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Preparation and characterisation of Si nanocrystallites embedded in a silica matrix†

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Si nanocrystallites embedded in a silica matrix have been prepared by the sol–gel route using triethoxysilane as the precursor. The different steps of formation of silicon during thermal treatment of the gels were observed by X-ray diffraction, Raman and ^{29}Si MAS NMR spectroscopy. The gels were first pre-heat-treated under vacuum at different temperatures (500 °C, 700 °C and 1000 °C) and then densified under pressure at 1320 °C. TEM and low frequency inelastic Raman measurements indicate that the size of the Si particles increases with the temperature of the pre-heat treatment. The only materials to show luminescence in the visible range were those containing residual Si–OH bonds.

1. Introduction

The discovery of porous and nanocrystalline silicon has shown that Si clusters of small dimensions might give strong room temperature photoluminescence[1] and electroluminescence.[2] Bulk crystalline silicon does not show such a property due to its indirect band gap which prevents radiative recombination of electrons and holes. The luminescence properties of Si clusters opened up the possibility of fabrication of optoelectronic devices based on silicon taking advantage of the already developed Si technology. A better understanding of the process underlying the observed phenomenon is needed to control the material property and to reach the eventual development of such optoelectronic devices. To date no agreement has been achieved to explain the involved process. The luminescence properties are either attributed to the small sizes of particles[3] or to their specific surface states.[4]

Many routes have been investigated for the production of Si clusters. Porous Si is obtained by anodic etching of crystalline Si with hydrofluoric acid solution.[5] Si nanocrystallites can be prepared by chemical-vapour deposition of silane,[4,6] co-sputtering,[7] ion implantation,[8] and high energy milling.[9] Recently Si nanocrystals were produced by ultrasonic fracturing of porous silicon and further embedded in various host matrices.[2]

A new method for producing Si nanocrystallites embedded in a silica matrix is proposed in this work. The method is based upon the sol–gel process and the use of triethoxysilane as the precursor for both the silica matrix and the Si crystallites. Previous work already showed that, under specific conditions the sol–gel route applied to trialkoxysilanes leads to modified silica gels containing Si–H bonds.[10] These hydrogenosilsesquioxane gels were shown to be hydrophobic and their high reactivity when heated under air,[10] ammonia[11] and argon[12] was investigated. In particular SiH_4 was formed when the gels were heated in an inert atmosphere. The developed process is based on the fact that silane decomposes at $T > 400$ °C and gives Si and H_2.[13] The second part of the work aimed at characterising the prepared materials and especially the Si crystallites by three experimental techniques, *i.e.* high resolution transmission electron microscopy (HRTEM), low frequency inelastic Raman scattering (LOFIRS) and photoluminescence measurements.

2. Experimental

2.1. Sample preparation

Various experimental conditions were tested in order to optimise the process. Acetone was preferred to alcohol as the solvent to obtain miscibility between the precursor triethoxysilane (Aldrich 95%) and water since it does not limit the hydrolysis reaction.

Since it is known that the Si–H bonds were broken during gelification in a basic sol,[10] all hydrolysis–condensation reactions were performed without a catalyst or under acidic conditions. Elemental analysis carried out at the central centre for chemical analysis from CNRS (Solaize, France) showed that most of the initial Si–H entities were maintained in the xerogels prepared using either one of these sets of initial conditions (*ca.* 90% under acidic conditions and 70% in neutral ones). ^{13}C NMR experiments were carried out on different xerogels dried at 60 °C. The lowest quantity of C residue was observed when working under acidic conditions with a large amount of excess water. For example, 1.5 wt.% of ethoxy groups were maintained in a xerogel prepared under acidic conditions with 10 moles of water per 1 mole of alkoxide compared to 3 wt.% when the xerogel was prepared with only 3 moles of water per 1 mole in alkoxide.

An optimised experimental procedure was then established. The solutions were prepared by dropping a solution of acidified water (10 moles, 0.1 M HCl) in acetone (5 moles) into a solution of triethoxysilane (1 mole) in acetone (5 moles) under strong stirring at room temperature for 1 hour. The solution was then allowed to stand at room temperature in a closed vessel and maintained under these conditions for one week after the gel was obtained. The gel was then dried at room temperature in air for 48 hours and at 100 °C for the same time. The resulting powders were kept in a dry atmosphere.

