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Depositing Mechanism of Metal Oxide Thin Film in the Liquid Phase Deposition Process

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The equilibrium reaction of fluorosilicate ion (SiF_6^{2-}) in the LPD method was investigated by the measurement of UV and IR spectroscopies, Raman spectroscopy. These measurements were carried out by adding the F- scavenger such as H_3BO_3 and Al metal which shifts the equilibrium reaction. Also, the concentration of Si dissolving species was measured after addition of fine α-Al_2O_3 powder. These species were estimated to be involved in the LPD process as intermediates and important for controlling the deposition process of metal oxide.

1. Introduction

The liquid phase deposition method is known as the direct deposition technique using ligand exchange hydrolysis of metalfluoro complex and F- consumption reaction with H_3BO_3 or Al metal(1-5). One of the characteristics of this technique is that it utilizes the shift of the equilibrium reaction as follows;

$MF_{x(x-2n)-} + nH_2O \leftrightarrow MO_n + XF^- + 2nH^+$ [1]
$H_3BO_3 + 4HF \leftrightarrow BF_4^- + H_3O^+ + 2H_2O$ [2]
$Al + 6HF \leftrightarrow H_3AlF_6 + 3/2H^2$ [3]

The formation of the metal oxides in the solution is thought to proceed via the equilibrium reaction [1], which shifts to right-hand side upon the addition of H_3BO_3 or Al metal (F- scavenger) which readily react F- ions to form more stable complex ions. The shift of the equilibrium reaction was precisely controlled by the amount of F- scavenger. This is one of the remarkable characteristics of the LPD method using F- complex ion, because it leads to lots of advantages including the precise control of the thickness, fabrication of the thick film and continuous deposition system.

Previously, various kinds of the metal oxide films were prepared by the LPD method(6-8). The metal oxide thin film deposits on the substrate materials through nucleus-growth and induction periods. Details of initial state of the LPD reaction have been studied in ref.8. Among of all, silicon dioxide thin film is the first material successfully prepared by this method, which has been industrially used for alkali passivation film for the substrate of LCD (Liquid Crystal Display) (9-10). The equilibrium reaction of SiO_2 system has been explained by following equation.

$SiO_2 \cdot xH_2O + 6HF \leftrightarrow H_2SiF_6 + (2+x)\ H_2O$ [4]

Although the equilibrium in the reaction solution is not known so much, it is worthwhile to investigate for improving the controllability of the system. However the detailed reaction has not been sufficiently investigated. A part of the reason is because the aqueous reaction system including F^- ion is very complicated. Intermediate species in the equilibrium reaction of SiF_6^{2-} anion and oxides have been studied for gaseous reaction using plasma(11), and surface finishing of Si wafer and its related materials(12) using various kinds of spectroscopic measurements. However, there are few studies for the equilibrium reaction of SiF_6^{2-} complex anion species in the oxide deposition in liquid phase, whereas the equilibrium condition and reaction constant have been studied in detail(13-15). In this study, we focus the dissolving species, SiF_4 which can be detected as the intermediate species in the gaseous phase with the vaporization of the reaction solution in the LPD process. We discuss the equilibrium reaction in the measurement of UV and IR absorption spectra, vapor pressure and electric conductivity.

Also, in order to discuss the effect of surface reaction area of the substrate, the various amounts of alumina powder samples were used as substrate. Influence of substrate, consumption of Si in the reaction solution, and deposition rate were investigated. Also, during the LPD reaction, the Raman spectra of reaction solution were measured in order to discuss the variation of the dissolving species.

2. Experimental

Various evaluation methods were combined to detect the molecular and ion species in H_2SiF_6 solution in this study. In order to identify the species, the equilibrium reaction was shifted by adding the materials involved in the reaction such as H_3BO_3 (Nacalai Tesque Co.), Al metal (Sun Aluminum Ind. Co.), SiO_2, HF (Stella Chemifa Co.). Each measurement method is described in the following section.

