

FLUORESCENCE BEHAVIOR OF BENZO[f]QUINOLINE DOPED IN LPD SILICA THIN FILMS

TOSHIAKI MABUCHI¹, SATOSHI SUZUKI*¹, TSUYOSHI NAKAJIMA¹, JUICHI INO², KAZUO TAKEMURA²
and ETSURO SHIMIZU³

¹Faculty of Engineering and Graduate School of Science and Technology, Shinshu University,
Wakasato, Nagano 380-8553, Japan

²Central Research Laboratory, Nippon Sheet Glass Co., Ltd., Konoike, Itami 664-8520, Japan

³Microcomponent Engineering Department, Olympus Optical Co., Ltd.,
Tatsuno, Kamiina, Nagano 399-0495, Japan

(Received 29 June 1998; accepted 25 August 1998)

Abstract— By using the liquid-phase-deposition (LPD) process, which has a potential of preparing organic-inorganic composite materials, samples doped with benzo[f]quinoline (BfQ) into silica thin films were prepared. We observed the fluorescence and fluorescence excitation spectra of the samples, as well as the fluorescence lifetimes and time-resolved fluorescence spectra. The comparison of the fluorescence spectra in pH-controlled buffer solutions yields the results that the dominant species of BfQ in the LPD silica films is a protonated one. The fluorescence band assigned to a hydrogen-bonded species was observed on the samples prepared from the dipping solutions of 3 and 2 M hexafluorosilicic acid. The band assignment was confirmed by the fluorescence lifetime measurement. The FT-IR data proved the existence of included water in silica films prepared from the LPD process. The appearance of the band corresponding to the hydrogen-bonded species within LPD silica phases was explained by the presence of included water. Depending on the preparation conditions of LPD silica films, the band assigned to protonated species shows band shifts in a wavenumber region between the peak of hydrogen-bonded and typical protonated species. This implies that there is some distribution of steric conformations of protonated species of BfQ interacting with adsorbing sites of LPD silica. The time-resolved fluorescence spectra suggest that some relaxation process is involved in the conformation of BfQ doped into the solid phase of LPD silica.

INTRODUCTION

The method of liquid phase deposition (LPD) is a wet process forming silica thin films on substrates such as glass plates.¹⁻⁵ The principal characteristics of the LPD process are summarized as follows:

- 1) The process forms hard and close silica thin films which is equivalent to the ones prepared by the thermal oxidation method.
- 2) The process forms films with very low impurity concentration. Taking into account the fact that the LPD process proceeds in water solutions, the water content in LPD films is surprisingly small.
- 3) The process proceeds at ordinary temperatures.
- 4) Some kind of organic molecules can be directly doped into LPD films.

The doping ability of some kinds of organic molecules is the most interesting feature of the LPD process.^{6,7} Owing to this feature, the LPD process has the probability of producing organic-inorganic hybrid materials. Although some attempt to prepare composite materials incorporating organic luminescent materials in inorganic

matrices have been made, little is known about the electronic properties of solid host matrices surrounding doped luminescent organic molecules.

Mabuchi *et al.* observed the fluorescence and excitation spectra of benzo[f]quinoline (BfQ) during the sol-gel-xerogel transitions and revealed that the doped species of BfQ in sol-gel silica reflect the conditions of microenvironment around the doped BfQ during the sol-gel reaction.⁸ Suzuki *et al.* observed the fluorescence spectra of acridine adsorbed on activated silica gel.⁹ They concluded that the dominant emitting species of acridine on silica gel are protonated ones which emerges from the interaction with silanol groups on silica gel surface. The spectroscopic evidence of electronic states may provide some useful information on the molecular species doped into LPD silica.

Suzuki *et al.* estimated the proton donating ability of internal silanol groups of silica solid phases prepared by the LPD method.¹⁰ They doped pH indicator dyes, methyl yellow and methyl orange, directly into LPD silica films from a dipping solution of 4 M hexafluorosilicic acid and observed absorption spectra of the doped samples. From the comparison of the absorption spectra of the doped dyes with those in pH-controlled buffer solutions, they concluded that the proton donating ability of silanol groups of LPD silica is

* To whom correspondence should be addressed.

