Preparation of Gold Colloid-Dispersed Silica Coating Films by the Sol–Gel Method

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Silica glass coatings containing dispersed colloidal gold particles have been prepared by dipping a slide glass substrate into acid-catalyzed tetraethoxysilane (TEOS) solutions containing $HAuCl_4 \cdot 4H_2O$, withdrawing it, and heating it at 500 °C. Effects of the amount of water and/or hydrochloric acid used for hydrolysis of TEOS on the size and state of the gold particles formed have been investigated. Higher HCl contents were effective in suppressing the escape of gold from the film on heating. Gel films derived from the highly acid-catalyzed TEOS solutions hydrolyzed with a larger amount of water were transformed into glass coatings containing dispersed gold particles larger in size; gold particles smaller than 200, 280, and 340 Å were formed in the silica coatings derived from the solutions of H_2O/TEOS mole ratios of 2, 4, and 10, respectively. Soaking of the gel coatings in monoethanolamine (MEA) vapor prior to heat treatment was found to be effective in suppressing the escape of gold from the film and in formation of silica coatings containing smaller gold particles. Silica glass coatings containing dispersed colloidal gold particles smaller than 80 Å in diameter could be prepared from highly acidic solutions through the amine vapor treatment.

Introduction

Glasses dispersed with gold colloid particles, as well as semiconductor-doped glasses, are attracting much attention because of their third-order nonlinear optical properties. The conjugate reflectivity of small gold particles in degenerate four-wave mixing (DFWM) was first reported by Ricard et al.,[1] where they measured a value of third-order nonlinear susceptibility of gold $\chi^{(3)}_m = 10^{-8}$ esu and a response time of <50 ps. A later paper by Hache et al.[2] reported the development of a model for third-order nonlinearities in metal particles. They realized large enhancements of the local field inside the particle at the plasmon resonance. A significant feature of the model is the strong size dependence of $\chi^{(3)}_m$, which is proportional to $1/r^3$, where r is the radius of the metal particle. They also showed that the nonlinear polarization that causes the nonlinear response of the gold–glass composites increases in proportion to the volume fraction of metal particles in the composite materials.[3] Other than the quantum size effect or the surface plasmon excitation mentioned above, hot electrons or Fermi smearing is recognized to be an important mechanism of the nonlinear response of the metal particles, where the size of the particles, however, has no effect in the nonlinear response.[4,5] Despite the contribution from the hot electrons, it is apparent that gold–glass composites having smaller gold particles in larger volume fraction would be ideal for potential application in nonlinear optical devices.

Conventionally, gold colloid-dispersed glass known as gold ruby glass has been prepared by the melt method using an aqueous solution of $AuCl_3$ as the Au source and appropriate thermoreducing agents like Sb_2O_3.[6,7] Because of the instability of Au^+ ions in the glass melt, it is difficult to make glasses containing gold colloids of high volume fraction without segregation of large gold particles. Besides, the volume fraction of the gold colloid in glass prepared by the melting method is generally limited to around 10^{-4}%.[6,7]

To achieve a high volume fraction of small gold particles in glass, Fukumi et al.[8] implanted Au^+ ions in silica glasses at an acceleration energy of 1.5 MeV and heated the Au-doped glasses, where glasses dispersed with gold particles of 58 Å in size and 7.6% in volume fraction were obtained. Wakabayashi et al.[9] applied RF sputtering to preparation of Au-doped silica glass with gold particles of 55 Å in size and 1% in volume fraction, which is calculated from their batch composition. Olsen et al.[10] prepared gold cluster laden polydiacetylenes, where a large metal volume fraction up to 15% was achieved with an average cluster size of 20 Å.

The sol–gel method is another candidate for making gold colloid-dispersed glasses. Matsuoka et al.[11] prepared

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[1] Recard, D.; Roussignol, P.; Flytzanis, C. *Opt. Lett.* **1985,** *10,* 511.

[2] Hache, F.; Ricard, D.; Flytzanis, C. *J. Opt. Soc. Am.* **1986,** *B3,* 1647.

[3] A phase conjugation (PC) signal is generated in DFWM, where two counter propagating pump beams of the electric field, E_f and E_b, and a weak probe beam, E_p, at a small angle with respect to the forward pump are incident upon the sample. In the model of Hache et al. for metal–glass composites the nonlinear polarization that causes the PC signal generation, $P^{(3)}_{NL}$, can be written as $P^{(3)}_{NL} = 3[pf^2|f|^2\chi^{(3)}_m]E_fE_p{}^*E_b = 3\chi^{(3)}E_fE_p{}^*E_b$, where p is the volume fraction of metal, f is the local field factor and $\chi^{(3)}$ is the third-order nonlinear susceptibility of the composite material. The local field factor f is defined as $f = 3\epsilon_d/[\epsilon_m + 2\epsilon_d]$, where ϵ_m and ϵ_d are the dielectric constant of the metal and the host material, respectively.

[4] Bloemer, M. J.; Haus, J. W.; Ashley, P. R. *J. Opt. Soc. Am.* **1990,** *B7,* 790.

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[6] Weyle, W. A. *Coloured Glasses;* The Society of Glass Technology: Sheffield, 1951.

