Sol−Gel Processing of Au Nanoparticles in Bulk 10% B_2O_3−90% SiO_2 Glass

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Bulk borosilicate glasses were prepared by the sol−gel process and doped with gold nanoparticles. First, a sol of the host glass (with nominal molar composition of 10% B_2O_3−90% SiO_2) was prepared, and then gold was introduced into the sol by means of a solution of a Au^{3+} complex. The resulting gels were dried at 60 °C and then heated in air at various temperatures up to 600 °C to nucleate the gold particles and sinter the glass matrix. Various gold ligands were tested, and thiourea was found to be the most effective ligand in preventing fast gold reduction and precipitation to the gel surface during drying. A model based on the formation of insoluble gold species during drying of the gel is discussed to explain the phenomenon of gold precipitation to the sample surface. The heated gels were studied by measurements of the BET specific surface area and of the apparent density, showing the densification of the matrix during the heat treatments. UV−vis optical absorption spectroscopy was used to monitor the formation of Au nanoparticles that was effective after heating the gel at 300 °C in air. TEM studies revealed that two kinds of Au particles were present, with mean sizes of 10 and 30 nm. The smaller particles have a lattice spacing corresponding to face-centered cubic Au, whereas electron nanodiffraction patterns of the larger particles exhibit features of orthorhombic Au_3Si.

1. Introduction

Small-sized material systems can display physical properties that are intermediate between those of the molecular and the solid state. For instance, the electronic properties can be remarkably affected if the number of atoms constituting the particles is such that the band structure of the particle is changed with respect to that of the bulk form of the material. In particular, in the last several years, the observation of nonlinear optical properties of metal nanoparticles in a dielectric matrix[1,2] has induced a noticeable effort toward the synthesis of this kind of materials.[3,4] In this context, the sol−gel process has appeared as a new and innovative technique for the synthesis of metal nanoparticles embedded in a dielectric host. A first advantage of the sol−gel process is the possibility of using low processing temperatures that reduce the loss of dopants by evaporation. Furthermore, it is possible to introduce in the starting sol dopant amounts that are not attainable with other techniques. It is also possible to have a wide choice of both the dopants and the embedding host, overcoming the limitations of other techniques. Many reports have concentrated on the sol−gel synthesis of Au nanoparticles,[5−15] and the routes developed can be divided into two different categories. The first route consists of the preparation of a gold sol that is subsequently added to a sol of the embedding matrix.[12,15] In

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(1) Ricard, D.; Roussignol, P.; Flytzanis, C. *Opt. Lett.* **1985**, *10*, 511.

(2) Hache, F.; Ricard, D.; Flytzanis, C. *J. Opt. Soc. Am. B* **1986**, *3*, 1647.

(3) Bradley, J.S., Persans, P.D., Schmid, G., Chianelli, R.R., Eds. *Chemical Processes in Inorganic Materials: Metal and Semiconductor Clusters and Colloids*; Materials Research Society: Warrendale, PA, 1992.

(4) Duncan, M. A. *Advances in Metal and Semiconductor Clusters*; JAI Press: New York, 1999; Vol. 4, Cluster Materials.

(5) Tseng, J. Y.; Li, C. Y.; Takada, T.; Lechner, C.; Mackenzie, J. D. In *Sol−Gel Optics II, Proceedings of The International Society for Optical Engineering (SPIE)*; Mackenzie, J. D., Ed.; The International Society for Optical Engineering (SPIE): Bellingham, WA, 1992; Vol. 1758, p 612.

(6) Matsuoka, J.; Mizutani, R.; Nasu, H.; Kamiya, K. *J. Ceram. Soc. Jpn.* **1992**, *100*, 599.

(7) Kozuka, H.; Sakka, S. *Chem. Mater.* **1993**, *5*, 222.

(8) Matsuoka, J.; Mizutani, R.; Kaneko, S.; Nasu, H.; Kamiya, K.; Kadono, K.; Sakaguchi, T.; Miya, M. *J. Ceram. Soc Jpn.* **1993**, *101*, 53.

(9) Sakka, S.; Kozuka, H.; Zhao, G. In *Sol−Gel Optics III, Proceedings of The International Society for Optical Engineering (SPIE)*; Mackenzie, J. D., Ed.; The International Society for Optical Engineering (SPIE): Bellingham, WA, 1994; Vol. 2288, p 108.

(10) Mennig, M.; Schmitt, M.; Becker, U.; Jung, G.; Schmidt, H. In *Sol−Gel Optics III, Proceedings of The International Society for Optical Engineering (SPIE)*; Mackenzie, J. D., Ed.; The International Society for Optical Engineering (SPIE): Bellingham, WA, 1994; Vol. 2288, p 130.

