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Redox Deposition of Silica Thin Films: Effect of Hydrogen Peroxide and Poly(vinylpyrrolidone) on Film Growth

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Effects of H_2O_2 and poly(*N*-vinylpyrrolidone) (PVP) additives on silica thin-film deposition by the redox reaction of an aqueous ammonium hexafluorosilicate (AFS) solution with reducing agent dimethylamine borane onto poly(ethylene terephthalate) (PET) and Si substrates were investigated. The trivial addition of H_2O_2 (a few percent) and PVP (1 ppm) greatly improved the rate of film growth and the stability of reaction solution. X-ray photoelectron spectroscopic and infrared spectroscopic analyses as well as surface (scanning electron microscopy) and inner phase (transmission electron microscopy) morphological characterization of the silica films were performed using varying concentrations of PVP. A model for the manner of the silica-film deposition based on the attractive or repulsive interaction among silica spherical granular, PVP, and PET substrate was proposed.

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Congruently with the development of transparent plastics [poly(ethylene terephthalate) (PET), poly(methyl methacrylate), and polycarbonate] as trendy replacements for glass substrates in the fields of optical devices, displays, and windows of buildings or automobiles, the demand for low-cost preparation methods of silica thin films as an antireflection material, gas barrier coatings, etc. are increasing.[1-5] Previously, we have cathodically prepared silica thin films from an aqueous solution of ammonium hexafluorosilicate $[(NH_4)_2SiF_6]$ onto metal substrates.[6] Moreover, for lower or nonconductive substrates involving PET, an electroless process with reducing agent dimethylamine borane (DMAB),[7] called redox deposition, has been proposed, and antireflection characteristics to PET have been investigated.[8,9] The redox deposition process includes an initial oxidation and reduction of DMAB and water to alkaline dimethylamine and H_2 gas, respectively, leading to the increase of pH (Eq. 1)

$$(CH_3)_2NHBH_3 + 3H_2O + H^+ \rightarrow (CH_3)_2NH_2^+ + H_3BO_3 + 3H_2 \qquad [1]$$

by which the formation (Eq. 2) and polymerization (Eq. 3) of hydroxide species is caused, resulting in silica film deposition

$$SiF_6^{2-} + 4OH^- \rightleftharpoons Si(OH)_4 + 6F^- \qquad [2]$$

$$Si(OH)_4 \rightarrow SiO_2 + 2H_2O \qquad [3]$$

The method can be characterized as an inorganic sol-gel process triggered by the electrochemical reaction (Eq. 1) in an aqueous media and using inorganic silicon source, where advantageous cost effectiveness of preferential silica formation in the vicinity of substrate, free from organic solvents, alkoxides, and heat-treatment, over the conventional sol-gel method can be claimed.

Our previous investigation on the time course of the redox deposition has shown that the essential film growth starts after an induction period that is shorter in the case of a higher initial concentration of DMAB.[8] Moreover, an excellent antireflection film (0.3% at 550 nm) was obtained by the two-step immersion process from comparable highly DMAB-concentrated ($200\ \text{mmol dm}^{-3}$) solutions.[9] Although higher initial DMAB concentration is effective for the initial reaction rate, the excess use of DMAB is costly and results in un-needed formation of silica particles in the solution bulk. Therefore, adequate agents activating DMAB decomposition and preventing the formation of silica particles in the solution are needed. Hydrogen peroxide (H_2O_2) is a leading candidate for the oxidation of DMAB because of its high potential[10]

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$

$$E_0 = 1.776 - 0.0591\ \text{pH} + 0.0293 \log[H_2O_2] \qquad [4]$$

Poly(*N*-vinylpyrrolidone) (PVP) is strikingly used in the sol-gel process for improvement of the various properties of the films or plates (gas barrier,[11] crack-avoiding,[12] composition with TiO_2 for optical waveguides,[13] and hybridization with organic functional materials)[14] because PVP is so amphiphilic that it easily interacts with the hydroxyl group of oxides in water/alcohol mixture media and then promotes the compatibility of the precursors in sols and the stress relaxation in the films. Moreover, the interaction of PVP with silica is beneficial to fabrication of nanostructural materials.[15,16] In light of these results, we have conceived of utilization of PVP as an interactive agent to silica particle inhibiting agglomeration of the precipitation in the solution. In the present paper, we investigated the effects of H_2O_2 and PVP addition on the film growth process by way of characterization of the films.

