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Infrared Spectra of SiO_2 Coating Films Prepared from Various Aged Silica Hydrosols

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Synopsis. Measurements have been made of the vibrational absorption bands of silica films. The results have been used to examine the importance of the polymerization of silica. Seven other absorption bands, which are related to the Si–O group, were clearly found in the region from 1300 to 400 cm^{-1}. A band at a wave number of 1069 cm^{-1} increased with increasing the viscosity of the hydrosol. The band at 974 cm^{-1} was substantially sensitive in intensity to the heat-treatment and the rehydration of silica film, can be assigned to the Si–O stretching vibration of the surface silanol since the intensity of its band is influenced by both the heat-treatment(dehydration) and rehydration.

It has been indicated by several workers[1–4] that silica-coating films can be prepared using several methods. Such silica films have been convenient for investigating the surface properties of silica, and may also be suitable for controlling the transmittance and refractive index in optics materials. It is known that the surface silanols on silicas, such as silica gel, pyrogenic silica and porous glass, play a central role as the active center regarding the adsorption properties, ion-exchange in solutions containing some cations, and surface modification of their materials using surface reactions.[5] Examinations using infrared spectroscopy have proved to be among the most effective means to investigate the bond nature of surfaces and substrate structures in materials.[6] The infrared spectra of such surface-active materials as silicas were normally taken in vacuo since the surface silanol is sensitive to the moisture in air, and the clearness of the spectrum is dependent on the sample preparation for infrared experiments.[7,8] The infrared spectra of the silicas can be clearly measured in the range of about 4000 to 3000 cm^{-1}, the wave number region of which corresponds to the stretching vibration of the O–H in surface silanols and the adsorbed water on such materials.[7] Indistinct spectra were found for the silicas when infrared measurements were carried out over a range of about 2000 to 400 cm^{-1}. This is due to the intense absorption efficiency of silica in this region. However, it could be expected that the problem has been solved by using silica films.

In order to understand the polymerization process of silica in its hydrosol stage, we measured the FT-IR spectra of silica films which were prepared by ageing the silica hydrosol obtained from the hydrolysis of tetraethyl orthosilicate. Moreover, the relationship between the formations of siloxane and the surface silanol and the remarkable feature of absorption bands is discussed in this report.

Experimental

Silica hydrosols were prepared by the hydrolysis of tetraethyl orthosilicate.[7] In this work, solutions of redistilled tetraethyl orthosilicate, ethyl alcohol, and distilled water adjusted to pH 2 by using a hydrochloric acid were mixed in volume ratio, $Si(OC_2H_5)_4$: C_2H_5OH: H_2O=5: 1: 0.5, and then heated at 65 °C for 60 min. After its sol had formed, the hydrolsol was allowed to stand for a long time at room temperature in air; that is, the hydrosol aged with the elapse of time. Metal plate (20×30 mm wide and 0.3 mm thickness), which is stainless steel (SUS 304) pretreated before use, was steeped in such hydrosol for 30 min in air, at a relative humidity of about 50%; its plate was then pulled from the hydrosol at a rate of 1.0 mm s^{-1} and dried at 170 °C for 1 h in air. A filmy specimen with the hues of a rainbow and about 0.9μm thickness, was obtained from the procedures mentioned above. For a pretreatment, the metal plate was immersed into a 2% NaOH solution, washed with distilled water, steeped in acid adjusted with sulfuric acid at 10%, washed with distilled water, and dried at 110 °C for 1 h. A Japan Spectroscopy Co. 5MP FT-1R spectrometer was used for the measuring on the silica films, spectra of which were taken with a polarizing reflection technique.[8]

Results and Discussion

Figure 1 shows the infrared absorption spectra of the silica coating films obtained from various ageing of the hydrosol. A number of absorption bands were found in the range from about 4300 to 400 cm^{-1}. A broad absorption band ranging from 3800 to 3000 cm^{-1}, which was ascribed to the O–H stretching vibration mode,[7,9] was found in a specimen aged for 1536 h. The intensity of this band depended on the time required for ageing. A few absorption bands around 2900 and 1400 cm^{-1}, which were assigned to C–H stretching and deformation vibrations, changed in intensity as a function of the ageing period. It can therefore be understood that the formation of the OH radical and the alkylation occurred at the same time on the surface of particles and that the contents of their chemical species in the films were dependent on the ageing. The very weak band at the water-bending vibration is ascribed to adsorbed water, since the band appeared at its wave number when the specimen was exposed to water vapor. The very strong bands at 1215 and 1069 cm^{-1} can be assigned to the asymmetrical stretching vibration of SiOSi in the layer structure of silica[10,11] and of the ≡Si–O–Si≡ bridge which is formed between particles or small spherical polymer, since the intensity of the band is enhanced with increased ageing with the elapse of time. The assignments of these bands are not in agreement with those found in the literature.[12] These bands were also indicated by Hino et al.,[13] the wave numbers of their bands are not clear due to an overlap of these bands as a result of the high concentration of Si–O species in a disordered structure. The specimens used in the literature[12,13] were of the silica xerogel, which consist of a rigid three-dimentional network of contiguous particles of colloidal silica; in the filmy silica used in this study it is quenched during the early or middle stage of polymerization. In the later case, when polysilicic acid is formed at low pH (the pH value of the present sol was about 2.8), polymer particles are formed, and the polymerization is sufficiently slow to allow the early stage. When the particles are not charged, they link together into branched chains to form three-dimension network regions in the sol. Such a polymerization process can be followed by taking the spectra of skeletal vibrations of filmy silica prepared from the sol. In a previous study,[8] it was suggested that the 1069 cm^{-1} band is mainly related to polymerization. Actually, the intensity of this band was substantially