(11) Innocenzi, P.; Kozuka, H.; Sakka, S. *J. Sol−Gel. Sci. Technol.* **1994**, *1*, 305.

(12) Yazawa, T.; Kadono, K.; Tanaka, H.; Sakaguchi, T.; Tsubota, S.; Kuraoka, K.; Miya, M. *J. Non-Cryst. Solids* **1994**, *170*, 105.

(13) Matsuoka, J.; Yoshida, H.; Nasu, H.; Kamiya, K. *J. Sol−Gel. Sci. Technol.* **1997**, *9*, 145.

(14) Matsuoka, J.; Naruse, R.; Nasu, H.; Kamiya, K. *J. Non-Cryst. Solids* **1997**, *218*, 151.

(15) Bharathi, S.; Fishelson, N.; Lev, O. *Langmuir* **1999**, *15*, 1929.

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this case, capping of the gold particles is achieved to avoid their aggregation, resulting in a broad particle size distribution and, ultimately, in gold precipitation. The advantage of this route is that particles are generated already at low temperature, so the heat treatment of the resulting material is avoided, thus preventing degradation of specific functionalities of the matrix. Furthermore, a narrow particle size distribution can be obtained by capping the starting gold sol. The use of low processing temperatures will not destroy the capping, so the particles will be kept separated in the final material, and the size distribution will not be remarkably affected. On the other hand, if the matrix has to be heated at high temperatures (for instance, to reduce the matrix porosity), the capping will be removed during heating, and aggregation of particles can occur even at low temperatures. In this respect, another synthesis procedure, consisting of the formation of gold particles within the already-formed matrix,[5−11,13,14] was developed and mainly applied to the synthesis of thin films. In this approach, Au is typically introduced into the matrix sol by means of a solution of Au^{3+} ions (commonly the tetrachloroaurate anion $[AuCl_4]^-$), and the nucleation of gold particles is achieved thermally by heating the doped film. A problem encountered with this procedure is the precipitation of metallic gold on the film surface.[8,9,11] Exposure of the films to monoethanolamine vapors prevented gold escape.[9] Films were also prepared starting from methyltriethoxysilane (MTES) and TEOS as silica precursors, and in this case, gold precipitation was prevented by using a suitable amount of MTES.[11] Gold precipitation has also been observed in TiO_2, ZrO_2, and Al_2O_3 matrixes.[13] In another work,[16] we developed a synthesis procedure belonging to the second category, which avoids gold precipitation in the sol and on the sample surface. The technique is based on the substitution of the chloro ligands of $[AuCl_4]^-$ with other ligands. With respect to the well-established use of functionalized silanes as ligands,[10] the use of unfunctionalized ligands allows for the stabilization of Au^{3+} ions in any matrix system and for the achievement of a broad range of stabilities of the gold complexes. In that work, a gold stability of about 1 week was reported in TiO_2 and ZrO_2 sols. The problem of obtaining a longer-lasting stability of gold ions remains open: this need is suggested by reproducibility requirements and, at least in this case, by the high cost of the dopant precursor. The accomplishment of this aim is at the same time an indication of the flexibility of the synthesis technique previously developed: depending on the matrix under investigation, it is possible to find a suitable stabilization of the gold ions. A bulk matrix was chosen because the observation of drying phenomena on a longer time scale and on macroscopic samples allows for a more precise model than the one previously used to explain the gold precipitation phenomena on the film surface[16] to be presented. Borosilicate glass was chosen because of its lower sintering temperature compared to that of pure silica. To our knowledge, Au-doped monoliths had not yet been prepared with the in situ nucleation technique.