Experimental

All chemicals were dissolved in water purified by deionization (Millipore Corporation Milli-RX12 Plus). Pretreatment and Sn–Pd catalyzation of a PET sheet (Toray Lumirror T60, thickness 250 μm) substrate and a silicon wafer [Electronics and Materials Co., n-type, (100)-oriented, 0.1–100 Ω cm] substrate were performed according to previously reported methods.[7,9] In a typical procedure, the catalyst-loaded substrates were immersed into an aqueous solution containing a $500\ \text{mmol dm}^{-3}$ ammonium hexafluorosilicate $[(NH_4)_2SiF_6$, Kanto Chemicals, >98%], a $20\ \text{mmol dm}^{-3}$ dimethylamine borane $[(CH_3)_2NHBH_3$, DMAB, Wako Pure Chemical Industries, 97%], a 2 vol % H_2O_2 aqueous solution (30%, Santoku Chemical Industries Co., Ltd.), and PVP (Nacalai, average molecular weight 24,500) at 333 K. The film samples on the PET substrate, SF0, SF1, and SF5, were prepared from the solutions containing 0, 1, and $5\ \text{mg dm}^{-3}$ PVP for 4, 4, and 8 h, respectively.

The silicon content in the films was determined by means of an X-ray fluorescent spectrometer (Rigaku RIX3100) and the fundamental parameter method[17] without a standard sample for the thickness. The calculation was performed using default mass-absorption coefficients of individual elements and assuming that there are SiO_2 films on the substrate containing C and O in the atomic ratio 7:3. The PVP adsorption to catalyzed PET substrate was detected by X-ray photoelectron spectroscopy (XPS, PHI ESCA 5700, mono-

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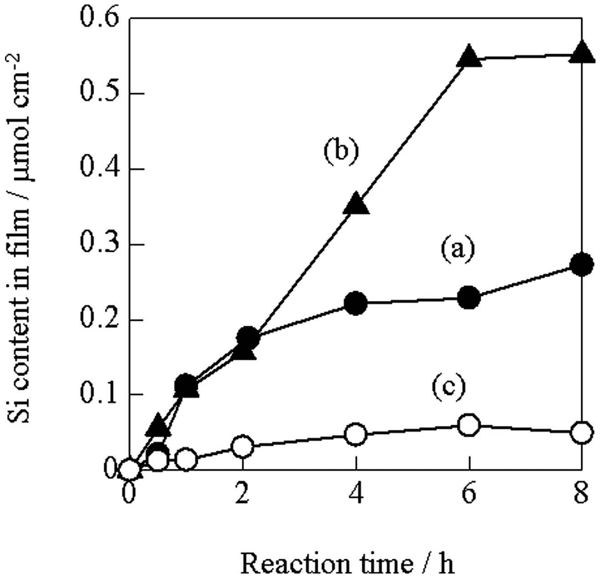

Figure 1. Time course of silicon contents in the deposits prepared by redox deposition from solutions containing H_2O_2, and various concentrations of PVP: (a, closed circles) 0, (b, closed triangles) 1, and (c, open circles) 5 mg dm^{-3}.

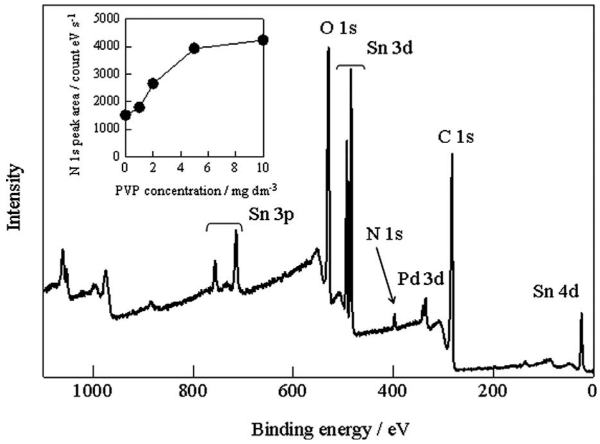

Figure 2. Wide-scan XPS spectrum of PET catalyzed and immersed in the solution containing 5 mg dm^{-3} PVP. The inset shows N 1 s peak area for concentration of PVP solution in which the catalyzed PET was immersed at 333 K.

chromated Al Kα source 1486.6 eV, 200 W) for the samples prepared by immersion of the catalyzed PET in the PVP solutions at 333 K. Atomic compositions of silica films for the surface and bulk phase were analyzed by XPS (non-monochromated Al Kα 1486.6 eV, 400 W) with alternative Ar^+ sputtering (acceleration energy 4 kV) and measurements of photoelectron spectra. Default sensitivity coefficients of a PC-ACCESS data treatment system of PHI ESCA 5700 were used for calculation of the atomic concentrations. The transmittance of reaction solution at wavelength 400 nm was measured in a quartz glass cell (inner light path of 1 cm) set up in a Shimadzu spectrophotometer UV-3150. Fourier transform infrared (FTIR) spectroscopy was performed for the film samples on Si-wafer substrates, SF0/Si, SF1/Si, and SF5/Si, prepared from 0, 1, and 5 mg dm^{-3} PVP solutions for 4h, and three cycles of catalyzation immersion for 8 h (24 h in total), respectively, on a Perkin–Elmer Spectrum GXI-R0. For the measurement of a standard PVP IR spectrum, the PVP powder was dried in vacuo at 423 K for 3 h and incorporated in a KBr disk. So as to determine the peak position, a raw spectrum was fitted to a Gaussian-type peak on linear background, adopting a least-squares method. The specular reflectance spectra of PET substrate and the film sample in the UV-visible region were obtained by means of a spectrophotometer (Ohtsuka Electronics FE-3000, incident angle of 11°). For the measurement of a reflection spectrum the film was prepared by a two-step process: the deposition from the solution containing $(NH_4)_2SiF_6$, 200 mmol dm^{-3} DMAB, and H_2O_2 for 1 h, followed by catalyzation and immersion in a new solution of the same components for 30 min.