[7] McMillan, P. W. *Glass-Ceramics;* Academic Press: London, 1964.

[8] Fukumi, K.; Chayahara, A.; Kadono, K.; Sakaguchi, T.; Horino, Y.; Miya, M.; Hayakawa, J.; Satou, M. *Jpn. J. Appl. Phys.* **1991,** *30,* L742.

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[10] Olsen, A. W.; Kafafi, Z. H. *J. Am. Chem. Soc.* **1991,** *113,* 7758.

[11] Matsuoka, J.; Mizutani, R.; Nasu, H.; Kamiya, K. *J. Ceram. Soc. Jpn.* **1992,** *100,* 599.

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Table I. Compositions of the Coating Solutions

	mole ratio				
solution no.	TEOS	H_2O^a	HCl	C_2H_5OH	Au^b
1	1	4	0.01	2	0.028
2	1	2	0.4	2	0.028
3	1	4	0.4	2	0.028
4	1	10	0.4	2	0.028

[a] H_2O originating from hydrochloric acid and $HAuCl_4 \cdot 4H_2O$ is included in the calculation. [b] $HAuCl_4 \cdot 4H_2O$ was used as the Au source.

gold colloid-dispersed silica coatings by using an acid-catalyzed tetraethoxysilane (TEOS) solution containing $NaAuCl_4 \cdot 2H_2O$ of molar composition, TEOS:C_2H_5OH:H_2O:HCl = 1:6:6:0.01, and heating the gel coatings. From the optical absorption measurement, they concluded that heat treatment of the gel coating films at 400 °C provides silica coatings containing dispersed gold colloids of about 80 Å in diameter, and the gold particle size decreases to about 70 Å when the coating film is heated further at 900–1000 °C, although direct observation of gold particles through electron microscopy was not performed. The mole ratio of Au/TEOS of their coating solution was 0.01, which corresponds to 0.37% in volume fraction of gold in the final film.

Silica gels prepared by the hydrolysis and polycondensation reaction of silicon alkoxides are porous in nature. If we can entrap appropriate gold salts in the gel pores of small diameter and reduce or decompose the salts confined in the pores, glasses dispersed with gold particles are expected to be formed. It should be stressed that the limited migration of gold species entrapped in the gel pores, which is not the case with gold ions in aqueous solutions or in glass melts, enables formation of small gold particles in high volume fraction without undesired aggregation on heating. It should also be emphasized that the pore size and the flexibility or rigidness of the host gel matrix, which would influence the final size of metallic gold particles, can be varied in the sol–gel process by controlling the conditions of hydrolysis and condensation of alkoxides.

On the basis of our concept mentioned above, it would be of interest to study the effects of the amount of water and acid used in the hydrolysis of the silicon alkoxide on the size and state of gold particles that would be precipitated in the silica matrix via heat treatment. The present authors have attempted to prepare silica coating films containing gold colloids using TEOS–H_2O–HCl–C_2H_5OH–$HAuCl_4 \cdot 4H_2O$ solutions of varying H_2O and HCl concentrations to study the size and state of gold particles precipitated in the heat-treated final products using optical absorption spectroscopy and TEM observation. In addition, we have found that soaking of the gel film in an amine vapor, which would change the properties of the gel matrix, has an effect on the size and state of the gold particles. Coating films containing gold colloids of 1% in volume fraction in the final products, which is a larger fraction than that of Matsuoka et al.,[11] have been prepared in the present study.

Experimental Section

Preparation of the Coating Films. Homogeneous tetraethoxysilane (TEOS) solutions containing $HAuCl_4 \cdot 4H_2O$ (Nacalai Tesque) as the gold source were prepared by adding a water–hydrochloric acid (Nacalai Tesque)–ethanol (Wako Pure Chemical Industries)–gold salt solution dropwise to a TEOS (Shinetsu Chemical)–ethanol solution under vigorous stirring in a beaker at room temperature. The molar compositions of the solutions are TEOS:H_2O:HCl:C_2H_5OH:Au = 1:2–10:0.01 or 0.4:0.028, where water originating from the hydrochloric acid and the gold salt was taken into account, as listed in Table I. Hereafter the mole ratios H_2O/TEOS and HCl/TEOS are represented by w and h, respectively. After stirring the solution for 5 min at room temperature, the beaker was tightly sealed and kept at 40 °C in a water bath for 120 min.

Table II. Color and Optical Absorption Peak Position of the Coating Films[a]

solution composition			
H_2O/TEOS	HCl/TEOS	color	abs peak position (nm)
	Without MEA Vapor Treatment		
4	0.01	very light red	522
2	0.4	slightly purplish red	539
4	0.4	slightly purplish red	542
10	0.4	light purplish blue	580
	With MEA Vapor Treatment		
4	0.01	light red	521
2	0.4	light red	521
4	0.4	light red	512
10	0.4	light red	519

[a] The coating films were wiped with tissue paper infiltrated with acetone to remove the gold precipitates that failed to be entrapped in the silica film.