2. Experimental Section

Au-doped bulk glasses, with a nominal 10% B_2O_3−90% SiO_2 molar composition (from now on, this composition will be indicated as borosilicate), and a Au/(SiO_2 + B_2O_3) molar ratio ranging from 0.014 to 0.112%, were prepared as follows. A borosilicate sol was first prepared by prehydrolizing tetramethyl orthosilicate [TMOS, $Si(OCH_3)_4$] with water acidified with concentrated HCl, in the molar ratio TMOS/H_2O/HCl = 1:4:10^{-3}. After the TMOS was hydrolyzed for 1 h, the prescribed amount of trimethyl borate [TMB, $B(OCH_3)_3$] dissolved in methanol was added (MeOH/TMB volume ratio was 2.5). The resulting mixture was stirred for 1 h, and then the gold solution was added. The latter was prepared as follows: the prescribed amount of $NaAuCl_4 \cdot 2H_2O$ was dissolved in MeOH, and then a solution of a Au^{3+} ligand dissolved in MeOH was added. The ligands tested were thiourea [TU, $SC(NH_2)_2$], dimethyl sulfide [DMS, $S(CH_3)_2$], and *N*-aminoethyl-3-aminopropyltrimethoxysilane [DAMO, $H_2N(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$] with molar ratios to Au of 10, 70, and 3, respectively. DMS was dissolved in tetrahydrofuran. The choice of the ligand/Au molar ratio was made to increase the stability of the corresponding gold complex. In the case of DAMO, the molar ratio was not increased to avoid precipitation in the sol. Gels were also prepared by using only $[AuCl_4]^-$ as the Au precursor. The Au^{3+} solution was poured into the borosilicate sol, and after the mixture was stirred for 15 min, an ammonia solution in water was added. Water was employed to obtain a final H_2O/Si molar ratio of 7, while a NH_3/Si molar ratio of 5×10^{-2} was reached. Casting of the sol in polyethylene containers was carried out 15 min after the addition of the water/ammonia solution. Gelation occurred at room temperature in the closed containers within 3 h. The gels were aged at room temperature for 3 days in closed containers; then, the syneresis liquid was removed, and the containers, covered with plastic sheets provided with pinholes, were placed into an air oven at 60 °C. Drying of the gels lasted for 3 days. The dried gels were heated in air in a tubular oven up to 120 °C with a heating rate of 60 °C/h and kept at the final temperature for 2 h. Then, the temperature was raised, with a heating rate of 120 °C/h, up to a final value ranging from 200 to 600 °C. The gels were kept at the various final temperatures for 1 h, except for the heat treatment at 500 °C, which lasted for 2 h for complete elimination of organic residuals. This last procedure was also used for the gels heated at 600 °C in He for 1 h. The heat treatment from 500 to 600 °C was carried out in a He atmosphere.

Specific surface area measurements with the BET method (Quantachrome, Nova 1000) were performed after the fractured gels were degassed in a vacuum at 150 °C for 16 h.

The density of the gels was measured by liquid picnometry, using isooctane as the buoyant liquid. The mean value of a set of five measurements for each sample was calculated.

Optical absorption measurements (Varian, Cary 5E) on the gels were carried out in the 200−750 nm wavelength range with air as the reference.

TEM observations were carried out with a Philips CM30 transmission electron microscope operated at 300 keV. The specimens were prepared by mechanically grinding the samples in an agate mortar and then dispersing the powder in ethyl alcohol. The dispersed powders were deposited onto a copper grid previously covered by an amorphous carbon layer.

3. Results and Discussion

(1) Preventing Gold Precipitation. After being dried at 60 °C, round-shaped monolithic samples were obtained, with a diameter of about 25 mm and a thickness of about 2 mm. Gels prepared with $[AuCl_4]^-$ as the Au precursor were red-purple and opaque after being dried at 60 °C, because of the formation of a lustrous gold-colored layer on the sample surface. This result can be explained by the formation of Au particles

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(16) Epifani, M.; Giannini, C.; Tapfer, L.; Vasanelli, L. *J. Am. Ceram. Soc.* **2000**, *10*, 2385.

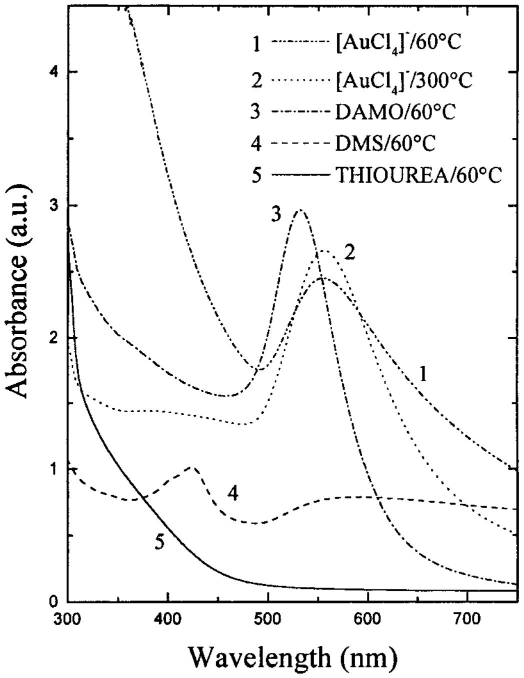

Figure 1. Optical absorption spectra recorded on gels dried at 60 °C and doped with the indicated Au^{3+} complexes.