2.1 UV spectrum

UV spectrum measurement was carried out in the wavelength range of 190 - 300 nm by using UV-Visible spectrometer (JASCO, UVIDEC-660). Aluminum oxide single crystal (sapphire) was used for UV window material. The other materials in contact with the H_2SiF_6 solution are made from Teflon and Viton for avoiding corrosion and contamination.

2.2 IR and Raman spectra

IR spectrum measurement was carried out in the wave number range of 4000-400 cm^{-1} by using IR Spectrophotometer (JASCO, A-302). The solution was sandwiched with a pair of KRS-5 plates. Raman spectra of the reaction solution were measured after the separation procedure by Horiba T-64000 excited by 532 nm Nd:YVO_3 second harmonic wave.

2.3 Deposition of SiO_2 on α-Al_2O_3 powder

For the substrate α-Al_2O_3 (Showa Denko K. K., 10.6 m^2 g^{-1}) were used. As a pretreatment, α-Al_2O_3 powders are calcinated at 400 ºC for 2 hours in the air. α-Al_2O_3

and treatment solution were mixed in the appropriate proportion ultrasonically or with pestle and mortar. Solid content, ϕ was determined as below.

$$\phi = \frac{W_{solid} / d_{solid}}{W_{liquid} / d_{liquid} + W_{solid.} / d_{solid}} \qquad [5]$$

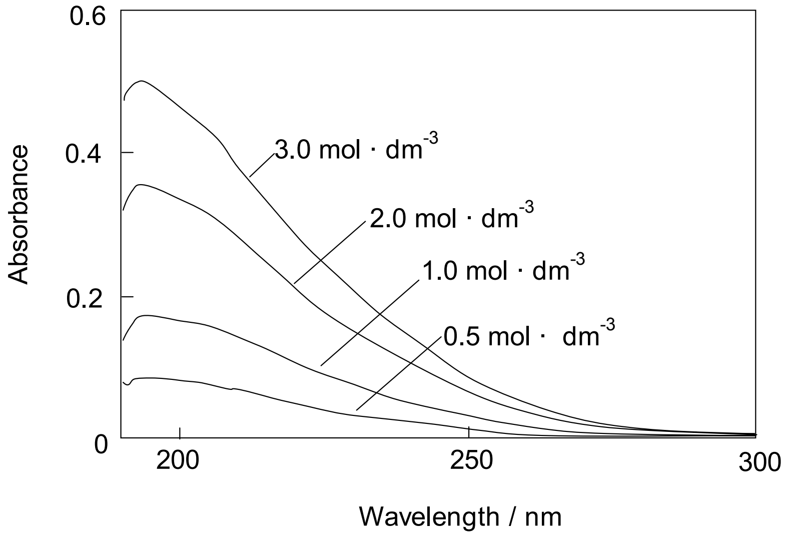
where W_{liquid}, d_{liquid}, W_{solid}, and d_{solid} are the weight of the liquid phase, the density of the liquid phase, the weight of the solid phase and the density of the solid phase, respectively.

The reaction cell was kept 30°C. When solid content was low and sedimentation of alumina might occur, reaction cell was under shaking condition. When solid content was high, reaction cell kept stationary.

After an appropriate reaction time, the reaction solution and precipitation were separated by either way of two. In the first way the solution was ion-exchanged water, and centrifuged at 12,000 rpm for 5 minutes, then supernatant was decantated. The precipitates were ultrasonically washed in ion-exchanged water, as to remove the reaction solution. The treatment was repeated by three times. In the other way the solution filtered by membrane filter and precipitates were washed by ion-exchanged water several times. Finally, the obtained powders were dried at 50 ºC in the air. The deposited SiO_2 was dissolved with dilute hydrochloric acid HCl (Nacalai Tesque Inc.). The amount of Si contained in deposition was measured by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES; HORIBA Ltd., ULTIMA 2000).

3. Results and Discussion

3.1. UV spectra



Fig,1. UV spectra of H_2SiF_6 solution

Fig. 1 shows the UV spectra of H_2SiF_6 solution. A broad absorption band appeared in the wavelength region less than 300 nm and increased as the concentration of H_2SiF_6 increased. Herein the absorption is assigned to the ion species in H_2SiF_6 solution. Fig. 2 shows the differential spectra of H_2SiF_6 solution when H_3BO_3 acid or HF acid were added to the solution, which can shift the equilibrium reaction of H_2SiF_6 solution as mentioned above. In this figure, the spectra were indicated by subtracting the spectrum before adding the additives. For adding H_3BO_3 acid, the absorption at around

240 nm increased with increasing the amount of additives. On the other hand, it decreased with the addition of HF acid.