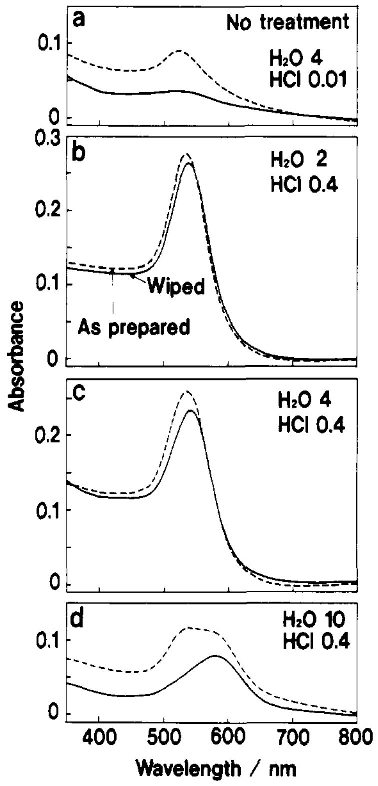

Figure 1. Optical absorption spectra of the as prepared (- - -) and wiped (—) coating films prepared without MEA vapor treatment. The samples were prepared from the solutions of w = 4 and h = 0.01 (a), w = 2 and h = 0.4 (b), w = 4 and h = 0.4 (c), and w = 10 and h = 0.4 (d).

A cleaned slide glass substrate (Matsunami Glass Industries, S-1112) was dipped into the solution and withdrawn at a constant rate of 3 cm/min to obtain a coating film, which was then transferred directly into a furnace of 500 °C and kept there for 10 min. For some of the samples, after withdrawing the substrate from the solution, the substrate was held above monoethanolamine (MEA, Wako Pure Chemical Industries) in a beaker for 1 min at room temperature prior to the heat treatment.

Measurements. Optical absorption spectra were measured for the coating films in the wavelength range 350–800 nm using a Hitachi Manufacturing Co. Model U-3500 spectrophotometer

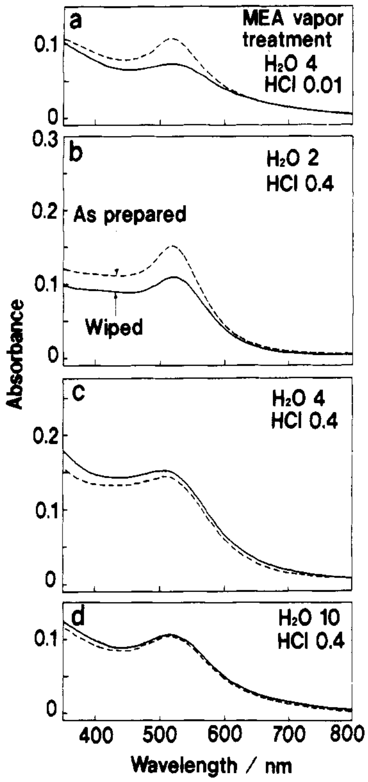

Figure 2. Optical absorption spectra of the as prepared (- - -) and wiped (—) coating films prepared with MEA vapor treatment. The samples were prepared from the solutions of w = 4 and h = 0.01 (a), w = 2 and h = 0.4 (b), w = 4 and h = 0.4 (c), and w = 10 and h = 0.4 (d).

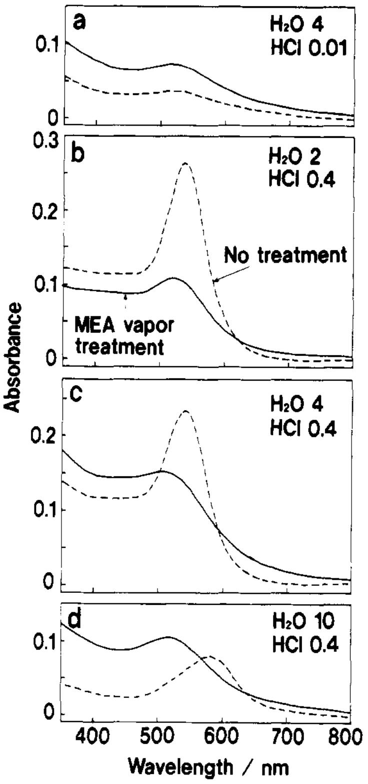

Figure 3. Optical absorption spectra of the wiped coating films prepared with (—) and without (- - -) MEA vapor treatment. The samples were prepared from the solutions of w = 4 and h = 0.01 (a), w = 2 and h = 0.4 (b), w = 4 and h = 0.4 (c), and w = 10 and h = 0.4 (d).

with a resolution of ±0.2 nm. A slide glass was used as a reference sample.

X-ray diffraction (XRD) measurement was carried out for the coating films by a Rigaku Co. Model RINT 1400 diffractometer using Cu Kα radiation operated at 40 kV and 200 mA. A Rigaku CN2651A2 thin-film attachment was used, and the glancing angle of the incident beam against the surface of the coating film was fixed at 1°. The diffracted X-ray was collected by scanning in 0.2° step and counting for 200 s.

The microstructure of the samples was observed by a Hitachi Manufacturing Co. Model HU-11D transmission electron microscope (TEM) at an acceleration voltage of 75 kV.