The surface morphological observations of the films were carried out with field-emission scanning electron microscopy (JEOL JSM-6700F). Cross-sectional transmission electron microscopic (TEM) images of the films on PET were obtained with a JEOL JEM-2100 (acceleration voltage 100 keV). The samples preparation procedures, Au particle mark deposition on the films surface, embedding in resin, and sectioning, were described in the preceeding paper.[9]

Results and Discussion

Figure 1 shows the effect of H_2O_2 and PVP on the film growth time course onto PET substrate. Assuming the density of the film to be 2.2 for amorphous SiO_2,[18] the thickness of the film for 8 h from the solution containing H_2O_2 and 1 mg dm^{-3} PVP was estimated to be 150 nm. In the absence of additives, the film deposition started after a long induction time (>4 h), and an extremely low amount of film (0.11 μmol cm^{-2} of Si content; data shown in the previous paper[8]) was deposited by immersion even for 8 h. The addition of H_2O_2 remarkably contributed to the enhancement of the initial film deposition rate, and the film grew without induction time. This disappearance of retention time is due to the generation of hordes of hydroxyl ions near the substrate originating from accelerated oxidation of DMAB by H_2O_2 (Eq. 1).

Moreover, by the addition of 1 mg dm^{-3} PVP (Fig. 1b), the film growth continued after 2 h and ceased after ca. 6 h, whereas in the case of only H_2O_2 addition (Fig. 1a) the rate of film deposition decreased after 2 h immersion. The decrease in film deposition rate is mainly due to the considerable and predominant formation of particles of silicon oxide/hydroxide species in the bulk solution, interfering with the film growth. Silica film formation by immersion for 4 h was enhanced, because until now the most Si content for 4 h was 0.16 μmol cm^{-2} in the case of the initial DMAB concentration of 0.05 mol dm^{-3}.[8] Figure 1 also shows the effect of PVP concentration on the deposition rate, representing that the excess addition (Fig. 1c) restrains the film deposition. As mentioned later, these effects of PVP seem to be based on adsorption of PVP molecules on the first catalyzed PET and interaction of PVP with silica particles in the solution.

The PVP adsorption on catalyzed PET is exhibited in an XPS spectrum (Fig. 2). In the wide-scan spectrum of PET catalyzed and immersed in the PVP solution (5 ppm) as a typical data, Sn 3d or Pd 3d peaks (including $3d_{5/2}$ and $3d_{3/2}$) and C 1s or O 1s photoelectron peaks attributable to the catalyst and PET, respectively, can be recognized. Because the N 1s peak corresponding to the amide group of PVP appears in the spectrum, C 1s and O 1s spectra barely include the peaks of PVP. The inset of Fig. 2 shows the increase of N 1s peak area for the catalyzed PET immersed in PVP solutions. The N 1s peak on the catalyzed PET immersed in pure water, corresponding to PVP concentration of 0 mg dm^{-3}, seems to be assignable to a contamination. The immersion in 1 mg dm^{-3} PVP solution resulted in a slight increase of N 1s peak area. According to PVP concentration, the peak area of N 1s region increased, implying PVP adsorption on the substrate.

In the course of reaction, the silica particles grew in the colloidal solution and the solution became white turbid. This change is represented by the decrease of transmittance of the solutions (Fig. 3). The film is thickened by settling of the granular silica on the PET substrate, and thereafter the precipitation becomes distinctive in the

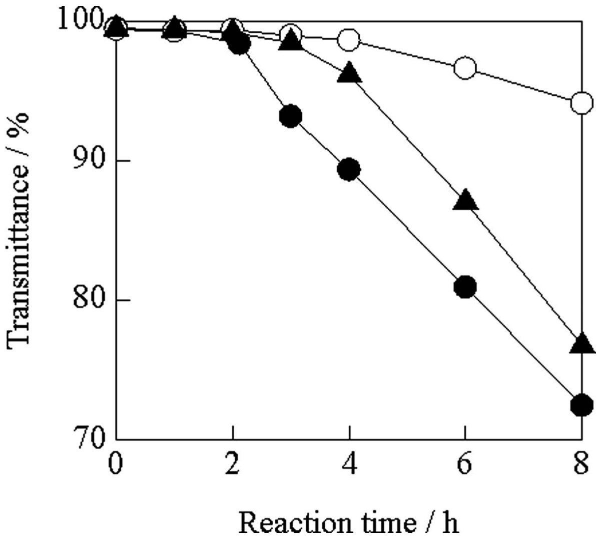

Figure 3. Time course of transmittance at 400 nm of solutions containing H_2O_2, and various initial concentrations of PVP: (a, closed circles) 0, (b, closed triangles) 1, and (c, open circles) 5 mg dm^{-3} during film-deposition reaction.