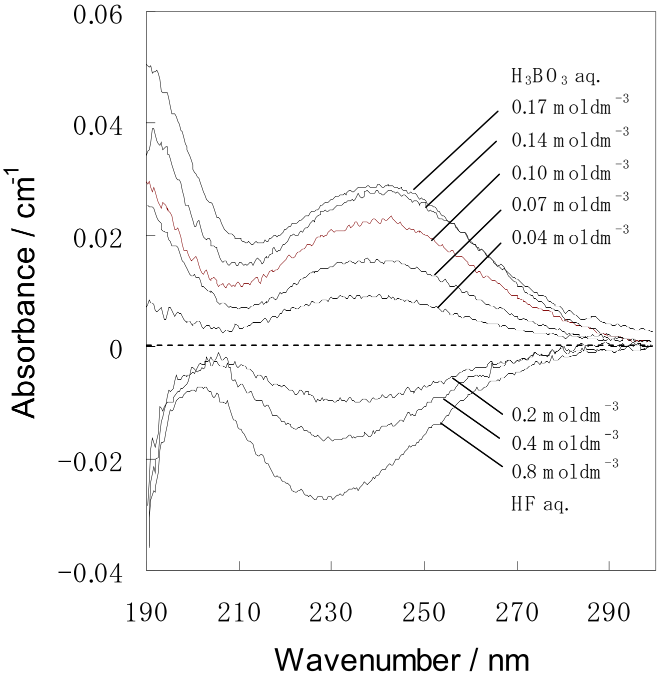


Fig.2. Effect of adding H_3BO_3 acid or HF acid on differential UV spectra. Concentration of H_2SiF_6 solution is 1 mol dm^{-3}.

Fig. 3 shows that the differential spectra of H_2SiF_6 solution when Al metal or SiO_2 acid were added to the solution. In this case, the spectra shows similar variation in the case of adding H_3BO_3 acid or HF acid. The fact that the variations of the absorbance appeared at almost same wavelength suggests that the absorption is attributable to the same ion species. However, the assignment of this UV absorption in the H_2SiF_6 solution has not been known generally. Thus, the possible ion species attributed to the absorption was tried to be estimated from the chemical equilibrium reaction. The shift of the equilibrium reaction brought from the additives was expressed by the following equation.

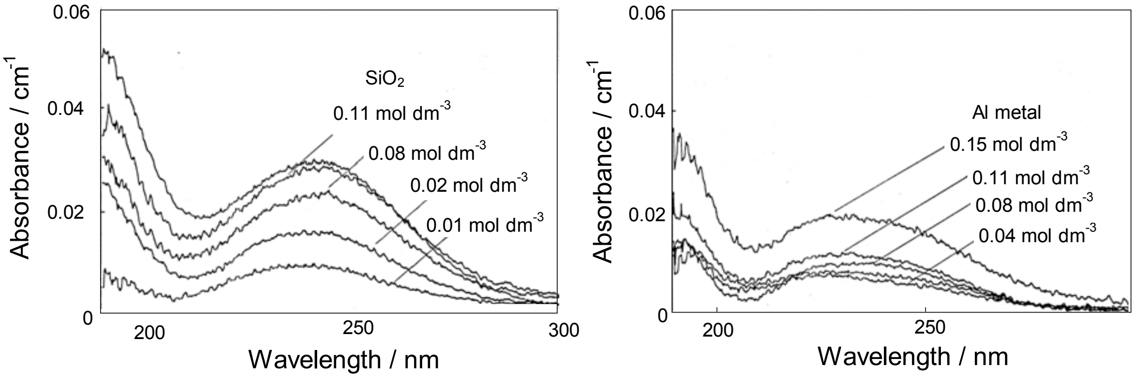
Adding H_3BO_3 or metal Al system (F- scavenger) (16),

$$SiF_6^{2-} + (2+x)H_2O \rightarrow SiO_2\ xH_2O + 6H^+ + F^- \qquad [6]$$

$$SiF_6^{2-} \rightarrow SiF_4 + + 2F^- \qquad [7]$$

$$2\ SiF_6^{2-} + 2H^+ \rightarrow [SiF_6 \cdot SiF_4]^{2-} + 2H^+ + F^- \qquad [8]$$

Here, F- was trapped by the F- scavenger according to the equations [2], [3].