† Abbreviations: LPD, liquid phase deposition; BfQ, benzo[f]quinoline.

equivalent to $\text{pH} = 3.5$, which is more acidic than the silanol groups of activated silica gel. They proposed the mechanism of the origin of strong acidity in which the formation of Si-F bond participates during LPD process. The high acidity of silanol groups of LPD silica may contribute much to the properties characteristic of LPD silica films.

This paper will make the assignment of doped molecular species and discuss the photophysical behavior of BfQ in LPD silica phases, based on the observation of fluorescence and fluorescence excitation spectra. It is concluded that the concentration of OH groups in silica phases increases with the decrease in the concentration of hexafluorosilicic acid (H_2SiF_6) in dipping solutions and that the photophysical behavior of doped molecules reflects the making conditions of silica films.

MATERIALS AND METHODS

Preparation Method of Sample Films. The SiO_2 saturated aqueous solution of hexafluorosilicic acid whose concentration are 4, 3, and 2 M ($1 \text{ M} = 1 \text{ mol dm}^{-3}$) were used in this study. BfQ was dissolved into the dipping solutions at a concentration of $2.0 \times 10^{-3} \text{ M}$. In order to start the deposition process, 1, 0.7, and 0.5 g Al powder were added to the 250 cm^{-3} solutions of hexafluorosilicic acid the concentrations of which were 4, 3, and 2 M, respectively. The glass plates used as substrates were immersed for 16 hours in the dipping solutions which were kept at 35°C in a thermostated water bath. After washing by water and drying in the air, the fluorescence and fluorescence excitation spectra of the samples were recorded on a Shimadzu RF-5000 fluorescence spectrophotometer. The data were transferred to an NEC PC-9800 personal computer through GPIB interface bus and were ready to any data processing.

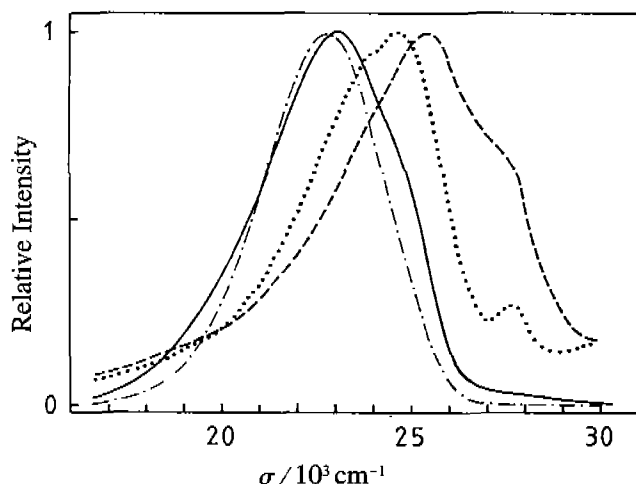


Figure 1. Fluorescence spectra of BfQ in LPD silica films prepared from the dipping solution of 4 M hexafluorosilicic acid (—), 3 M hexafluorosilicic acid (·····), 2 M hexafluorosilicic acid (----), and in 1 M HCl solution (-·-·-). Excitation wavelength: 320 nm.

RESULTS AND DISCUSSION

In protic solvents, BfQ shows the fluorescence band with regularly spaced vibrational structures.⁸ BfQ in ethanol has three vibrational bands at 28500, 27200, and 26000 cm^{-1} . In water, the fluorescence band is slightly displaced to the red and is situated at 28200 and 27100 cm^{-1} . The fluorescence excitation spectra of BfQ observed in these solvents corresponds to the absorption spectra of BfQ in the same solvents and shows typical mirror symmetry relation to the fluorescence band described above. The fluorescence band with vibrational structures having the highest peak at 27200 cm^{-1} can be assigned to the hydrogen-bonded species of BfQ.