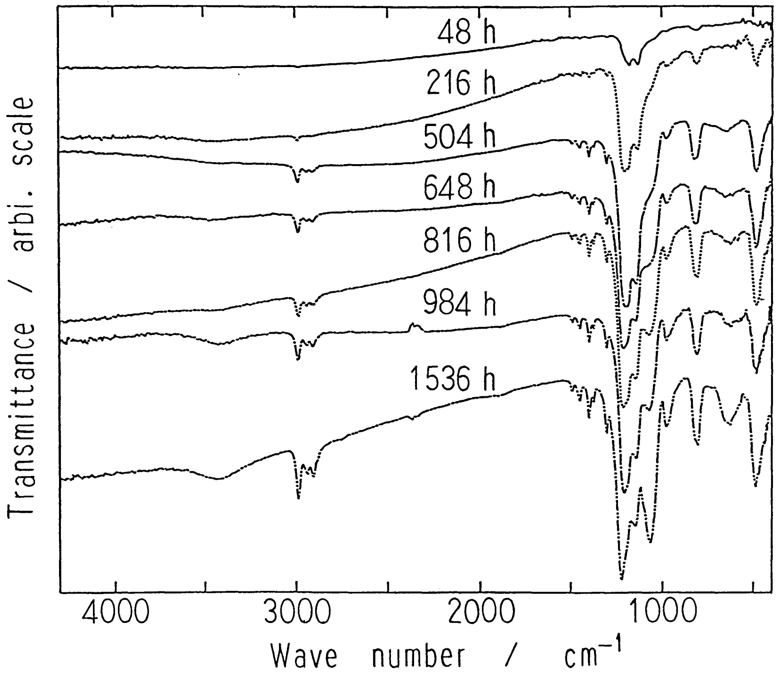

Fig. 1. Spectra of the silica films prepared from the silica hydrosol.

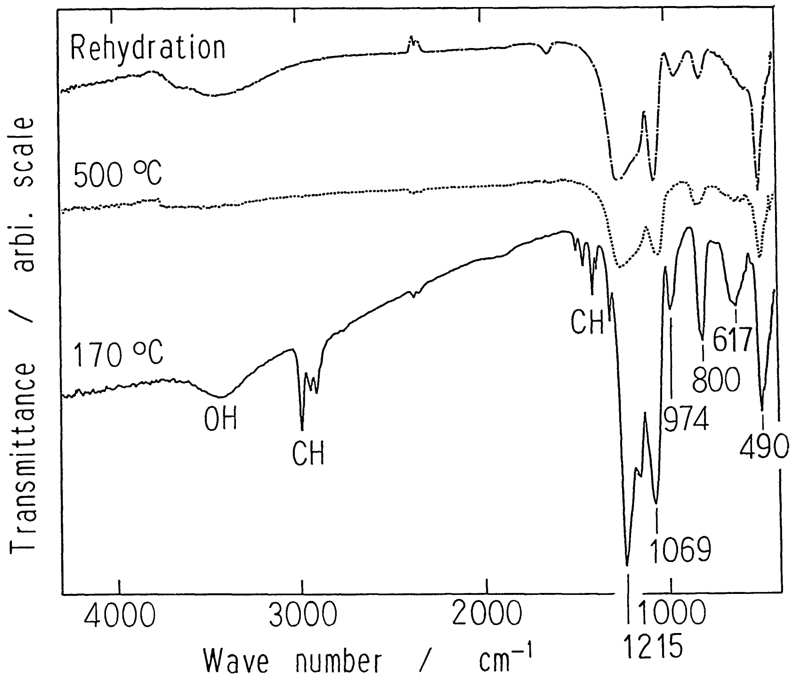

Fig. 2. Spectra of the silica films heat-treated at 500 °C in air and rehydrated with saturated water vapor after its heat-treatment.

sensitive to the elapse of time, as can be seen in Fig. 1. It is therefore thought that a measurement of the intensity change of such a band can be used as an indication of the polymerization rate.

In order to determine the nature of the bands in the lower wave number region of about 1000 to 400 cm^{-1}, a heat-treatment and rehydration experiments were performed on film specimens; their spectra are shown in Fig. 2. When heating a specimen at 500 °C for 1 h in air, both the O–H and the C–H bands disappeared, and the bands at 974 and 617 cm^{-1} also faded out. It is known that the 974 cm^{-1} band weakens as Si–OH groups condense to form Si–O–Si bands.[12,13] When such a specimen is exposed to saturated water vapor, a band at 974 cm^{-1} is recovered and, of course, the O–H stretching broad band at about 3800—3000 cm^{-1} is also observed, though the band at 617 cm^{-1} and the C–H vibration bands are not restored. These results indicate that the bands at 974 and 617 cm^{-1} can be assigned to the Si–O stretching vibration of the silanol and the absorption band related to the C–H vibration, respectively. The assignment of the 974 cm^{-1} band is in good agreement with values found in literature.[12,13] Though the sharp bands at about 800 and 490 cm^{-1} are not clear regarding their origins, they are probably associated with the typical structure of four-coordinate silica.

Stable silica films were formed on a metal plate surface by a dip-coating method from the silica hydrosol obtained from the hydrolysis of tetraethyl orthosilicate. The FT-IR spectra were measured on those films. Two remarkable bands were found at 1069 and 974 cm^{-1}. Among them, the band at 1069 cm^{-1}, which can be assigned to the stretching vibration of the ≡Si–O–Si≡ bridge, is related to the polymerization of silica particles, by which smaller molecular units are linked together into large ones. On the other hand, the band at 974 cm^{-1} is assigned to Si–O stretching vibration of the silanol and in sensitive to a thermal treatment and the rehydration.

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