in the gel that were subsequently driven to the surface during the drying process to form a thin surface layer. This hypothesis was confirmed by UV−vis optical absorption spectroscopy, as Au particles in a dielectric matrix exhibit a characteristic absorption in the visible range through the excitation of surface plasmon oscillations in the metal particle.[17] The absorption spectrum of the gel prepared with $[AuCl_4]^-$ (curve 1 in Figure 1) indeed shows an absorption band that can be attributed to the Au surface plasmon. Heating the sample at 300 °C did not produce drastic changes in the curve (curve 2 in Figure 1), showing that Au^{3+} ions have already been totally reduced after the samples are dried at 60 °C. To avoid gold formation in the early stage of gel processing, we applied the technique already used for Ag and Au nanoparticles in thin films. The chloro ligands bound to the Au^{3+} ions were substituted by other ligands, in an attempt identify a ligand capable of stabilizing the Au^{3+}ions in such a way to avoid their fast reduction and aggregation. The formation of complexes was monitored by the change of the color of the $[AuCl_4]^-$ solution upon addition of the various ligands. The color turned from yellow to orange in the case of DAMO, whereas for DMS and TU, the solution turned very light yellow and colorless, respectively. The main factor discriminating the effectiveness of the various ligands is the thermodynamic stability of the various complexes, and on this basis, the results in Figure 1 can be explained. Because Au^{3+} is a soft acid, the stability of its complexes increases with increasing softness of the ligand, so it is expected that amino complexes are less stable than thio complexes. Thus, DAMO is much less effective than DMS and TU in stabilizing Au^{3+}, and substantial particle formation is shown by the intensity of the Au surface plasmon band of curve 3 in Figure 1. Consequently, these samples are also opaque, like those prepared with $[AuCl_4]^-$. The optical absorption curve for the case of DMS shows a much less intense surface plasmon band (curve 4), and the sample is more transparent if compared to those with $[AuCl_4]^-$ and DAMO, but some precipitation is still observed. For this reason, TU was also tested, and it proved to be extremely effective in preventing gold formation, which is demonstrated by curve 5 in Figure 1, in which the surface plasmon band is completely absent. Only an increasing absorption is seen in the short-wavelength range of the spectrum, which is responsible for the yellow color of the dried samples and which we attribute to charge transfer in the Au^{3+} complex and/or to intraligand charge transfer in TU. It is instructive that the gels became colored during the last stage of drying, when the more polar water/methanol species tend to disappear. The gels with TU were exposed to sunlight at room temperature for more than 1 year without any change in appearance. Thus, the aim of long-term stabilization of the gold ions was achieved, taking advantage of the flexibility of the synthesis technique. DMS was effective in the case of thin films, but in the case of bulk materials, the 60 °C drying process destabilized the corresponding Au^{3+} complex. To solve this problem, it was necessary only to find a more effective ligand, which was not difficult starting from the extensive coordination chemistry of Au^{3+}. It is now remarked that the preparation of doped monoliths can generally present inhomogenity problems because of the migration of dopants with the syneresis liquid. This problem can be solved through the use of suitably functionalized silanes. Here, DAMO was not effective because of the low thermal stability of the corresponding Au^{3+} amino complex during the drying of the monoliths, but it was useful to indicate the influence of the stability of the Au^{3+} complex on the precipitation problems. Nevertheless, it is expected that a thiosilane[10] might provide better results than DAMO, because of the generally higher affinity of sulfur-containing ligands for the Au^{3+} ion. A thiosilane was not employed in the present work because our aim was the achievement of gold precursors with improved stability through a general method, applicable even when the matrix is not silicate-based.

As stated in the Introduction, the other aim of this work was further elucidation of the problem of surface precipitation of Au, which has been reported by many authors. Recently, Matsuoka et al.[13] proposed a model for thin films based on the idea that the electrostatic interaction between the gold species and the matrix oxide influences the retention of gold particles within the matrix. We proposed another explanation,[16] which we review here before treating the case of monoliths. This explanation is based on the hypothesis of accumulation of gold species near or on the surface already after drying of the film. Here, “drying” is used to mean the whole process starting from film deposition to oven standing at 80 °C for the complete elimination of solvents, and the term “species” is used to indicate any chemical species containing gold ions or particles. A first factor to be discussed is the thermal stability of Au precursors. The easy decomposition of $[AuCl_4]^-$ might result in particle formation at low temperatures, when the gold particles can form aggregates before thermal

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[17] Vollmer, M.; Kreibig, U. *Optical Properties of Metal Clusters*; Springer Series in Material Science; Springer-Verlag: Berlin, Germany, 1995.