Fig. 1 shows the fluorescence spectra of BfQ in LPD silica films prepared from a dipping solution in which the concentration of hexafluorosilicic acid is 4, 3, and 2 M, as well as in a 1 M HCl solution. Fig. 2 shows the excitation spectra of BfQ in LPD films prepared from the dipping solution of 4, 3, and 2 M hexafluorosilicic acid, as well as in a 1 M HCl solution.

The fluorescence spectra of BfQ in buffer solutions with various pH are shown in Fig. 3. The corresponding fluorescence-excitation spectra of BfQ in pH-controlled buffer solutions are shown in Fig. 4. At a pH higher than 6, BfQ in buffer solutions shows the fluorescence band with vibrational structures at around 27000 cm^{-1} , which is situated at the same spectral region of the hydrogen-bonded species and has similar vibrational structures to those of the hydrogen-bonded species. On lowering pH, the fluorescence band with vibrational structures disappears and a broad band appears at about 23000 cm^{-1} . The broad fluorescence band observed under acidic conditions can reasonably be assigned to the protonated species of BfQ.

In LPD silica films prepared from the dipping solution of

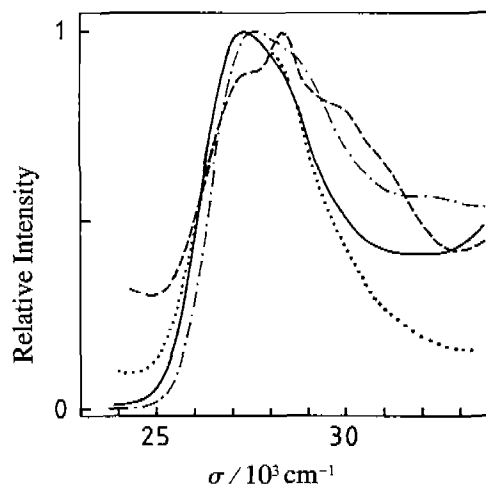


Figure 2. Excitation spectra of BfQ in LPD silica films prepared from the dipping solution of 4 M hexafluorosilicic acid (—), 3 M hexafluorosilicic acid (-·-·-), 2 M hexafluorosilicic acid (----), and in 1 M HCl solution (·····). Observation wavelength: 450 nm.

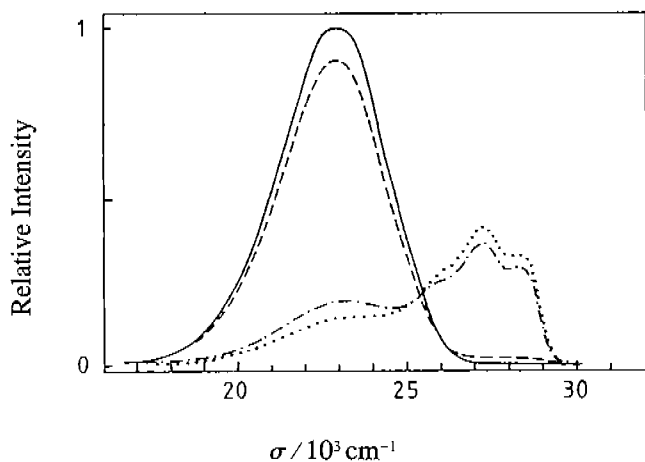


Figure 3. Fluorescence spectra of BfQ in pH-controlled buffer solutions. pH = 1.75 (—), pH = 4.03 (----), pH = 6.56 (-·-·-), pH = 9.32 (·····).

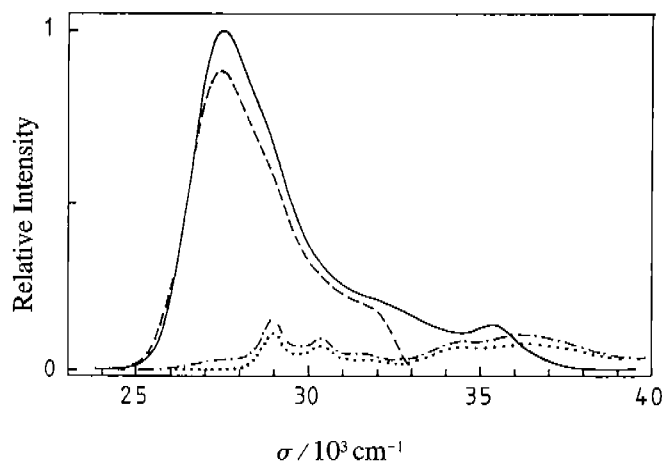


Figure 4. Fluorescence excitation spectra of BfQ in pH-controlled buffer solutions. pH = 1.75 (—), pH = 4.03 (----), pH = 6.56 (-·-·-), pH = 9.32 (·····).