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The gel was further heat-treated at various temperatures. The powder was either put inside a silica tube sealed under vacuum (10^{-5} Torr) or in an open crucible. In this case, the crucible was either maintained in a flow of an inert gas (Ar) or under a dynamic vacuum maintained by continuous pumping. The powder was brought to the desired temperature ranging from 200 °C to 1000 °C with a heating rate of 0.5 °C min^{-1}, maintained at this temperature for half an hour and then cooled to room temperature.

The heat-treated powders were further densified by hot-pressing using an apparatus described elsewhere.[14] The powder was heated under vacuum with two stages at 400 °C and 700 °C for 30 min to allow the dehydration of the gels. A pressure of 35 MPa was then applied to the sample while the temperature was increased. The densification was completed at a temperature of 1320 °C.

2.2. Characterisation of gels and of densified samples

The degradation of the gel during heat treatment was studied by X-ray diffraction, Raman and ^{29}Si NMR spectroscopy. X-Ray diffraction patterns were obtained using a diffractometer Seifert MZ VI θ–2θ with a Cu-Kα monochromator. The Raman spectra were recorded using a OMARS 89 Dilor spectrophotometer. The 514.5 nm line of an Ar ion laser was used as the excitation source with a power of 150 mW. The NMR studies were performed using a Bruker MSL 400 spectrometer under magic angle spinning conditions (rotor speed = 4 kHz). The ^{1}H decoupling technique was applied when the proton content in the gels was still important, *i.e.* for powders treated at low temperature <400 °C. About 160 scans were recorded using a $\pi/4$ pulse and a relaxation delay of 8 min.

The presence and characteristics of Si crystallites in the densified samples were studied by HRTEM and LOFIRS. TEM experiments were carried out on powders obtained by grinding the bulk samples. A Topcon EM002B electron microscope operating at 200 kV with a point-to-point resolution of 1.8 Å was used for the investigations. Conventional transmission electron microscopy (CTEM) was used to observe a representative area of the sample. These observations helped in determining the size distribution of crystallites from an image analysis method. Information about the nanocrystal structure was obtained from diffraction patterns (DP) and HRTEM images. The image analysis method is based upon the following procedure. Micrographs were digitised with an overall resolution of 0.425 nm per pixel and a classical granulometry by openings was performed. Before any measurement, digitised micrographs were slightly noise filtered and all particles with diameters smaller than 2 nm were removed. The size distribution for a sample results from measurements performed on several TEM micrographs. A five grating Dilor Z40 monochromator was used to measure the low frequency inelastic Raman spectra. Such measurements close to the Rayleigh line are made possible by the high rejection rate of the monochromator. Visible lines of an Ar ion laser (514.5 nm) and of a Kr ion laser (647.1 nm) were used for excitation using a power of 50 mW. The scattered light was collected parallel and perpendicular to the excitation line in order to measure polarisation effects.

3. Results and discussion

3.1. Characterisation of the heat treated gels before densification

Several xerogels heat-treated at different temperatures ranging from 100 °C to 1320 °C were characterised by X-ray diffraction, ^{29}Si NMR and Raman spectroscopy in order to check whether Si crystallites were indeed produced. It appeared that no Si crystallites were detected by any of the three selected characterisation techniques when the heat treatment was performed in an open atmosphere. On the other hand amorphous or crystalline Si could be detected after heat treatment in the powders placed in a silica tube sealed under vacuum. Fig. 1 shows the Raman spectra of these gels. A broad peak at 480 cm^{-1} indicative of Si–Si vibrations in amorphous silicon[15,16] appeared for gels heated at temperatures between 500 °C and 650 °C. It supports the assumption that SiH_4 was first formed in the gels then decomposed and gave some Si at $T > 400$ °C. Such an explanation is also in agreement with the fact that no Si was obtained when the heat treatment was performed in an open atmosphere. One can indeed expect the silane gas to leave the gel prior to its decomposition. Amorphous Si crystallised when heated at $T > 650$ °C as indicated by the narrowing and displacement of the Raman peak at about 510 cm^{-1}.[15,16] At the same time, peaks indicative of crystalline silicon appeared in the X-ray diffraction patterns of the gels (Fig. 2). A last point concerning the Raman spectra should be underlined. The Raman peak of crystalline bulk Si is expected to be symmetrical and to appear at 520 cm^{-1}. The fact that the Raman peak of the Si present in the gels is asymmetrical and shifted to lower frequency might be the signature of nanocrystallites.[17,18] Fig. 3 shows the ^{29}Si NMR spectra of several gels. Owing to the long relaxation time of ^{29}Si [$T_1(SiO_2) = 40$ min and T_1 (Si) = 3 min] quantitative NMR experiments could not

