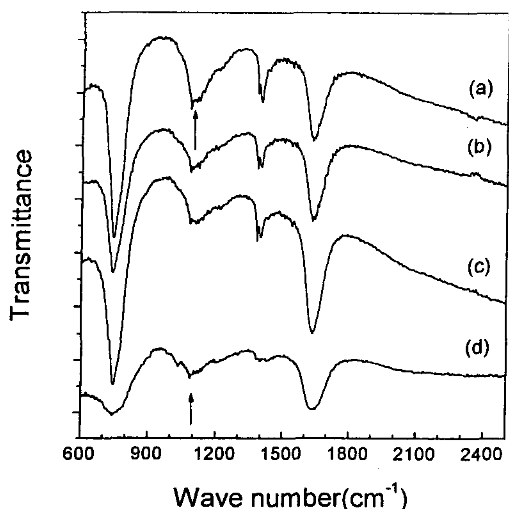


Fig. 2. FT-IR spectra of LPD SiO_2 films formed with different immersion time; (a) 1hr, (b) 3hr, (c) 5hr, (d) 15hr

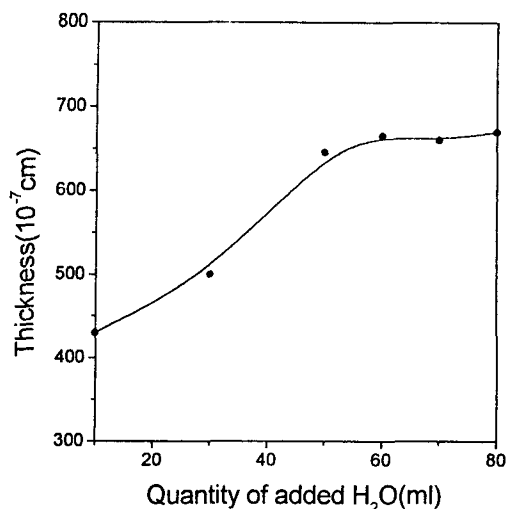


Fig. 4. Effect of added amount of H_2O on the thickness of LPD SiO_2 film.

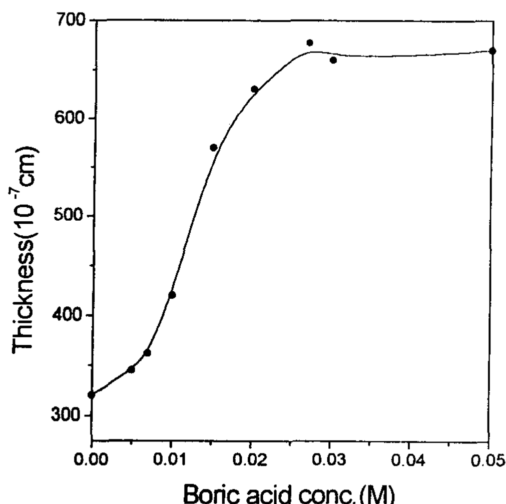


Fig. 3. Effect of boric acid solution on the thickness of LPD SiO_2 film.

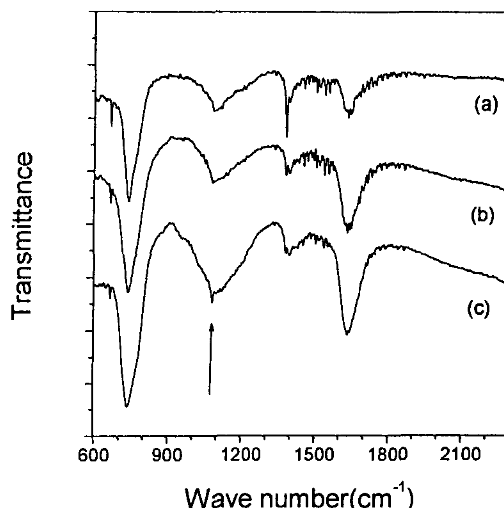


Fig. 5. FT-IR spectra of LPD SiO_2 films formed with different added amount of H_2O ; (a)20ml, (b)40ml, (c)60ml per 100ml immersion solution.