Results

Optical Absorption Spectra of the Coating Films. The coating solutions were transparent and yellow in color, and the gel-coating films looked transparent and colorless. The coating films heat-treated at 500 °C were transparent and colored. Some of the samples had very light brown precipitation on the surface of the coating films, which could not be seen by the naked eye without very careful observation and seemed not to affect the transparency of the films. It was found that these surface precipitates could be removed by wiping the coating film, and they showed sharp X-ray diffraction peaks attributed to metallic gold. These indicate that these precipitates are metallic gold species that failed to be entrapped in the silica film and escaped from the gel matrix on the heat treatment. The colors of the coating films of which the surface precipitates were removed by wiping with tissue paper infiltrated with acetone are summarized in Table II.

To evaluate the degree of the escape of gold species from the silica matrix, optical absorption spectra were compared between the as-prepared and the wiped samples in Figure 1. A significant reduction in absorbance in the wavelength range of 500–600 nm, which is due to gold colloids,[12] by wiping is observed for the samples derived from the solution of w = 4 and h = 0.01 (Figure 1a) and that of w = 10 and h = 0.4 (Figure 1d). On the other hand, a less amount of reduction of the absorbance by wiping is seen for the sample prepared from a larger amount of acid of h = 0.4 as can be seen in the spectra of the samples prepared from the solutions of w = 4 (Figure 1c), indicating that much larger portion of gold could be entrapped in the silica film for this sample.

Figure 2 shows the absorption spectra of the samples that were prepared by soaking in the MEA vapor treatment before heating. A comparison of Figure 1 with Figure 2 shows that the reduction of absorbance resulting from wiping is decreased by the MEA vapor treatment except for the sample from the solution of w = 2 and h = 0.4. This effect is significant for the sample from the solution of w = 10 and h = 0.4 (Figure 2d), and a negligible reduction in absorbance by wiping is seen in the spectra of the samples from the highly acid-catalyzed solutions of w = 4 and 10 (Figure 2c, and d), indicating that the MEA vapor treatment has a great effect in suppressing the escape of gold from the gel matrix on heating. For the sample from the solution of w = 2 and h = 0.4, however, the reduction of absorbance by wiping increases through the amine vapor treatment (Figure 2b).

Dependence of the optical absorption due to the entrapped gold on the starting solution composition can be seen in the absorption spectra of the wiped samples

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[12] Creighton, J. A.; Eadon, D. G. *J. Chem. Soc., Faraday Trans.* 1991, *87*, 3881.

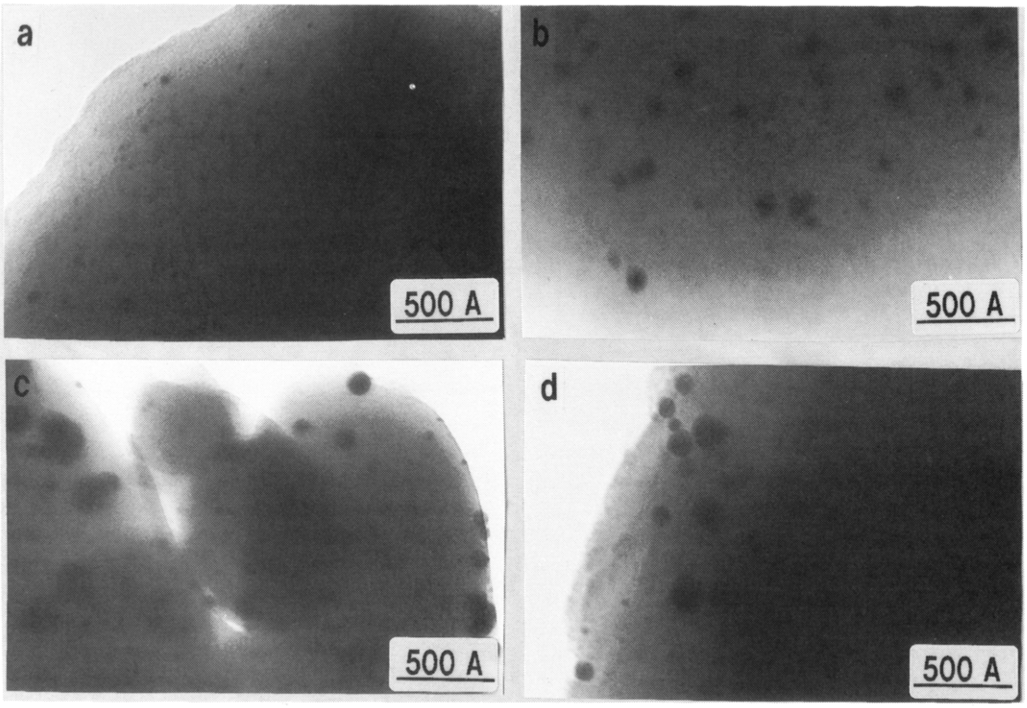

Figure 4. TEM photographs of the wiped coating films prepared without MEA vapor treatment. The samples were prepared from the solutions of $w = 4$ and $h = 0.01$ (a), $w = 2$ and $h = 0.4$ (b), $w = 4$ and $h = 0.4$ (c), and $w = 10$ and $h = 0.4$ (d).

without the amine vapor treatment (Figure 1). In the samples from the highly acidic solutions of $h = 0.4$, the absorption band shifts to longer wavelength as the water content of the solution is increased. For the samples from the solutions of $w = 4$, the band shifts to longer wavelengths when the acid content is increased from $h = 0.01$ to 0.4. These tendencies are more clearly seen in the peak position data summarized in Table II. Much lower absorbance of the samples from the solution of $w = 4$ and $h = 0.01$ and that of $w = 10$ and $h = 0.4$ is attributed to the higher amount of the gold particles removed through wiping as described previously.