4 M hexafluorosilicic acid, the fluorescence spectrum of BfQ shows a broad band having a band maximum at around 23000 cm^{-1} and a slight shoulder at a higher wavenumber side of the peak. The fluorescence band of BfQ in LPD silica films is located at nearly the same wavenumber as that observed in acidic conditions. The excitation spectra of BfQ in LPD films prepared from a 4 M dipping solution show broad bands and are situated at nearly the same location as in acidic conditions. These findings indicate that the dominant emitting species of BfQ doped in LPD silica films prepared from 4 M dipping solutions is a protonated one in its ground state.

A pK_a value of BfQ is reported being 4.2 in its ground state and increasing up to 10~11 in its excited state.¹¹ This implies that BfQ is a weak base in its ground state and a strong base in its excited state. Suzuki *et al.* estimated the effective acidity inside the LPD silica phase to be equivalent to pH = 3.7.¹⁰ By assuming the pK_a of a solute to be 4.2 and a solvent to be 3.7, we can estimate the population of the protonated species of BfQ in LPD silica phases; 76 % of BfQ exists as a protonated species and 24 % as a hydrogen-

bonded one in LPD silica phases. The fluorescence band corresponding to the hydrogen-bonded species can not be observed in a buffer solution of pH = 4.03, however this estimation is consistent with the assignment that the dominant emitting species of BfQ is the protonated one in LPD silica phases.

On lowering the concentration of hexafluorosilicic acid in dipping solutions, the fluorescence bands are displaced to the blue. In a LPD silica film prepared from the dipping solution of 3 M hexafluorosilicic acid, the fluorescence spectrum of BfQ shows a broad band with a band peak at about 25000 cm^{-1} and a small peak at a lower wavenumber side about 27500 cm^{-1} . In a LPD silica film prepared from the dipping solution of 2 M hexafluorosilicic acid, the band maximum is further blue-shifted up to near 25500 cm^{-1} and the band at around 27500 cm^{-1} appears as a shoulder.

A typical FT-IR spectrum of LPD silica thin films deposited on a silicon wafer is shown in Fig. 5. The dominant vibrational band near 1100 cm^{-1} is assigned to the stretching vibration of Si-O-Si group constituting the framework of SiO_2 . Three bands appear in the FT-IR spectra of LPD silica films, which can not be observed in pure silica films such as thermally grown silica films. Weak absorption bands assigned to SiOH group and incorporated water are observed in a region over 3000 cm^{-1} . A band also appears at about 950 cm^{-1} , which has been assigned to SiF group. These findings conclude that the LPD silica films has silanol groups and it contains a small amount of water. These groups are considered to specify the specific features of LPD silica thin films.

Fig. 6 gives the dependence of the apparent absorption coefficients of various vibrational bands of LPD silica films which were deposited onto silicon substrates upon the concentration of hexafluorosilicic acid in dipping solutions. It is seen from the figure that the absorption coefficient of the band at 1100 cm^{-1} is increased and the ones at 3400 and 3650 cm^{-1} is decreased, with increasing the concentration of

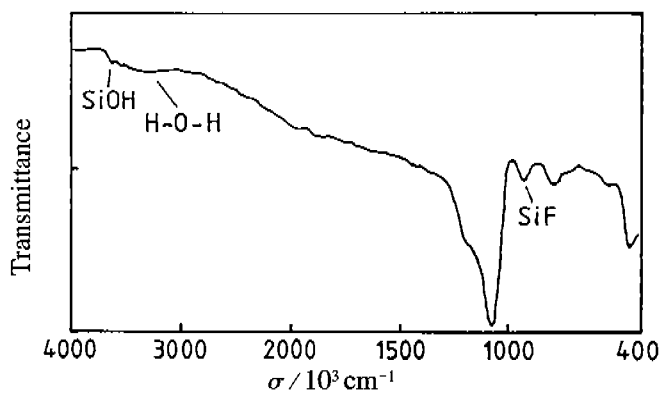


Figure 5. Typical FT-IR spectra of LPD silica thin films grown on a silicon wafer.