solution bulk. The accordance of time course of decreasing transmittance of the solutions with lowering of the deposition rate (Fig. 1) indicates that the growth of silica particles in the solution interrupts the growth of the film. PVP addition by 1 mg dm^{-3} delayed the growth of silica particles in the solution and maintained film growth. The excessive addition of PVP (5 mg dm^{-3}) suppressed the film growth despite stabilizing the solution.

Figure 4 shows the surface morphology of the films on PET prepared from the solutions with and without PVP. On the surface of the film prepared without PVP (SF0), considerable spherical particles having a diameter of ca. 100 nm, corresponding to the silica particles causing turbid in the solution, were observed. Cross-sectional TEM images of sliced film samples are shown in Fig. 5. Fine dark particles are Au markers for the discrimination of the film surface. The image of SF0 exhibited homogeneous film deposition before the precipitation of spherical silica particles. Contrastingly, SF1 possessed defects mainly in the substrate/film interface region (Fig. 5b), indicating laterally fragmentary formation of the film. In the image of SF5, such outstandingly large defect was not observed. The difference between the construction of SF1 and SF5 is supposedly explained in terms of the chemical species of which the films are composed, as well as of PVP molecules adsorbed on the substrate shown in Fig. 2, as exhibited below in the characterization of the films and discussed later in an inclusive model.

Figures 6-8 compare the elemental components in the three films, SF0, SF1, and SF5, for the amount of PVP addition. The atomic ratios of oxygen to silicon (O/Si) in the inner phase of the films, within which Si concentration is higher than 50% of maximal value, were commonly 2.2–2.5. Although the atomic concentrations are based on the default sensitivity factors (used without refinement), the main components of all films can be identified to SiO_2 (silica), and the comparison among miner components (C, N, F, Sn, and Pd) is valid. A negligible signal of F 1s in the films implies sufficient decomposition of SiF_6^{2-}. The reason why Sn was observed in the substrate/film interface region despite the absence of Pd is not clear. However, the presence of both Sn and Pd on the catalyzed PET surface shown in Fig. 2 can lead to the guess that the difference of the depth region in which the Sn and Pd exist is responsible for the finding. The absence of N in SF1 shown in Fig. 7 (bottom) suggests that the contribution of PVP to film growth does not result from intruding into but existing outside of the film. In the inner phase of SF5 [Fig. 8 (bottom)], C and N were noticeably observed, whereas

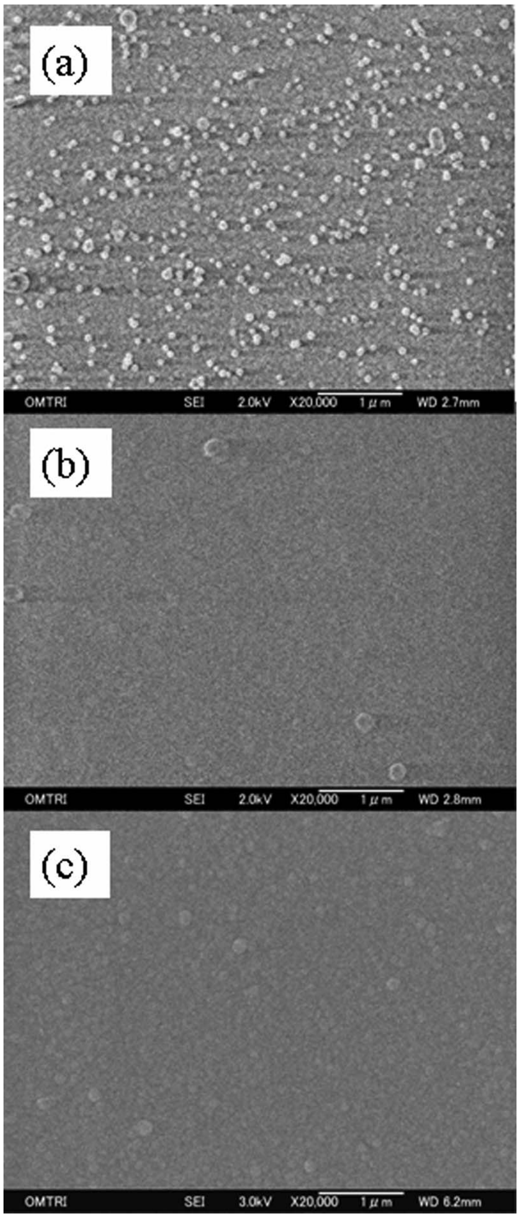

Figure 4. SEM photographs of surface of silica thin films: (a) SF0, (b) SF1, and (c) SF5.

they were not recognized in SF0 and SF1, indicating the inclusion of PVP in SF5. Comparably high concentration of N near the substrate/film interface probably indicates that the film growth seems to proceed with the aggregation of silica particles to which PVP clings on initially adsorbed PVP on the substrate.