(a) SiO_2 adding system

(b) Al metal adding system

Fig.3 Effect of adding SiO_2 or Al metal on differential UV spectra.

Adding SiO_2 system

$$2\ SiF_6^{2-} + 4H^+ + SiO_2 \cdot \rightarrow 3\ SiF_4 + 2H_2O \qquad [9]$$

The presence of the equation [8] showing the existence of $[SiF_6 \cdot SiF_4]^{2-}$ was reported in the previous research by Busey et al.(17) The shift by adding the HF acid is explained by the inverse reactions of Eqs.[6-8]. Considering these reactions, the possible ion species that increase or decrease by the additives are $SiO_2 \cdot xH_2O$, SiF_4 and $[SiF_6 \cdot SiF_4]^{2-}$. Among them, $SiO_2 \cdot xH_2O$ is not considered theoretically to have absorption at around the 240nm. And the Rayleigh scattering come from polysilicic acid is also difficult to explain, because the scattering should increase exponentially with the wavenumber. Therefore, there is a possibility that SiF_4 or $[SiF_6 \cdot SiF_4]^{2-}$ are assigned to the absorption. These species come from equilibrium reactions [7], [8] may have a roll as intermediates in the LPD process according to the following equation.(18)

$$SiF_4 + 2H_2O \rightarrow SiO_2 + 4F^- + 4H^+ \qquad [10]$$
$$[SiF_6 \cdot SiF_4]^{2-} + 2H_2O \rightarrow 2SiO_2 + 10F^- + 4H^+ \qquad [11]$$

Therefore, the reaction is considered to be very important in controlling the LPD process. In the following sections, we will focus on these ion species through the measurement of other properties.

3.2 IR absorption spectrum – contribution of $[SiF_6 \cdot SiF_4]^{2-}$ to equilibrium of dissolving species

Fig.4 shows the IR spectra of H_2O and H_2SiF_6 solution at the wavelength of 4000 - 1500 cm^{-1}. In H_2SiF_6 solution, broadened absorption appeared at around 2800cm^{-1} and 1800cm^{-1} beside the H_2O absorption spectrum. Giguere et al.[18)] reported that the absorption at 2900cm^{-1} and 1730cm^{-1} absorption arisen from H_3O^+ in acid solution shift to low wavelength side and high wavenumber side respectively in HF acid due to a strong interaction between H_3O^+ and F^-. Also the absorption at around 3600 - 3200 cm^{-1} shift to high wavenumber in comparison with that of H_2O absorption. It is caused that H-F stretching bands exist in HF – H_2O molecular complex. These results show the presence of free HF species in H_2SiF_6 solution, which is consistent with the discussion at the vapor pressure. Fig.5 shows the IR spectra of H_2SiF_6 solution adding Al metal or SiO_2 at the wavenumber of 600 – 400cm^{-1}. Strong ν_4 absorption band of SiF_6^{2-} was observed at 740cm^{-1} and clearly shifted to lower wavenumber with adding the additives.