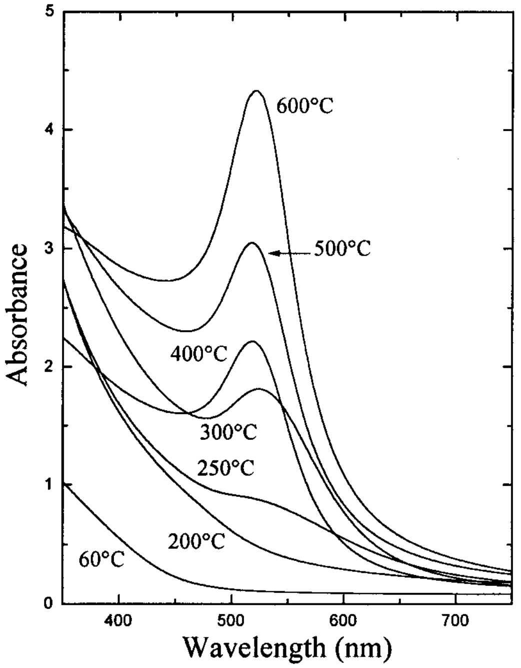

Figure 2. Optical absorption spectra recorded on gels heated in air or He (600 °C sample) at the indicated temperatures.

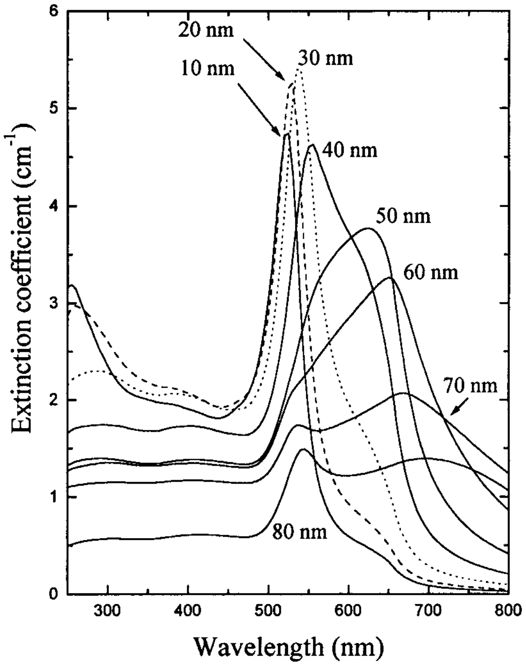

Figure 3. Theoretical optical extinction curves calculated by the theory of Mie for gold spheres embedded in a silica host, for the indicated values of the particle radius.

diffusion can better disperse them. Large Au precipitates might result, as they can aggregate more easily than within the film structure. Actually, surface precipitation was reported in other works[8] in SiO_2 films where Au was introduced as $[AuCl_4]^-$ and effective particle nucleation started at 300 °C, a temperature that should better promote the diffusion of gold species. On the other hand, Au-doped TiO_2 and ZrO_2 thin films were prepared in our previous work using Au complexes other than $[AuCl_4]^-$. Compared to SiO_2, such films displayed Au particle formation after being heated at only 100 or 200 °C, without any surface precipitation. Thus, the thermal stability of the Au complex does not seem to be the determining factor. The solubility of the metal itself in the matrix during the heat treatments could be used as an explaination for this behavior, and indeed, this might be the case for silica. In fact, we have also prepared Au-doped SiO_2 monoliths using thiourea, and after the gels were heated at 500 °C in air, a very thin gold colored layer was observed on the surface. This did not occur after the gels were heated at 300 °C, when the amount of gold particles was lower and the gold particles were smaller than those obtained after heating at 500 °C, as seen from the optical absorption spectra (not shown). These observations are consistent with the presence of a solubility limit of Au in SiO_2. Nevertheless, we did not observe precipitation for other hosts even for doping levels higher than those that resulted in precipitation in other works (ref 13, ZrO_2 thin films). Thus, it is concluded that the better solubility of complexes other than $[AuCl_4]^-$ in the matrix seems to play an important role in preventing surface precipitation by avoiding the formation of any gold species deposits on the film surface. The influence of the electrostatic interaction between the complex and the matrix, as suggested by Matsuoka et al.,[13] can be taken into account to explain the solubilities of the various complexes. Nevertheless, other factors must play a role, because, in the case of TiO_2 and ZrO_2 thin films, we did not observe any surface precipitation, even though the inner surface of such oxides should be positively charged, as suggested by Matsuoka et al.,[13] and should repel, for instance, the positively charged DMS$-$Au^{3+} complex.