The PVP inclusion only in SF5 is also exhibited in the IR spectrum of the film on Si substrate (Fig. 9) as a characteristic peak around 1650 cm^{-1} assigned to the stretching band of amide carbonyl group (C=O) of PVP. On the basis of our previous atomic force microscopy observations,[7,9] the films on both PET and Si substrates were composed of silica spherical grains and can be treated as identical in quality. The peak position of the carbonyl group for the film (Fig. 9c) shifted to low frequency by ca. 7 cm^{-1} from standard PVP (Fig. 9d); suggesting the interaction of C=O group of PVP and terminal silanol (Si–OH) of silica as hydrogen bonding.[19] Compared with the other works (10–40,[20] 20,[14] and 25.5 cm^{-1}[21]) this shift is small, corresponding to the weak interaction. This supposedly originates from the interaction among C=O groups of associated PVP

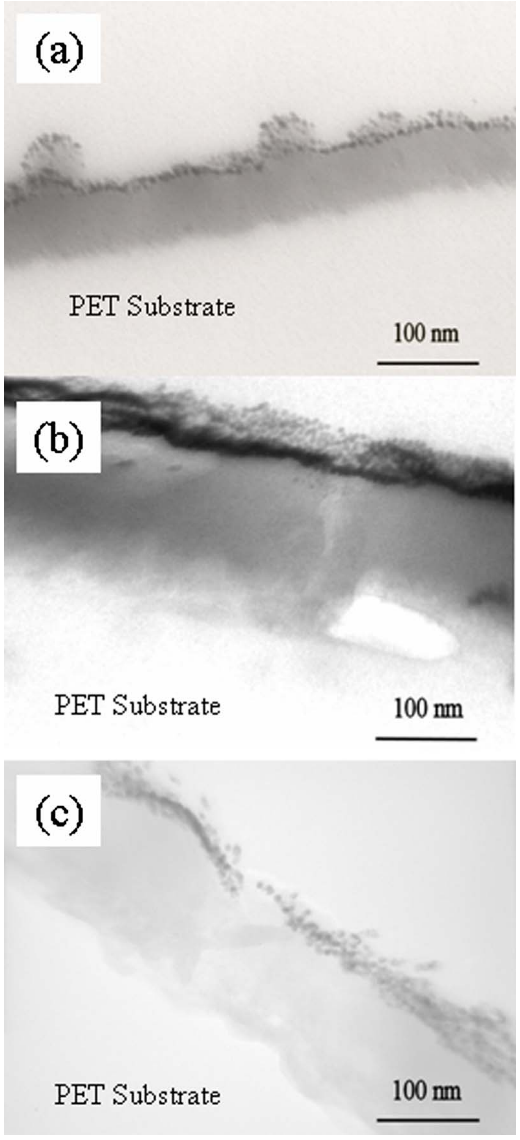

Figure 5. (Color online) Cross-sectional transmission electron micrographs of silica films on PET substrate: (a) SF0, (b) SF1, and (c) SF5.