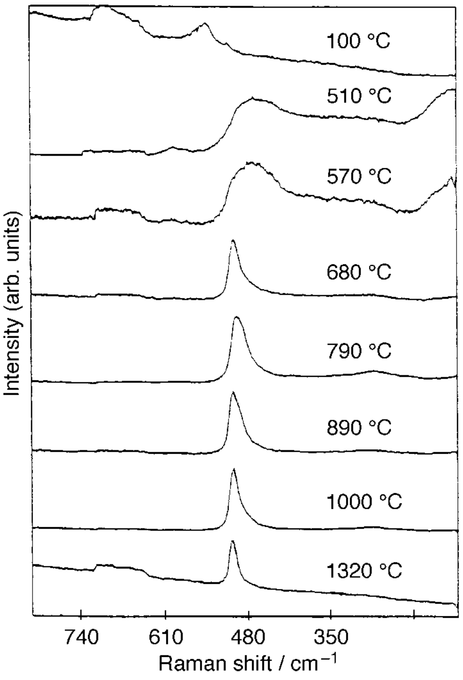

Fig. 1 Raman spectra of gels prepared with triethoxysilane as the precursor and heated at different temperatures under confined vacuum.

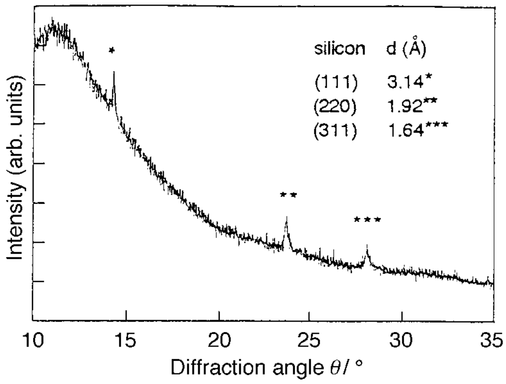

Fig. 2 X-Ray diffraction pattern of a gel heat-treated at 680 °C.

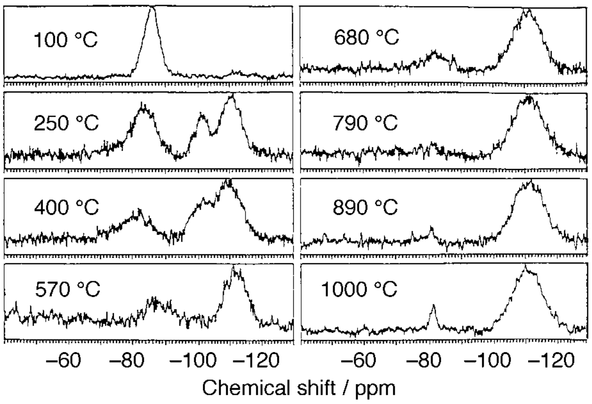

Fig. 3 ^{29}Si NMR spectra of gels prepared with triethoxysilane as the precursor and heated at different temperatures under confined vacuum.

be carried out. However the degradation of the gel during heat treatment was qualitatively studied. The gel treated at 100 °C clearly contained $HSiO_{3/2}$ units as indicated by the peak at -85 ppm.[19] The intensity of the peak slowly decreased when the heat treatment temperature of the gel was increased and the peak was no longer observed for gels treated at $T > 700$ °C. Peaks in the range -100 ppm to -120 ppm indicative of the formation of silica[20] by a hydrolysis–polycondensation process appeared in NMR spectra of gels treated at 250 °C. The peak at -100 ppm characteristic of Q^3 units was present for gels treated at intermediate temperatures (250 °C to 400 °C). For gels treated at even higher temperature only the peak at -110 ppm indicative of Q^4 units remains. The presence of crystalline Si at $T > 700$ °C is indicated by the peak at -81 ppm.[21]

3.2. Characterisation of Si crystallites existing in the densified gels

To date two densified samples were studied by TEM. They result from the densification of two gels pre-heat-treated at 500 °C and 700 °C respectively. A typical TEM micrograph is shown in Fig. 4. Crystallites are homogeneously dispersed throughout the material. Diffraction patterns confirmed their Si structure. The average size and size distribution of crystallites were measured by image analysis of several micrographs. Fig. 5 shows the resulting distributions of equivalent diameters, *i.e.* diameters of circles of the same surface as the observed particles, for the two investigated samples. Assuming a gaussian distribution of sizes, a mean value for the size and the standard deviation of size distributions were calculated. The results are given in Table 1. They indicate that the particles grow when the heat-treatment temperature increases, probably owing to a diffusion–agglomeration process. HRTEM images indeed showed that the sample pre-heated at 500 °C mainly contained small isolated particles similar to that shown in Fig. 6(a). On the other hand the sample pre-heated at 700 °C contained both isolated particles and larger ones resulting from aggregation of smaller particles as shown in Fig. 6(b).