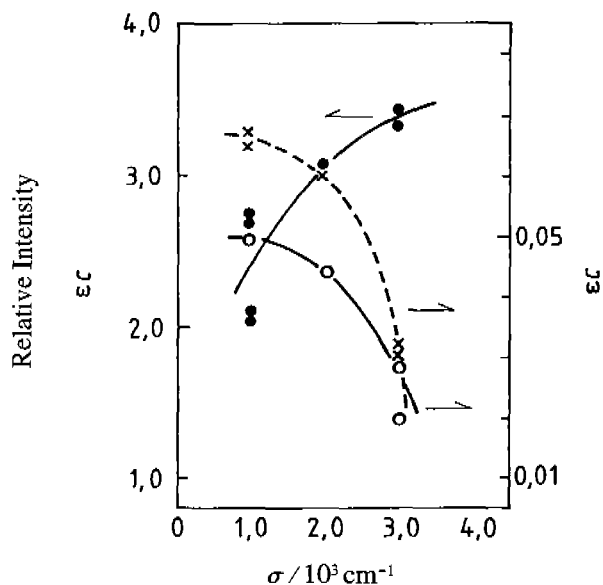


Figure 6. Absorption coefficient of Si-O-Si species (●) at 1100 cm^{-1} , Si-O-H (○) species at 3650 cm^{-1} and included water (×) at 3400 cm^{-1} in $1.0\text{ }\mu\text{m}$ thick LPD silica films on silicon substrate prepared from the dipping solutions with various concentrations of hexafluorosilicic acid.

hexafluorosilicic acid in dipping solutions.

The band at 3650 cm^{-1} is assigned to Si-OH stretching vibration and therefore the amount of silanol groups in LPD silica films is increased with the decrease in the concentration of hexafluorosilicic acid. The apparent absorption coefficient of the band at 3400 cm^{-1} , which is assigned to adsorbed water, is also increased with the decrease in the concentration of hexafluorosilicic acid. The data lead to the conclusions that the LPD silica films contain a detectable amount of water and the amount of water in LPD silica films is increased with decreasing the concentration of hexafluorosilicic acid in dipping solutions.

It is well accepted that in protic solvents the strength of stronger acids are leveled by the solvents (Leveling effect).¹² The intrinsic acid strength of Si-OH in LPD silica phases as proton donors is weaker than H_3O^+ as a protic solvent, so that the leveling effect will not affect the effective acidity of Si-OH in LPD silica even in the presence of water.

As described above, the fluorescence spectra of BfQ in ethanol and water are situated at around 27000 cm^{-1} and have vibrational structures. The peak or shoulder appeared at the same spectral region of hydrogen-bonded species of BfQ in LPD silica films prepared from 3 or 2 M dipping solutions. The emitting species contributing to the peak or shoulder may be assigned to the hydrogen-bonded species of BfQ. The spectral findings suggest that a hydrogen-bonding site with low acidity exists in LPD silica phases. It is highly probable that the included water forms hydrogen bonds with Si-OH groups and the acidic strength of Si-OH