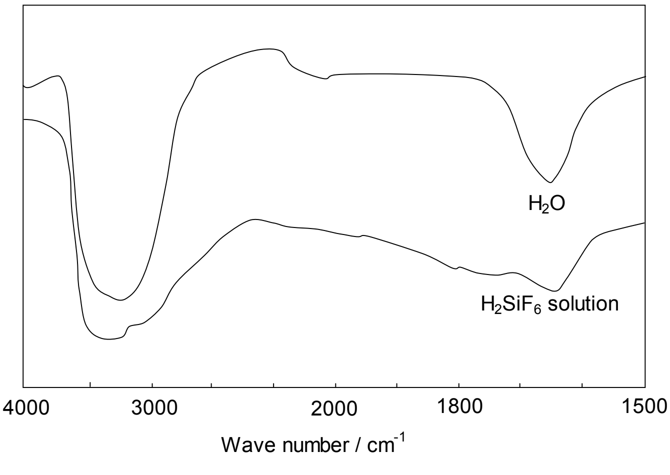


Fig 4. IR spectra of H_2O and H_2SiF_6 solution at the wavenumbers of 4000 - 1500 cm^{-1}.

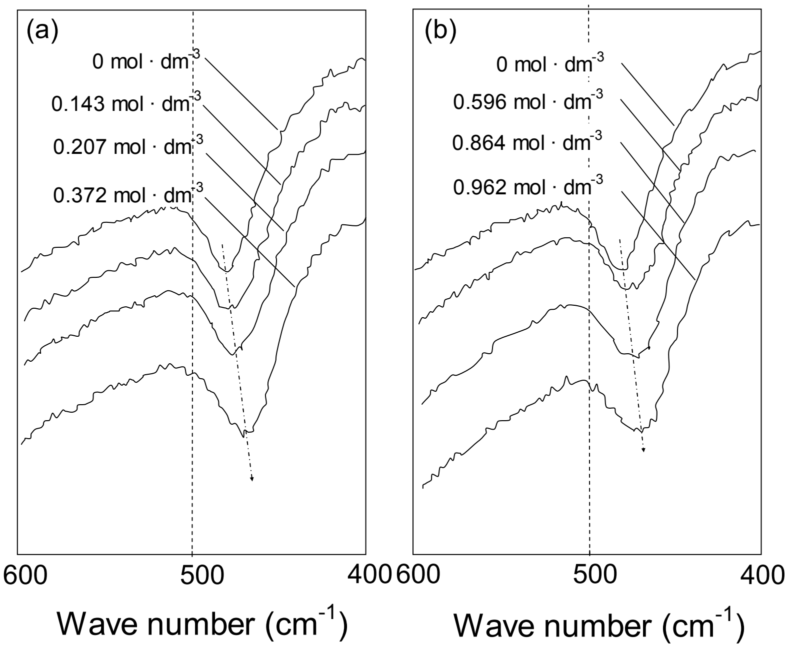


Fig.5. IR spectra of H_2SiF_6 solution adding (a)Al metal or (b)SiO_2 at the wavenumber of 800 – 600cm^{-1}.

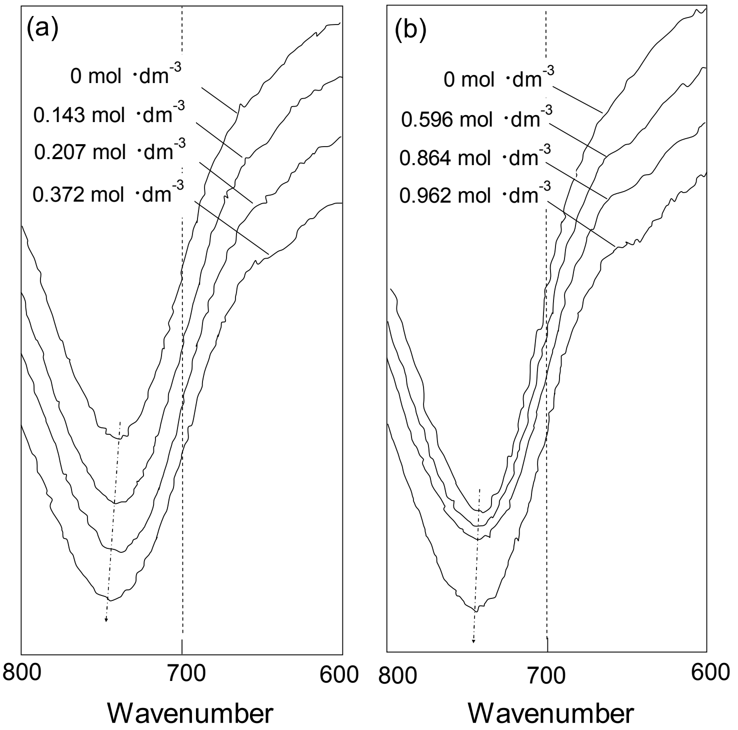


Fig.6. IR spectra of H_2SiF_6 solution adding (a) Al metal or (b) SiO_2 at the wavenumber of 600 – 400cm^{-1}.