The study of doped monoliths made it possible to propose a more precise phenomenological model than the one previously proposed for thin films, showing that, in the case of monoliths, the stability of the Au precursor plays a more evident role. In fact, the gels that were opaque at the end of drying were red-purple during the aging stage, showing the early formation of gold particles. In this stage, the gels were also transparent and remained so during the first stage of drying, when the gels underwent only partial shrinkage. Opacity of the gel began to appear when shrinkage stopped, and it became more and more evident during the last drying stage, when no more shrinkage was observed. In this last stage, the pore liquid starts to recede into the gel structure, until the pores begin to empty. Consequently, the decrease of liquid in the pores lowers the solubility of the metal species dispersed within the liquid. These species are then driven by the liquid flow to the outer surface of the gel, where they accumulate. When Au^{3+} ions are complexed with TU, particle formation is completely hindered during aging and drying, and surface precipitation is prevented. As mentioned above, particle formation occurs during aging at room temperature, so the complex decomposition is attributed to the exposure of gels to sunlight. Aging the gels in the dark would reduce the possibility of gold reduction, but the use of TU is more effective because it makes it possible to process and expose the gels or sols to sunlight without any undesired gold particle formation. In conclusion, surface precipitation in thin films is attributed to the expulsion of gold species from the film during the early stages of film processing, and complexation of Au^{3+} with different ligands helps to retain the gold precursor in the matrix. In the case of the bulk matrix, precipitation

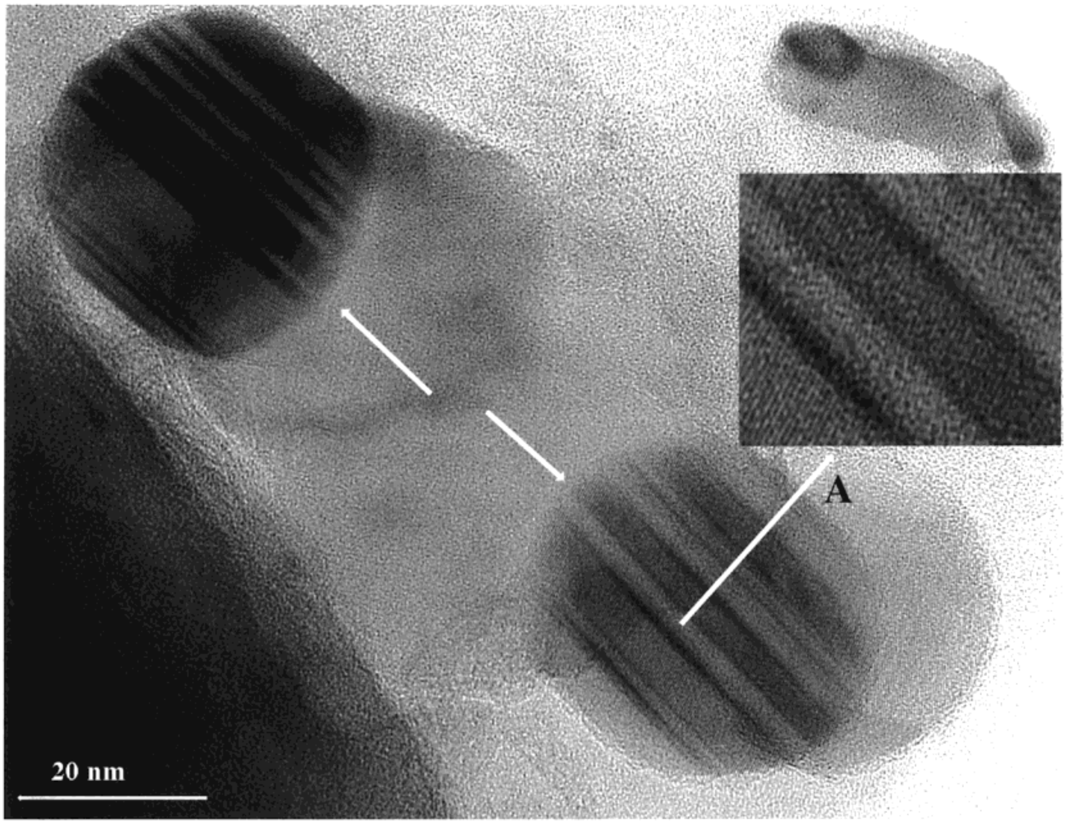

Figure 4. HRTEM image of larger particles observed in a sample doped with the Au^{3+}–TU complex and heated in air at 400 °C. The arrows indicate two larger particles. The sharp contrast variations inside the particles are due to regions of different structures. Arrow A marks the area shown at the higher magnification in the inset. The distortion of the lattice fringes across zones of different contrast is evident.