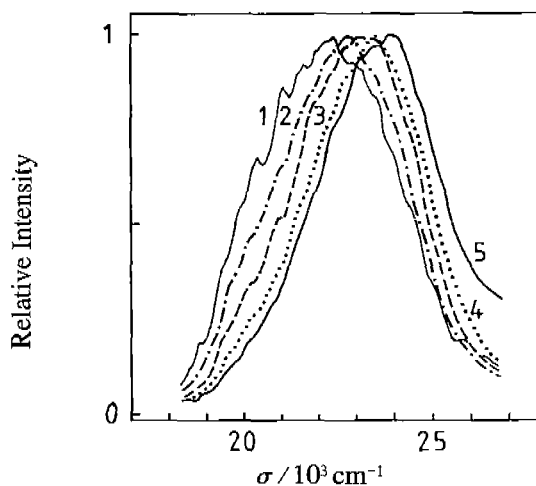
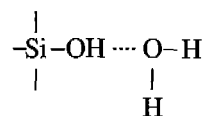


Figure 7. Time-resolved fluorescence spectra of BfQ in LPD silica films. Excitation wavenumber: 24674 cm^{-1} (337 nm). 1: 0-4 ns, 2: 4-10 ns, 3: 10-20 ns, 4: 20-40 ns, 5: 40-100 ns.

in LPD silica phases is moderated by the bridged water; the hydrogen-bonding site with lower acidity emerges in LPD silica phases due to the presence of included water.



In pH-controlled buffer solutions, two emitting species of BfQ, namely hydrogen-bonded and protonated ones, can be identified. In LPD silica films, the broad fluorescence bands corresponding to protonated species can be identified in the LPD silica films prepared from a 4 M dipping solution. The fluorescence band corresponding to the hydrogen-bonded species is also identified as a shoulder in LPD silica films from a 2 M dipping solution.

The main peak of the fluorescence band of the samples shifts to the blue on lowering the concentrations of dipping solutions and the wavenumber of the peak is situated at a wavenumber between that of typical protonated and hydrogen-bonded species. The spectral shape resembles to that of protonated species, but the peak position is displaced to the blue compared with that of typical protonated species. The broad fluorescence bands which were observed in the LPD silica films prepared from 3 and 2 M dipping solutions at a wavelength region between the peaks of protonated and hydrogen-bonded species can not be observed in pH-controlled buffer solutions. This implies that such broad bands can be observed only in solid phases not in fluid solutions. The emitting species contributing to the bands seem to be protonated species, which are observed only in the solid LPD silica phases.

The evidence of inclusion of water into LPD silica phases was detected on FT-IR spectra, but only a little amount of water was incorporated in the LPD films. The mobility of water in the solid phase of LPD silica seems to be highly

Table 1. Fluorescence Lifetime of BfQ in LPD Silica Films.

λ_{ex}/nm	τ_1/ns	τ_2/ns	τ_3/ns	k_1	k_2	k_3
400	5.3	8.6	44.3	1.0	1.25	0.17
450	5.3	8.6	44.3	1.0	4.48	0.78

restricted. Furthermore, LPD silica phases are amorphous and have inhomogeneous composition. As the result of this, there will be some extent of fluctuation in the proton-donating ability of interacting sites with BfQ.

The fluorescence decay curves of BfQ in LPD silica films can be convoluted by a three-component decay. The best fit data are shown in Table 1. The k_i 's are the preexponential factors corresponding to τ_i 's and the value of k_1 was set to be 1.0. By analogy with solution data, the τ_1 component can be assigned to the hydrogen-bonded species with silanol groups and τ_2 to the protonated species. The assignment of long-lived species τ_3 has not been fixed yet. The fluorescence band of protonated species is situated at a lower wavenumber than that of hydrogen-bonded one. The k_2 value observed at 450 nm is larger than that observed at 400 nm; this is consistent with the band assignment that the fluorescence band of protonated species situates at lower wavenumber than that of hydrogen-bonded one. The observed data on fluorescence lifetimes support the assignment of the fluorescence bands of BfQ in LPD silica films described above.

Time-resolved fluorescence spectra of BfQ doped in LPD silica films prepared from 4 M dipping solutions are given in Fig. 7. At the shortest time range, the fluorescence band is a broad one with the peak at about 24000 cm^{-1} and the band corresponding to the hydrogen-bonded species can not be observed. The probable reason is that the lifetime difference between τ_1 and τ_2 is too small to resolve these two bands. On increasing the time range, fluorescence bands is shifted to the red continuously. At intermediate time ranges, the band have a maximum at around 23000 cm^{-1} . At a longest time range, the band is further shifted to the red and has a maximum at about 22000 cm^{-1} . All these bands may be assigned to protonated species of BfQ. Such a spectral shift is considered to reflect the fact that some relaxation processes in which included water participates are involved in the decay process of protonated BfQ in LPD silica phases.