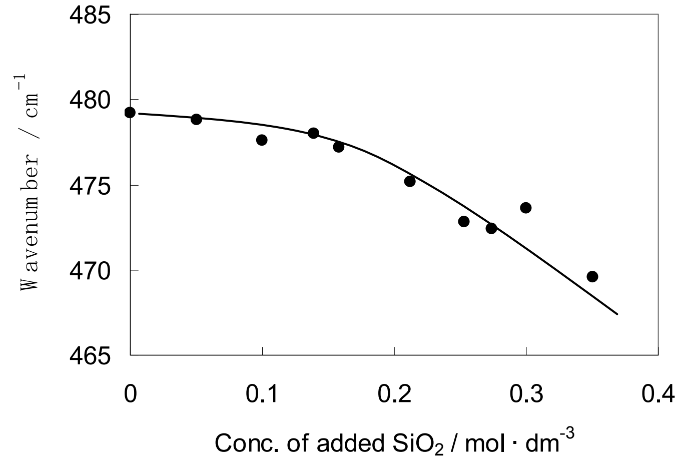


Fig.7. Plots of the maximum wavenumber of ν_4 absorption of SiF_6^{2-} as a function of SiO_2 content.

Fig. 6 shows the IR spectra of same system at the wavenumber of 600 – 400cm^{-1}. Strong ν_3 absorption band of SiF_6^{2-} was observed at 480 cm^{-1} and in this case shifted to higher wavenumber with adding the additives. These results can by also explained by the presence of the strong interaction between the SiF_6^{2-} and SiF_4. Fig 7 shows the plot of the maximum wavenumber of ν_4 absorption of SiF_6^{2-} as a function of SiO_2 content. The wavenumber steeply increased above 0.15 mol·dm^{-3}. It is also explained by the idea that free HF species dissociated from SiF_6^{2-} are present in the solution.

3.3 Deposition of SiO_2 on α-Al_2O_3 powder

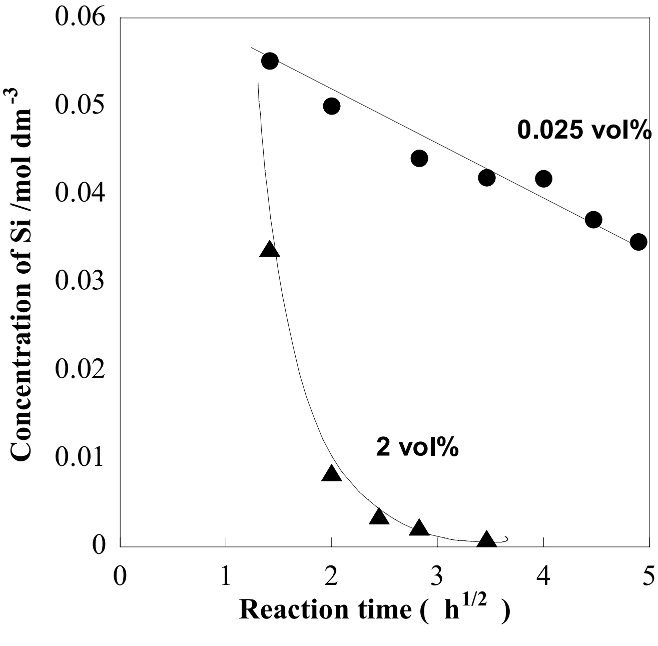


Fig. 8. Variations of concentration of Si with the reaction time in LPD reaction solution after adding H_3BO_3 solution.