Absorption spectra are compared between the wiped samples prepared with and without the amine vapor treatment in Figure 3. It can be seen that the absorption band shifts to shorter wavelengths by the amine vapor treatment (Figure 3b,c,d) except for the sample from the weakly acidic solution ($h = 0.01$) of $w = 4$ (Figure 3a). It is seen that for the samples through the MEA vapor treatment the absorption bands are centered around 520 nm irrespective of the amount of water and hydrochloric acid used in the hydrolysis of TEOS. The peak position data are listed in Table II.

TEM Observation and Distribution of Gold Particle Size. Figure 4 shows TEM photographs of the samples prepared without the amine vapor treatment. Figure 5 shows the distribution of gold particle size that were determined by measuring the size of 200–300 gold particles on the TEM pictures. Small gold particles of about 50 Å in size and a small number of larger particles are seen in the sample from the weakly acidic solution of $w = 4$ (Figure 4a and Figure 5a). An increase in the gold particle size is found when the acid content h is increased from 0.01 to 0.4 for the samples from the solution of $w = 4$ (Figure 4c and Figure 5c).

In the samples derived from the highly acidic solutions of $h = 0.4$, an increase in the particle size is observed when the water content w is increased (Figure 4b–d). For the sample from the solution of $w = 2$, particles of 40–200 Å are seen. Particles of 40–280 Å are observed in the sample from the solution of $w = 4$. For the sample from the

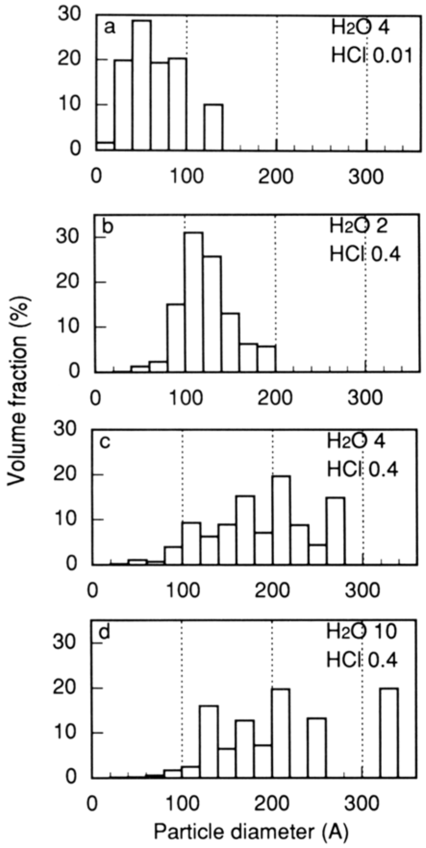

Figure 5. Distribution of gold particle size in the wiped coating films prepared from the solutions of $w = 4$ and $h = 0.01$ (a), $w = 2$ and $h = 0.4$ (b), $w = 4$ and $h = 0.4$ (c), and $w = 10$ and $h = 0.4$ (d).