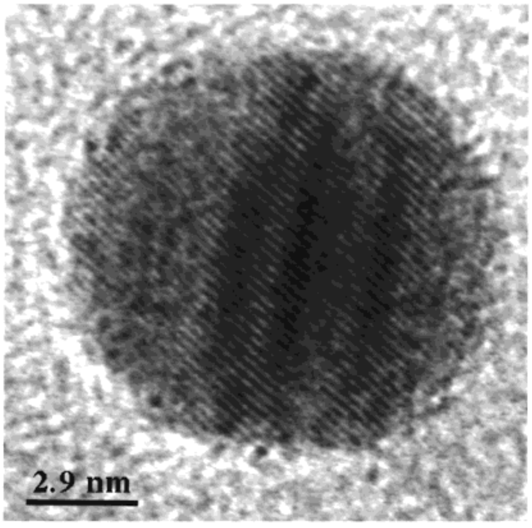

Figure 5. HRTEM image of a smaller aggregate observed in the same sample as shown in Figure 4.

is due to the low solubility of Au particles in the pore liquid, and complexation of Au^{3+} is necessary to control the photochemistry of the gold precursor. It is difficult to determine the mechanism that would lead, in the case of thin films, to the early formation of precipitates on the surface.

(2) Nucleation of the Gold Particles and Optical Properties of the Gels. We focused our attention only on the gels prepared with TU and with 0.014% Au content. After being heated at 200 and 250 °C, they were dark yellow, whereas after being heated 300 °C, they became red-colored. The color intensity increased after heating at higher temperatures. These observations are summarized by the UV–vis optical absorption spectra reported in Figure 2. When the gel is heated at 200 °C, partial decomposition of the organic residuals occurs, so the corresponding curve shows an increased absorp-

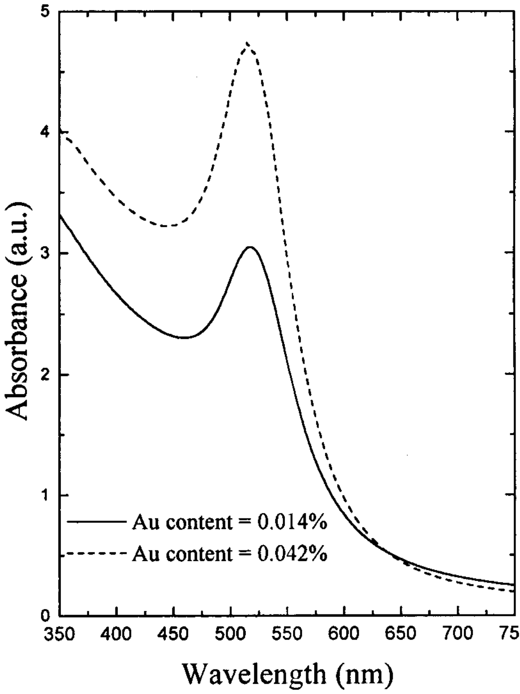

Figure 6. Optical absorption spectra measured on gels doped with the indicated Au contents and heated in air at 500 °C.

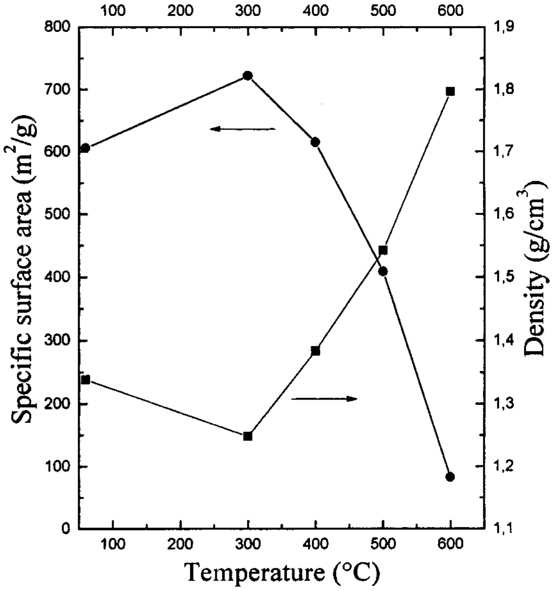

Figure 7. Evolution with heating temperature of the BET specific surface area and the density of the gels with 0.014% Au content.