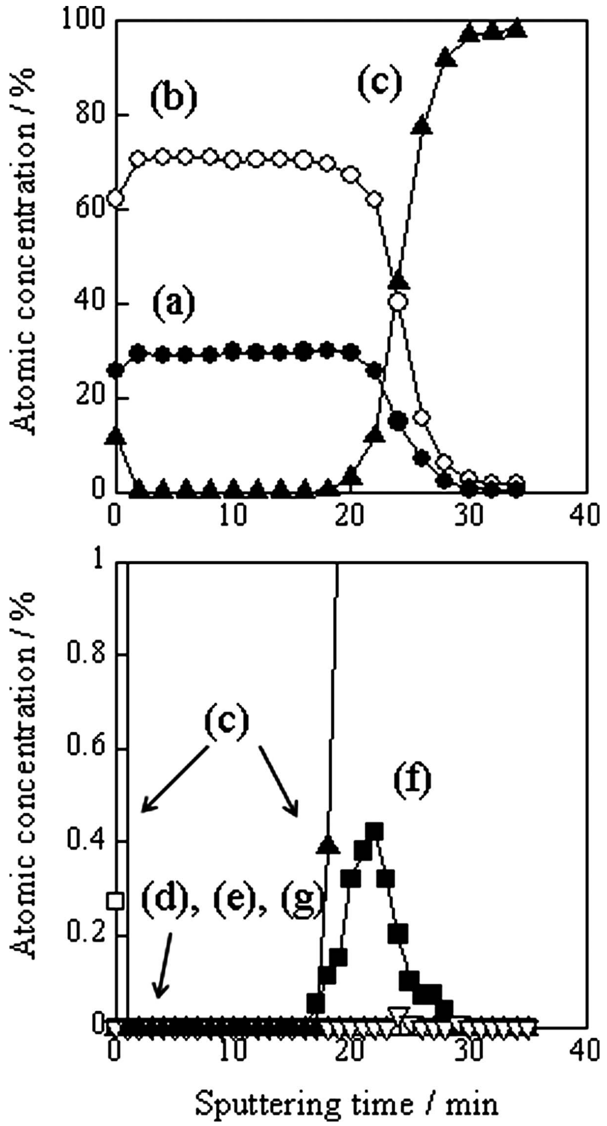

Figure 6. XPS depth distribution profile of composition of (a, closed circles) silicon, (b, open circles) oxygen, (c, closed triangles) carbon, (d, open triangles) fluorine, (e, open squares) nitrogen, (f, closed squares) tin, and (g, open inverted triangles) palladium of SF0. Full scale of bottom figure was expanded 100 times that of top.

molecules in SF5, which are closely similar to the interaction in the standard PVP powder sample. It is probable that the aggregation of PVP molecules in SF5 is intimated by the detection of PVP signals (N and C) by XPS mainly near the substrate [Fig. 8 (bottom)] and can be introduced by PVP molecules adsorbed on the substrate (Fig. 2). Because direct evidence of this interpretation, e.g., with cross-sectional TEM (Fig. 5c), has not been obtained due to insufficient magnification and contrast, further investigation is needed.

To sum up the above results, the effect of H_2O_2 and PVP addition on film deposition is speculated as Fig. 10 based on two factors for granular form silica, activity for the production of the silica in the solution and affinity of the silica with the substrate surface. The H_2O_2 promotes rapid pH increase represented by Eq. 1, leading to speedy growth of silica particles both near the substrate and in the solution (Fig 10a). The contact angle value, 77.0° (Kyowa Interface Science Co., Ltd. CA-X150), for bare PET substrate against water was remarkably decreased to 35.8° by catalyst deposition. This sufficient hydrophilicity of catalyzed substrate surface contributes to smooth coverage with silica film. In PVP-added solutions (Fig. 10b and c), a silica-PVP complex is formed and the growth of silica particles is restrained to a degree, as shown in Fig. 3. The size of PVP in the solution was estimated to be 12.5 nm by dynamic light scattering (Ohtsuka Electronics DLS-6000HLC) in terms of diameter of the sphere of huddled polymer chains, denoting that the special region, within which the hydrophobicity of PVP has effects, is more than 12 nm. Because the amount of PVP molecules placed on the silica surface and of C═O groups in a PVP molecule interacting with Si–OH groups are unclear, the connection between PVP and silica is abstractly illustrated in the scheme. In the case of comparably low concentrations of PVP (1 ppm, Fig. 10b), although PVP molecules are scatteringly adsorbed on the substrate, a large part of the surface is active for silica deposition. Moreover, PVP-free silica particles are prevented from aggregation in the solution by silica-PVP complex and then tend to be deposited on the silica film, followed by the duration of film growth. As for the defective spots in the film, an explanation can be put forward that PVP molecules adsorbed on the substrate produce a hydrophobic field near the substrate, from which hydrophilic silica particles are excluded because the hydrophilic amide group of PVP is capped by substrate. This "silica-phobic" effect of PVP on the substrate causes a difference in