Variation of Si amount in dissolving species in reaction solution with reaction time is shown in Fig.8. The amount of Ti ion decreases with the raction period and depends on the amount of alumina powder. An increase of the amount of alumina caused the rapid decrease of the amount of Ti ion. It is suggested that the deposition reaction is induced by the existence of the surface of hetero-phase in the reaction solution which promotes the LPD deposition reaction.

Additionally, for the elucidation of the deposition mechanism, the reaction solutions were investigated by Raman spectroscopy in order to gain information about the behavior of chemical composition. In Fig.9, variation of the Raman spectra for LPD reaction solution with reaction time at 30ºC. Raman spectroscopy confirmed that H_3BO_3 reacts with F^- to

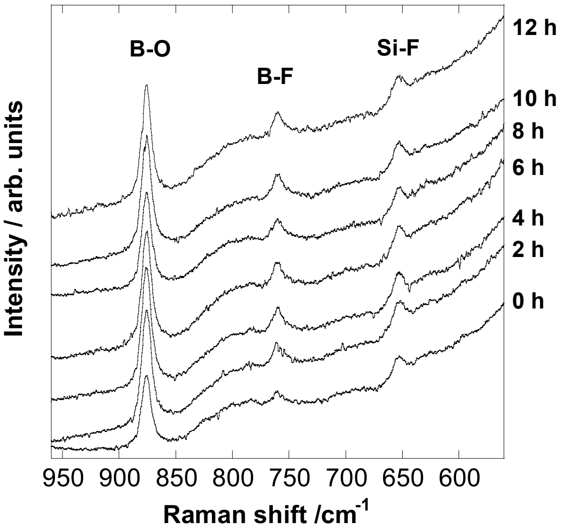


Fig. 9. Variation of Raman spectra for LPD reaction solution with reaction time at 30°C.

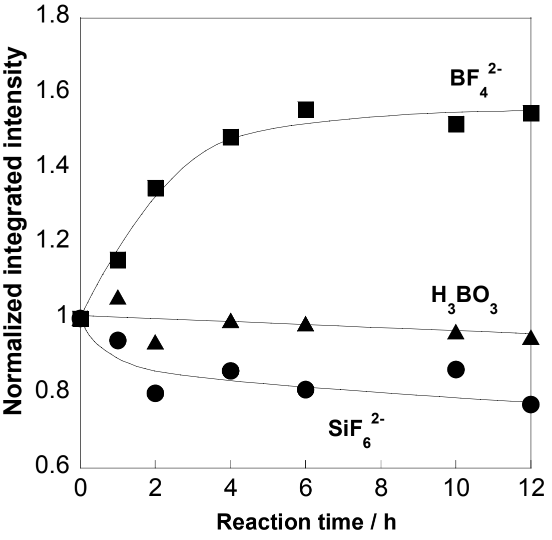


Fig.10. Variations of integrated intensities of Raman bands assigned to each dissolving species normalized by the initial intensities for LPD reaction solution with the reaction time.

form stable BF_4^-, which indicated that H_3BO_3 plays a crucial role as F^- scavenger. The scattering bands at 653, 761, and 878 cm^{-1} are assigned to Si-F, B-F, and B-O stretching bands, respectively. These bands indicate the existence and the variations of their amounts. In order to confirm the process of the LPD reaction, we calculate the ratio of BF_4^-/H_3BO_3.

Variations of integrated intensities of Raman bands assigned to each dissolving species normalized by the initial intensities for LPD reaction solution with the reaction time is shown in Fig.10. This intensity of BF_4^{2-} rapidly increased with the reaction time. It is suggested that the formation of the more stable species such as BF_4^- ion promote the liquid phase deposition.

4. Conclusion

The equilibrium reaction of SiF_6^{2-} ion as a dissolving species in the LPD process was investigated by the measurement of UV and spectroscopic measurement. The measurement was carried out by adding the F^- scavenger such as H_3BO_3 and Al metal which can shift the equilibrium reaction. In the beginning of the LPD reaction, the BF_4^{2-} was rapidly generated in the reaction solution, and contributed the forming thbe oxide. The fluoride complex species were estimated to be involved in the LPD process as intermediates. Therefore, the reaction is considered to be very important in controlling the LPD process.

Acknowledgments

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