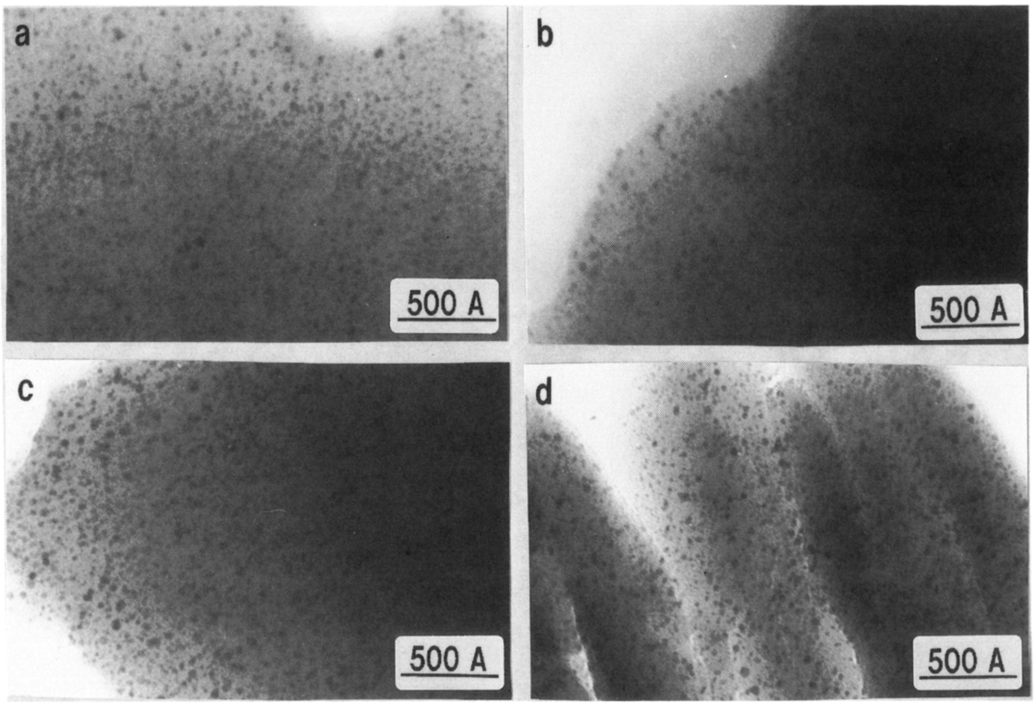

Figure 6. TEM photographs of the wiped coating films prepared with MEA vapor treatment. The samples were prepared from the solutions of $w = 4$ and $h = 0.01$ (a), $w = 2$ and $h = 0.4$ (b), $w = 4$ and $h = 0.4$ (c), and $w = 10$ and $h = 0.4$ (d).

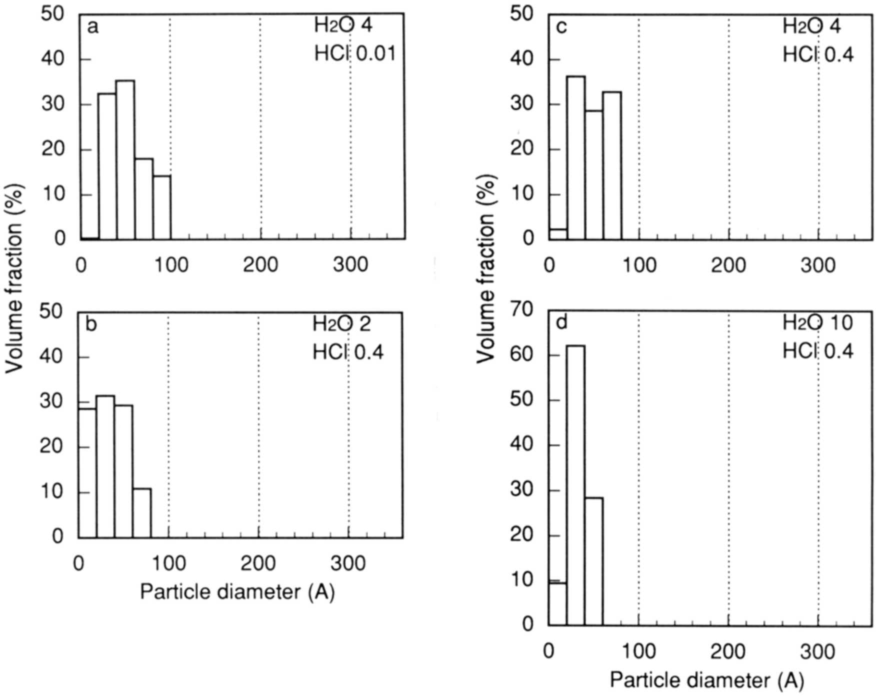

Figure 7. Distribution of gold particle size in the wiped coating films prepared with MEA vapor treatment. The samples were prepared from the solutions of $w = 4$ and $h = 0.01$ (a), $w = 2$ and $h = 0.4$ (b), $w = 4$ and $h = 0.4$ (c), and $w = 10$ and $h = 0.4$ (d).

solution of $w = 10$, distribution of the particle size is broader and particles of the size ranging from 60 to 340 Å are observed.

Figure 6 and 7 show TEM photographs of the samples obtained through the amine vapor treatment and the distribution of gold particle size, respectively. In all samples, the size of gold particles is less than 60–100 Å. It is seen that the distribution of the particle size is much sharper for the samples prepared with the amine vapor treatment compared with those without the treatment.

XRD Patterns of the Coating Films. Figure 8 shows the XRD patterns of the coating films prepared from the solution of $w = 4$ and $h = 0.4$ with and without the amine vapor treatment. To exclude the information on the gold particles that failed to be entrapped and were precipitated on the surface of the silica film, the surface gold precipitates were removed by wiping the sample prior to the measurement. Peaks at $2\theta = 38.15°$ and $44.25°$, corresponding to (111) and (200) planes of metal gold, are clearly seen in the pattern of the sample prepared without the amine treatment. The two peaks are much broader in the sample prepared with the amine treatment. The crystallite size of gold, calculated on the basis of Scherrer's equation using half height widths of the Au (111) peak, was 114 ± 2 and

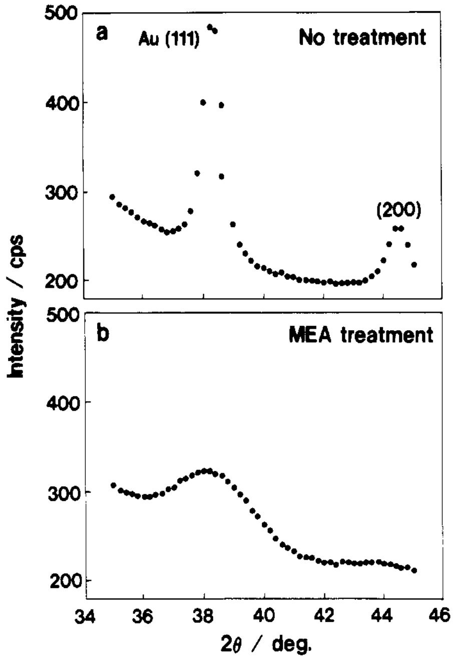

Figure 8. X-ray diffraction pattern of the wiped coating films prepared from the solution of $w = 4$ and $h = 0.4$ without (a) and with (b) the MEA vapor treatment.