CONCLUSIONS

Benzo[f]quinoline can be doped into LPD silica films. The dominant emitting species doped from dipping solutions of 4 M hexafluorosilicic acid are assigned to protonated ones. This is consistent with the facts that the effective acidity inside LPD silica phases prepared by the same conditions is equivalent to $\text{pH} = 3.7$ and the $\text{p}K_a$ value of BfQ in fluid solutions is 4.2 in its ground state.

The dominant emitting species prepared from 3 and 2 M

dipping solutions are also assigned to protonated ones. The peak or shoulder assigned to hydrogen-bonded species were observed at a higher wavenumber side. The presence of the band was supported by the fluorescence lifetime measurement. The appearance of the fluorescence band of the hydrogen-bonded species in acidic surroundings of LPD silica phases can be explained by the presence of included water.

In the solid phase of LPD silica, the band maximum of the protonated species varies between 22000 and 24000 cm^{-1} , depending on the concentration of dipping solutions. This suggests that there is some distribution in conformations of protonated species of BfQ in solid LPD silica phases.

REFERENCES

- Nagayama, H., H. Honda and H. Kawahara (1988) A new process for silica coating. *J. Electrochem. Soc.* **135**, 2013-2016.
- Goda, T., H. Nagayama, A. Hishinuma and H. Kawahara (1988) Physical and chemical properties of silicon dioxide film deposited by new process. *Mat. Res. Soc. Symp. Prog.* **105**, 283-288.
- Kawahara, H. (1990) Synthesis of silica films by means of the reaction in aqueous solutions, *Yoyuen (Molten Salt)*, **33**, 7-23.
- Hishinuma, A., T. Goda, M. M. Kitaoka, S. Hayashi and H. Kawahara (1991) Formation of silicon dioxide films in acidic solutions. *Appl. Surf. Sci.* **48/49**, 405-408.
- Kawahara, H., Y. Sakai, T. Goda, A. Hishinuma and K. Takemura (1991) Formation of SiO_2 film on plastic substrate by liquid phase deposition method. *SPIE Proceedings Series* **1513**, 198-203.
- Ino, J. (1992) Organic dye containing SiO_2 films. *New Glass* **7**, 283-286.
- Ino, J., K. Takemura and H. Kawahara (1992) Preparation and properties of SiO_2 film doped with organic molecules by LPD method. *Rivista della Staz. Sper. Vetro* 15-19.
- Mabuchi, T. and T. Fujii (1993) Fluorescence and fluorescence-excitation spectra of benzo[f]quinoline during sol-gel-xerogel transitions of mixed silicon-aluminum alkoxide systems. *Bull. Chem. Soc. Jpn.* **66**, 2174-2181.
- Suzuki, S. and T. Fujii (1989) Photophysics of acridone, N-methylacridone acridine, and pyrene adsorped on silica gel. In *Photochemistry on Solid Surface* (Edited by M. Anpo and T. Matsuura), pp.89-92. Elsevier, Amsterdam.
- Suzuki, S., N. Tokou, T. Mabuchi, T. Nakajima, J. Ino, K. Takemura and H. Kawahara (1995) The absorption spectra of pH indicator dyes doped in silica thin films prepared by the method of liquid phase deposition and the spectroscopic estimation of effective acidity of internal hydroxyl groups of silica. *Bull. Chem. Soc. Jpn.* **68**, 1275-1279.
- Marzacco, C. J., G. Deckey, R. Colarulli, G. Siuzdak and A. M. Halpern (1989) Excited-state protonation and photo-physical properties of azaphenanthrenes. *J. Phys. Chem.* **93**, 2935-2939.
- King, E. J. (1965) *Acid-Base Equilibria*, Pergamon Press, Oxford.