tion with respect to that of the 60 °C dried sample. After the heating at 250 °C, gold particles are formed, as indicated by the appearance of a shoulder at the wavelength of 530 nm, which can be attributed to the gold surface plasmon. Heating at 300 °C promotes more effective Au particle formation, as evidenced by the increased intensity of the characteristic band. Heating at higher temperatures results in an even more effective gold particle nucleation, and the intensity of the band progressively increases. The optical absorption spectra were analyzed with the help of the theory of Mie,[17] which describes the light-scattering behavior of a suspension of spheres in a dielectric host. In Figure 3, as an illustrative example, the calculated[18] optical extinction curves are shown for Au nanoparticles with the indicated radii embedded in a fused-silica host. These calculations are generally only indicative, because the real sample contains a size distribution of particles and a refractive index distribution at the matrix−particle interface and because the particles might display dielectric properties different from the bulk values (quantum size effect). It is nevertheless necessary to point out that the theory of Mie is useful for obtaining insight about the particle growth, for instance. Thus, it is possible to say that the amount of gold in the form of nanoparticles increases with the heating temperature in Figure 2 because, according to the theory of Mie, the optical absorption is proportional to the metal volume fraction. Furthermore, according to the theory, an increase in the particle size causes a red shift in the peak position of the surface plasmon band. This feature is clear in Figure 3. Thus, from the evolution of the surface plasmon peak position in Figure 2, it is concluded that the mean particle size is unchanged for heating temperatures ≥400 °C because the peak position remains constant at 520 nm. Consequently, increasing the heating temperature promotes a more effective particle nucleation, as evidenced by the increased absorbance, without changing the mean particle size. A hypothesis for explaining this result is suggested by the TEM observations. TEM studies of a gel heated to 400 °C reveal the presence of two different kinds of particles: (i) small particles with a size of about 10 nm and with a regular, spherical shape and (ii) larger particles with a diameter of 30 nm and a less regular shape. In Figure 4, images of the larger particles are shown, which are characterized by a structure of different contrast and with highly distorted lattice fringes, as can be seen in the inset where the region marked by the arrow A is shown at higher magnification. The presence of internal domains is evidenced by the sharp contrast variation inside the particles, as shown by the low-magnification, high-resolution image of Figure 4. The formation of regions with different chemical compositions and crystalline structures can be hypothesized. Indeed, the nanodiffraction pattern acquired for the cluster (not shown) shows a reciprocal lattice symmetry and a lattice spacing that can be attributed not to Au but to an orthorhombic Au_3Si alloy. Figure 5 shows a high-resolution image of a small particle. Again, domains with different contrasts are easily observed. Here, the measured lattice spacing corresponds to the value of face-centered cubic Au, as seen from a fast Fourier transform pattern (not shown). A possible explanation for the structural differences of the two kinds of particles is that the larger Au particle size favors the dissolution of Si from the matrix in the particle to such an extent that it is revealed in the nanodiffraction results. The different domains in the particles can provide an interpretation of the behavior of the optical spectra. In particular, the presence of Si contamination in the larger particles might result in such dielectric properties of the particles that make them no longer able to sustain a surface plasmon oscillation or that cause its fast damping. Thus, raising the heating temperature would increase the intensity of the plasmon band in Figure 2 only because it produces a higher density of small particles. It is also interesting that, from TEM studies, the particle nucleation is seen to be inhomogeneous, as there are regions of the sample with relatively high numbers of particles and other parts where no particles are observed. This result could be due to the low Au content of the gels and the low heating temperature.

Figure 6 shows that even increasing the Au concentration from 0.014 to 0.042% does not influence the peak position and, thus, the mean particle size. Only the intensity of the absorption increases with respect to that of the lowest doping.

(3) Matrix Evolution with the Heat Treatments. Figure 7 shows the evolution of BET specific surface area (SSA) and the density of the gels with the heating temperature. As expected, the BET SSA decreases with increasing heating temperature, whereas the opposite behavior is observed for the density. The SSA value of the doped gel heated at 600 °C shows that a borosilicate matrix allows a substantial sintering of the gel to be obtained at low temperatures in contrast to pure silica gel. The presence of gold particles influences the structural evolution of the gels, as indicated by the bursting of the gels heated for 2 h in air at 500 °C and for 1 h in He at 600 °C. Heating in He atmosphere further densifies the gel with respect to those undergoing in-air heating, because He is much more soluble in the

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(18) Epifani, M. Unpublished results.

borosilicate matrix. Thus, bursting could be due to water entrapped in the collapsed gel structure, but silanol condensation is expected not to be extensive (as evidenced by FTIR spectra, not shown). It should be mentioned that crystallization of the gel might also cause bursting; however, at such a heating temperature, the gel is amorphous (as evidenced by XRD, not shown). In addition, an undoped gel did not burst, so we can conclude that competition between gel shrinkage and the presence of Au particles induces strains in the structure that are released through the formation of cracks in the gel, which yield finally to its bursting.

To conclude the part concerning the matrix characterization, we finally remark that, as in the work by Irwin et al.,[19] a white precipitate, identified by those authors as boric acid, was observed on the gel surface when it was exposed to the atmosphere after heat treatments at low temperatures. The problems disappeared after heat treatment at 600 °C. Furthermore, FTIR studies (not shown) indicated the formation of borosiloxane bonds (B−O−Si).

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(19) Irwin, A. D.; Holmgren, J. S.; Zerda, T. W.; Jonas, J. *J. Non-Cryst. Solids* **1987**, *89*, 191.