LPD SiO_2 film was increased as the boric acid concentration was increased. It was fixed to ca. 650±20Å in the range from 0.03 to 0.05M. But the supersaturated hydrofluorosilicic acid solution became gelation over 0.05M of boric acid. Clearly, more boric acid consumed more hydrofluoric acid and led to larger deposition rate. Moreover, the LPD SiO_2 film was formed in the absent of boric acid. This indicates the importance of the saturation level in the solution for the selective deposition.

Figure 4 shows the thickness of formed LPD SiO_2 film with the added amount of H_2O. The thickness of LPD SiO_2 film was increased with the increasing of added amount of H_2O. It was uniformly maintained by ca. 620Å over 60ml of H_2O. But, the crack was generated on LPD SiO_2 film from the excess adding amount of H_2O.

Figure 5 shows that the peak intensity of Si-O-Si band(1090cm^{-1}) in LPD SiO_2 film was increased with the increasing of added amount of H_2O. From the results of Figure 4 and Figure 5, the formation of LPD SiO_2 film was affected from the added amount of H_2O. Otherwise, initially formed LPD SiO_2 film was not affected from the added amount of H_2O.

The formation mechanism of LPD SiO_2 film was investigated in each solution and mixed solution of hydrofluorosilicic acid and boric acid from Raman spectra in Figure 6. The band at 650cm^{-1} is highly polarized and strongest. This indicates that the species responsible for the 650cm^{-1} band have a highly symmetric structure. Raman peaks at 400, 487, and 656cm^{-1} (strong) in $(NH_4)_2SiF_6$ and at 400, 475, and 662cm^{-1}

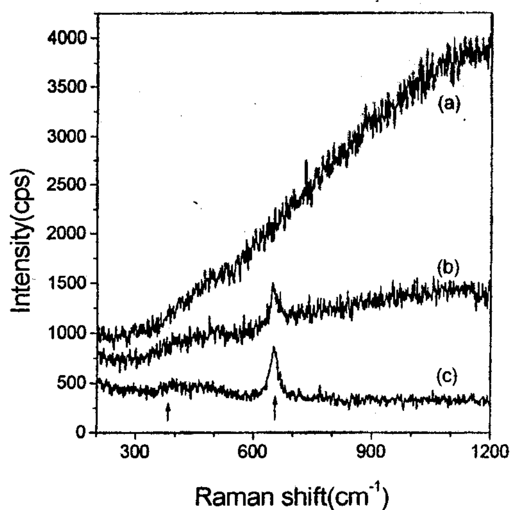
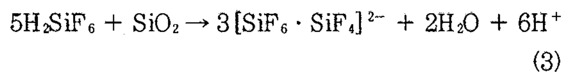
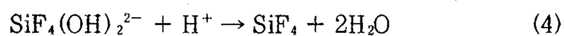


Fig. 6. Raman spectroscopy spectra of (a) boric acid solution, (b) supersaturated solution with silica and boric acid, and (c) hydrofluorosilicic acid solution.

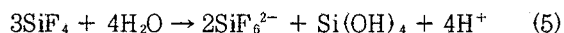
(strong) in $Li_2SiF_6 \cdot 2H_2O$ were reported.[10] Therefore, peaks at 390, 460, and 650cm^{-1} could be causedby SiF_6^{2-}. It could be considered that silicon existed as SiF_6^{2-} due to the single peak at 650cm^{-1}. These Raman results support the reaction model stated in reaction (3), (4), and (5).



$$5H_2SiF_6 + SiO_2 \rightarrow 3[SiF_6 \cdot SiF_4]^{2-} + 2H_2O + 6H^+ \quad (3)$$