38 ± 2 Å for the samples prepared without and with the amine vapor treatment, respectively.

Discussion

Effect of the Solution Composition and the MEA Vapor Treatment on the Extent of the Escape of Gold Particles. It has been found from the comparison between the optical absorption spectra of the as-prepared and the wiped samples (Figure 1) that a quite large amount of gold failed to be entrapped in the film and escaped from the film on the heat treatment for the samples from the weakly acidic solution of $h = 0.01$ and the highly acidic solution containing a high water content of $w = 10$. The use of a higher acid content in the solution and the amine vapor treatment, however, has been demonstrated to be effective in suppressing the escape of gold from the film, while it was not effective for the sample from the highly acidic solution of $w = 2$.

Schematic illustration of the transformation of the gel film into the gold-silica composite film is shown in Figure 9. In the gel film, the gold salt species may be dissolved in the liquid phase in the gel pores (Figure 9, step 1). It is known that $HAuCl_4{\cdot}4H_2O$ is decomposed in air when heated in the following way:[13]

$$HAuCl_4{\cdot}4H_2O \xrightarrow{100\ °C} AuCl_3 \xrightarrow{160\ °C} AuCl \xrightarrow{200\ °C} Au$$

Because ethanol can act as a reducing agent,[14] formation of metallic gold at lower temperatures than 200 °C would be possible. The following processes would take place in the gel film on heating: (1) evaporation of the liquid phase in the pores; (2) decomposition of the gold salt and formation of metallic gold within the pores; (3) condensation reaction between silanols and/or ethoxyl groups, which further develops the siloxane linkages; (4) shrinkage and collapse of the pores.

Silica gel network with a smaller degree of the cross-linking of siloxane bonds are more mechanically flexible, which would lead to a larger shrinkage on heating. A larger shrinkage of the gel film may squeeze the liquid phase in the pores out of the film (Figure 9a, step 2), resulting in decomposition of gold species not within but on the surface of the film (Figure 9a, step 4). This should be the reason why a larger amount of gold precipitated on the surface of the film for the sample from the weakly acidic solution than for the highly acidic solution. A more rapid hydrolysis and polycondensation reaction of TEOS[15] and hence a more rigid gel network structure are expected for the more highly acid-catalyzed solutions. Because of the higher rigidness of the gel network derived from the high acid solution, a less amount of gold would escape from the film (Figure 9b).

Among the samples from the solutions of $h = 0.4$, that from the solution of $w = 10$ showed the highest extent of the escape of gold from the silica film (Figure 1d). Higher water contents in the TEOS solution would result in formation of larger pores in the gel structure, because gel network is more colloidal than polymeric when prepared with a larger amount of water.[16] Larger open pores would accelerate the evaporation of the liquid phase, which induces a higher degree of escape of gold from the film on heating.

The role of the MEA vapor treatment in suppressing the escape of gold from the film has been considered as follows. The exposure of gel films to a basic atmosphere arising from MEA accelerates the polycondensation reaction between unreacted silanols and/or ethoxyl groups that are left in the gel film. The condensation rate of silicates is known to increase when pH of the solution increases from 2 to 7.[17] As a result, the cross-linking of the siloxane bonds in the silica gel film develops further and the rigidness of the gel film increases. This reduces the extent and rate of shrinkage of the film in the heating process and permits gold species to be decomposed and transformed into metallic gold within the pores (Figure 9c).

Another possible explanation is that the MEA vapor accelerates the conversion of gold chloride into tiny solid particles of gold hydroxides within the pores. They are fixed and entrapped more stably than the salt dissolved in the pore liquid, which reduces the escape of gold from the film.

Effect of the Solution Composition and the MEA Vapor Treatment on the Gold Particle Size. It is known that gold particles of the size much smaller than the wavelength of lights show the optical absorption band centered around 520 nm and the band shifts to longer wavelengths as the particle size increases.[18] Absorption bands of much longer wavelength than 520 nm, found in the samples from the highly acidic solutions without the amine vapor treatment (see Table II), can be attributed to the large gold particles formed in the films, as seen in the TEM observations (Figures 4 and 5).

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(13) Johnson, B. F. G.; Davis, R. *Comprehensive Inorganic Chemistry*; Bailar Jr., J. C., Emeleus, H. J., Nyholm, R., Trotman-Dickenzon, A. F., Eds.; Pergamon: New York, 1973; Vol. 3, p 129.

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(15) Pope, E. J. A.; Mackenzie, J. D. *J. Non-Cryst. Solids* **1986**, *87*, 185.

(16) Sakka, S.; Kozuka, H. *J. Non-Cryst. Solids*, **1988**, *100*, 142.