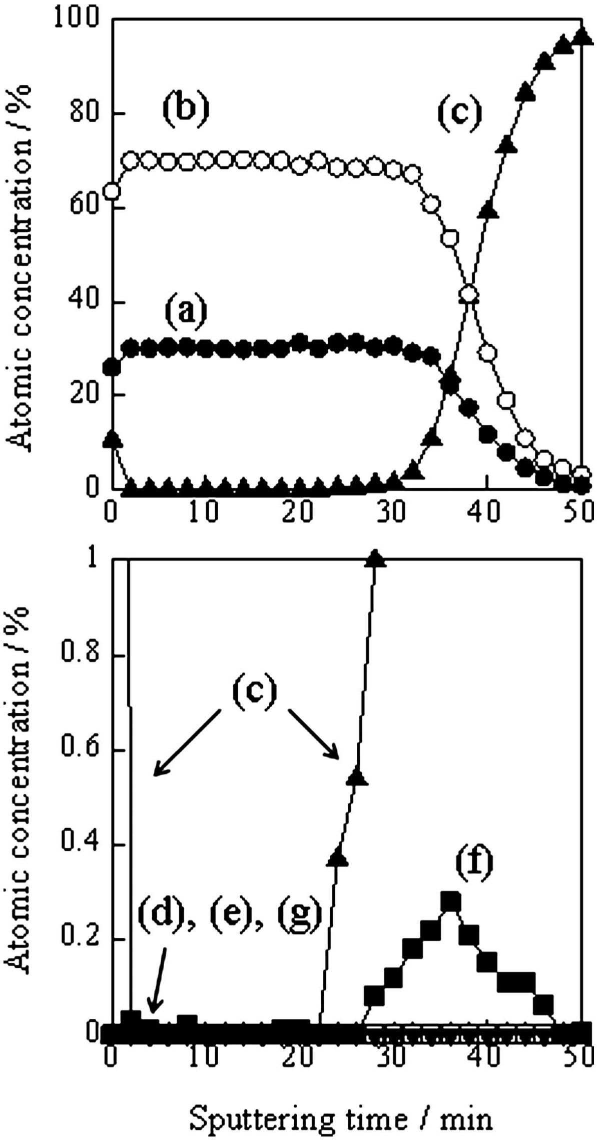

Figure 7. XPS depth distribution profile of composition of (a, closed circles) silicon, (b, open circles) oxygen, (c, closed triangles) carbon, (d, open triangles) fluorine, (e, open squares) nitrogen, (f, closed squares) tin, and (g, open inverted triangles) palladium of SF1. Full scale of bottom figure was expanded 100 times that of top.

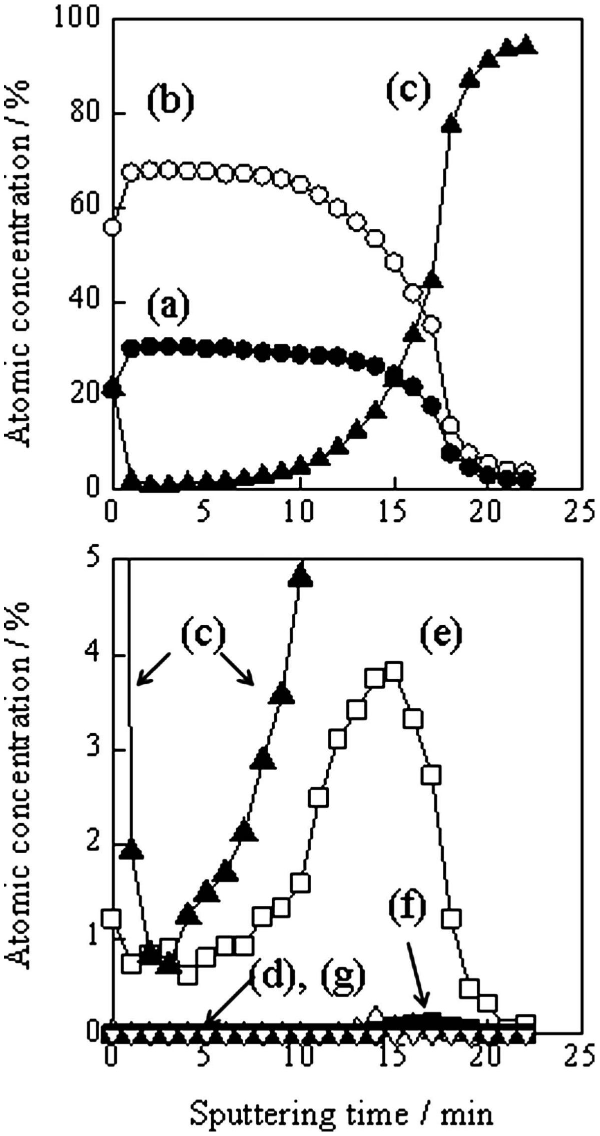

Figure 8. XPS depth distribution profile of composition of (a, closed circles) silicon, (b, open circles) oxygen, (c, closed triangles) carbon, (d, open triangles) fluorine, (e, open squares) nitrogen, (f, closed squares) tin, and (g, open inverted triangles) palladium of SF5. Full scale of bottom figure was expanded 20 times that of top.

briskness of the film growth on the substrate and lateral discontinuity in the deposition. Additionally, the slow-pace deposition in the case of concentrated PVP (5 ppm, Fig. 10c) originates from the relatively large amount of silica-repellent PVP adsorbed on the substrate and the interruption of silica particle growth in the vicinity of the substrate. Because the PVP molecules on the substrate can have affinity with another PVP molecule, the growth of the film mainly relies on the "PVP-philicity" between the PVP molecules on the substrate and that on the silica particles in the solution, and then PVP is introduced into the film.

Figure 11 exhibits the antireflection property of a silica film from an H_2O_2-added solution. The lowest reflection (0.3% at 574 nm) and the broad-band antireflection (<2%) in the visible range (380–800 nm) for the silica film (Fig. 11b) were closely similar to the results of the film prepared for 6 h from a solution without H_2O_2 reported in our preceding paper. The result indicates that H_2O_2 can accelerate the preparation rate of a suitable film by four times, and further investigation on reducing DMAB concentration is now underway.