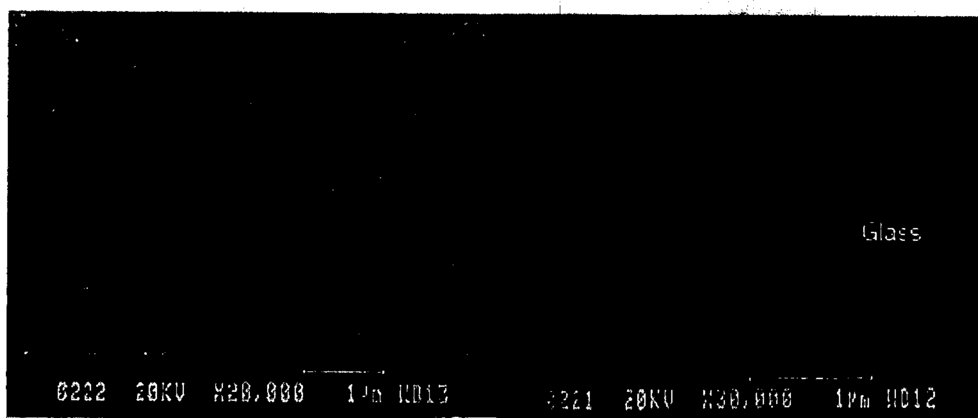


$$SiF_4(OH)_2^{2-} + H^+ \rightarrow SiF_4 + 2H_2O \quad (4)$$

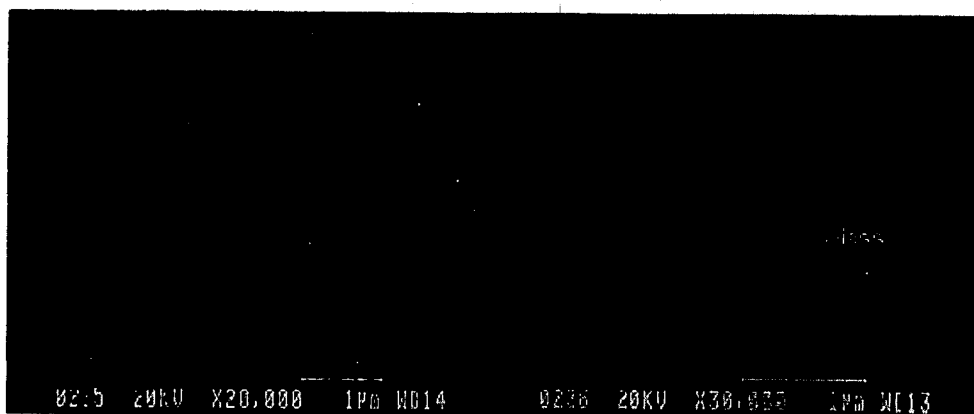


$$3SiF_4 + 4H_2O \rightarrow 2SiF_6^{2-} + Si(OH)_4 + 4H^+ \quad (5)$$

Figure 7 shows the SEM photographs of plane-sectional and cross-sectional view of LPD SiO_2 film on the substrate with the boric acid concentrations, respectively. The particle of LPD SiO_2 was irregularly grown with the increasing of boric acid solution in the plane-sectional view. And LPD SiO_2 film was formed thickly and unsmoothly in the cross-sectional view. This indicates that the boric acid concentration have an



(a)



(b)

Fig. 7. SEM photographs of the plane-sectional and cross-sectional view of LPD SiO_2 film with boric acid concentration; (a) 0.01M, (b) 0.03M

effect on the LPD SiO_2 film formation.

It was difficult to prepare the homogeneous LPD SiO_2 film on the substrate. Further study was required for the preparing of homogeneous LPD SiO_2 film and applicable reproducibility.

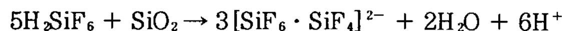
4. Conclusions

The formation of SiO_2 film was investigated by liquid phase deposition (LPD) method in silica-saturated hydrofluorosilicic acid solution with the addition of boric acid and H_2O.

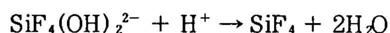
1) The formation of LPD SiO_2 film was influenced by the initial reaction time, the boric acid concentration, and the added amount of H_2O in supersaturated hydrofluorosilicic acid solution.

2) LPD SiO_2 film was formed on the substrate in the range from 0 to 0.05M of boric acid solution and from 0 to 80ml of added amount of H_2O.

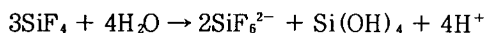
3) Silicon was existed as SiF_6^{2-} in the silica-saturated solution by Raman spectroscopy. This result support the following reactions models;



$$5H_2SiF_6 + SiO_2 \rightarrow 3[SiF_6 \cdot SiF_4]^{2-} + 2H_2O + 6H^+$$



$$SiF_4(OH)_2^{2-} + H^+ \rightarrow SiF_4 + 2H_2O$$



$$3SiF_4 + 4H_2O \rightarrow 2SiF_6^{2-} + Si(OH)_4 + 4H^+$$

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