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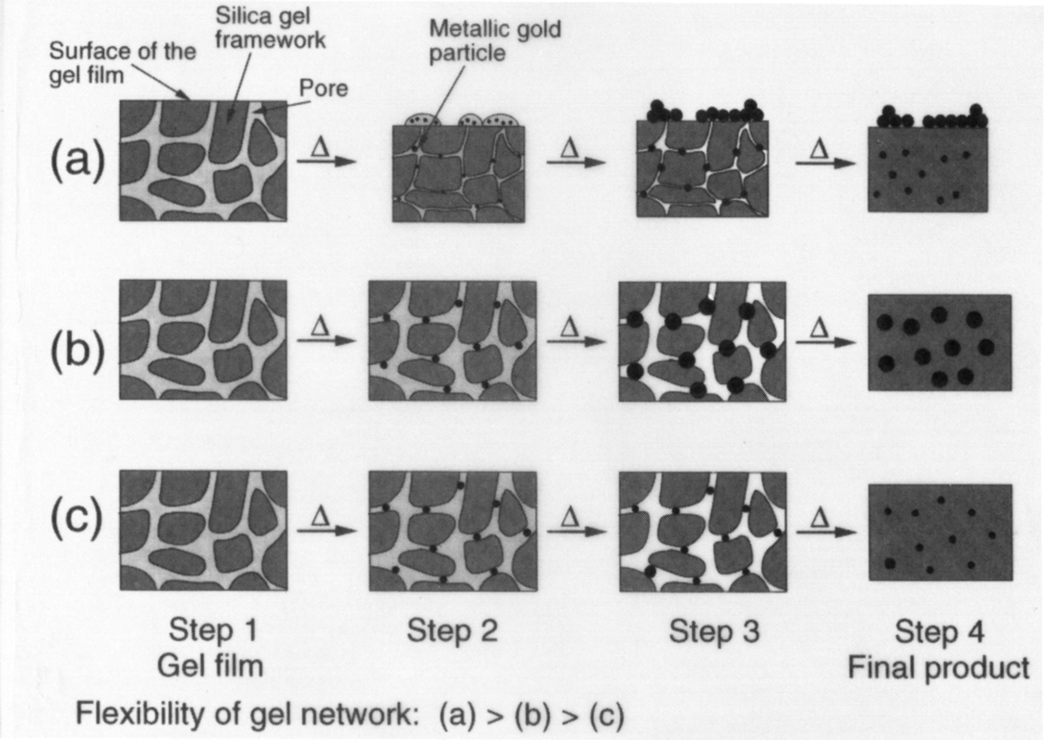

Figure 9. Schematic illustration of transformation of the gel coatings into the glass coatings on heating. The cross section of the coating films is shown.

As discussed previously, higher acid contents of the starting solutions may give rise to more rigid gel network, which shrinks less on heating than that from weakly acidic solutions. This may explain why the higher HCl content results in precipitation of larger gold particles in the samples of $w = 4$ (Figure 9a,b). As discussed previously, higher water contents also produce larger pores and so allow formation of larger gold particles, as seen in the samples from the solutions of $h = 0.4$.

The MEA vapor treatment promotes the condensation reaction in the gel films, giving rise to more rigid gel network. Because of the higher rigidness of the gel network, the size of the metallic gold particles formed on heating is limited by the size of the gel pores (Figure 9c). In the sample without the MEA vapor treatment, the lower rigidness of the gel network allows growth of the gold particle to the larger size than the pore size (Figure 9b).

Evaluation of the Volume Fraction of Metallic Gold Particles in the Coating Film. The volume fraction of the metallic gold particles in the coating films was evaluated for the samples prepared from the highly acidic solutions ($h = 0.4$) of $w = 4$ and 10 and with the MEA vapor treatment, which showed no reduction of absorbance in the optical absorption spectra when wiped. The evaluation was made by counting the number and measuring the size of the gold particles in a specific area on the TEM photographs, which gives us the total volume of the gold particles, and dividing the total volume of the gold by the volume of the film, where the thickness of the sample observed in TEM is assumed to be 130 or 260 Å. The assumption of the thickness of the sample is made on the basis of the fact that the sample containing gold particles larger than 260 Å in size gave very dark image of the silica matrix on the TEM observation. We adopted relatively bright TEM image as the data. The volume fraction of gold thus obtained is 1.9 and 1.0% for the samples of $w = 4$ and 10, respectively, when the thickness is assumed to be 130 Å, and 1.0 and 0.5% for the samples of $w = 4$ and 10, respectively, when the thickness is assumed to be 260 Å. Taking account of the experimental error and error in the assumed thickness, we can conclude that the gold particles are contained in the film in volume fraction close to 1%.

Conclusions

Silica coating films dispersed with gold colloids occupying 1% volume fraction have been prepared from acid-catalyzed TEOS solutions containing $HAuCl_4 \cdot 4H_2O$ as the gold source. The high acid contents of the TEOS solutions and soaking of the gel film to monoethanolamine vapor prior to heat treatment were found to be effective in suppressing the escape of gold from of the film on heating. The higher water contents resulted in the formation of larger gold particles; gold particles smaller than 200, 280, and 340 Å were formed in the silica coatings derived from the highly acid-catalyzed TEOS solutions of H_2O/TEOS = 2, 4, and 10, respectively. The amine vapor treatment was found to reduce the gold particle size. Silica coating films containing gold particles less than 80 Å in size could be prepared by using the highly acidic solutions and the amine vapor treatment.

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