Conclusions

In this paper, the addition of H_2O_2 has been found to remarkably improve the initial rate of redox deposition of silica thin films and to suppress the use of costly DMAB. Shortened film formation time by H_2O_2 gives rise to the high possibility of the rapid preparation of excellently antireflective films (<1%) to PET substrate. It has also been clarified that PVP prohibits inefficient particle sedimentation in the bulk solution by interaction with silica particles and brings about remarkable changes in the growth manner and the structure of silica films in no more than parts-per-millions order. In the case of a comparably low amount of addition, the high amphiphilicity of PVP adsorbed on PET substrate caused ambivalence silica film deposition to form, on one part of the substrate enhanced film deposition and on the other part produced silica-phobic field remaining void parts in the film. This finding raises important problems for the quality of films, continuity, adhesiveness, and strength, giving rise to the necessity of alternatives in which surfactants are involved, and the investigation is now in progress. The XPS and FTIR character-

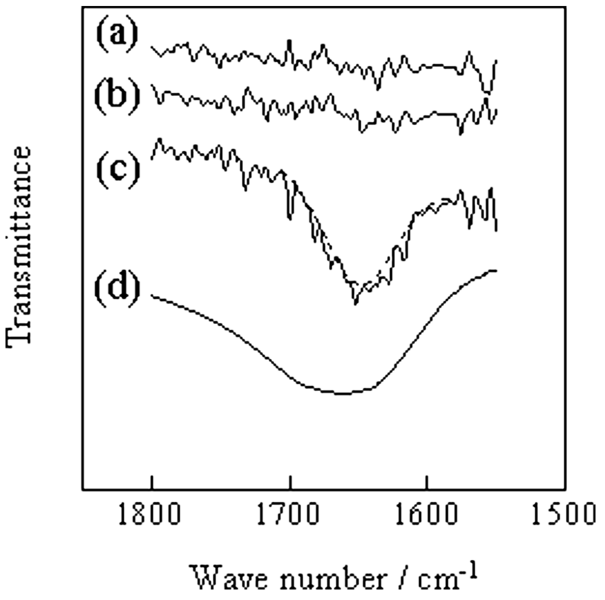

Figure 9. (Color online) FTIR transmission spectra of silica films on Si-wafer substrates: (a) SF0/Si, (b) SF1/Si, and (c) SF5/Si and (d) standard PVP powder. A Gaussian-type fitting curve (dotted line) is also exhibited for SF5/Si.

izations on the void-free film from comparably PVP-concentrated solution have revealed that PVP is incorporated in the film with the hydrogen bonding of C═O group of it to the terminal OH group of silica. The PVP-silica interaction demonstrated in this study proposes the possibility of redox preparation of size-controlled silica spherical particles and thereafter fabrication of ordered structure, e.g., photonic crystals.

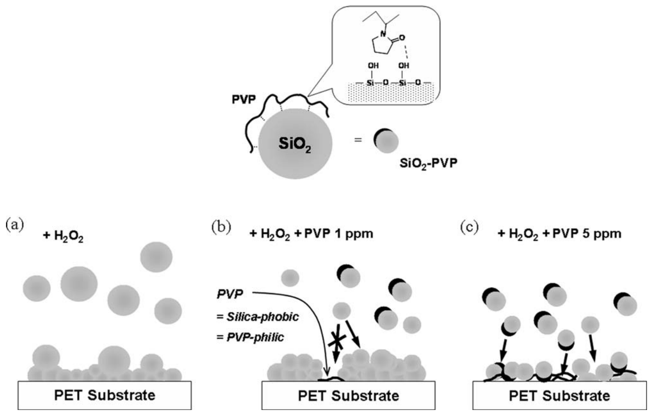

Figure 10. (Color online) Schematic mechanisms of the redox growth of silica films on PET substrates from solutions containing H_2O_2 and PVP: (a) 0, (b) 1, and (c) 5 mg dm^{-3}.

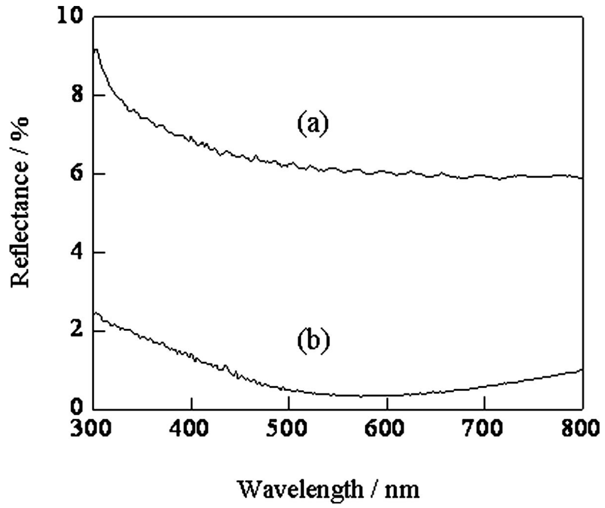

Figure 11. UV-visible specular reflection spectra of (a) untreated and (b) silica-coated PET substrate.

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