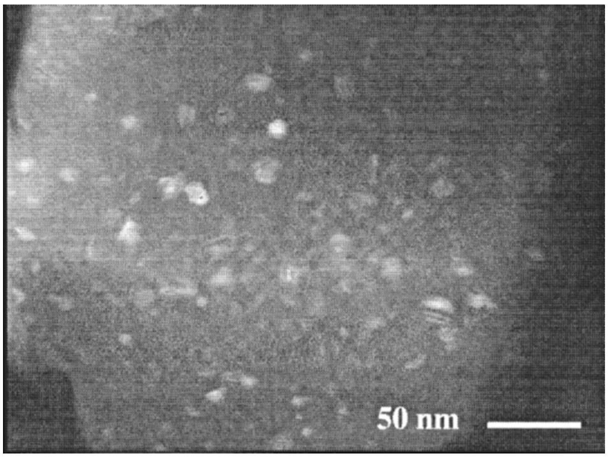

Fig. 4 TEM micrograph of a densified sample pre-heat-treated at 500 °C (magnification = 200 000).

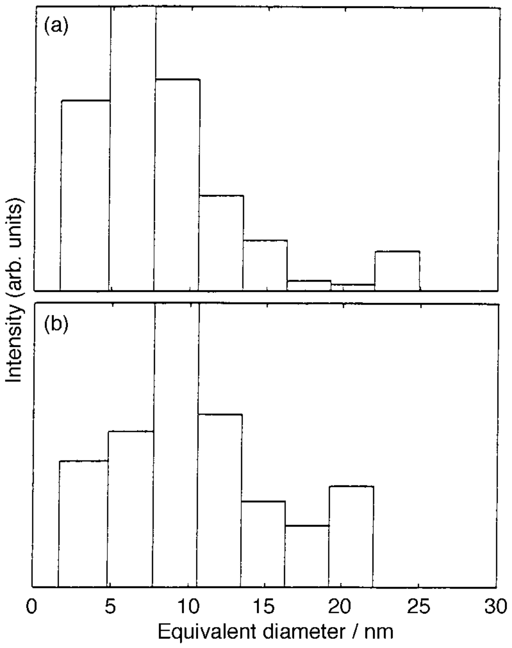

Fig. 5 Nanocrystal size distributions measured from TEM micrographs of densified samples pre-heat-treated at 500 °C (a) and 700 °C (b).

Table 1 Sizes and size distributions of the Si nanoparticles present in densified gels pre-heated at 500 °C and 700 °C (as calculated from TEM measurements)

Sample	Mean equivalent diameter/nm	Dispersion
Pre-heat treated at 500 °C	6.8	3.5
Pre-heat treated at 700 °C	9.3	4.5

The low frequency inelastic Raman scattering can be used for estimating the size of semiconductor crystallites in glasses. It indeed reveals the interactions of the laser light with the low-frequency vibration modes of the crystallites. According to the LOFIRS theory developed by Duval *et al.*[22] the frequencies of these vibration modes are inversely proportional to the diameter of the particles. LOFIRS experiments were mainly used for the study of CdX (X = S, Se) nanocrystallites.[23,24] They were recently extended to the characterisation of Si nanocrystals prepared by co-sputtering.[25] Three densified samples pre-heat-treated at 500 °C, 700 °C and 1000 °C were studied by this technique. Results are reported in Fig. 7. The spectrum obtained for the sample treated at 1000 °C does not show any significant signal which is probably due to particles too large to be measured by this way. On the other hand a low frequency line is observed at 13 cm^{-1} and 9 cm^{-1} in the spectra of the samples pre-heat-treated at 500 °C and 700 °C respectively. A rough estimation of the sizes of the particles can be made with the following assumptions: (i) because of the depolarisation of the signal, it was attributed to $l = 2$ modes; (ii) the value of the sound velocity in the $\langle 100 \rangle$ direction was used for calculation. In this case the energy ω of the low frequency lines can be calculated as a function of the particle diameter d, *i.e.* $\omega\ (cm^{-1}) \approx 1600/d$ (Å). Therefore, the Raman spectra of the samples pre-heat-treated at 500 °C

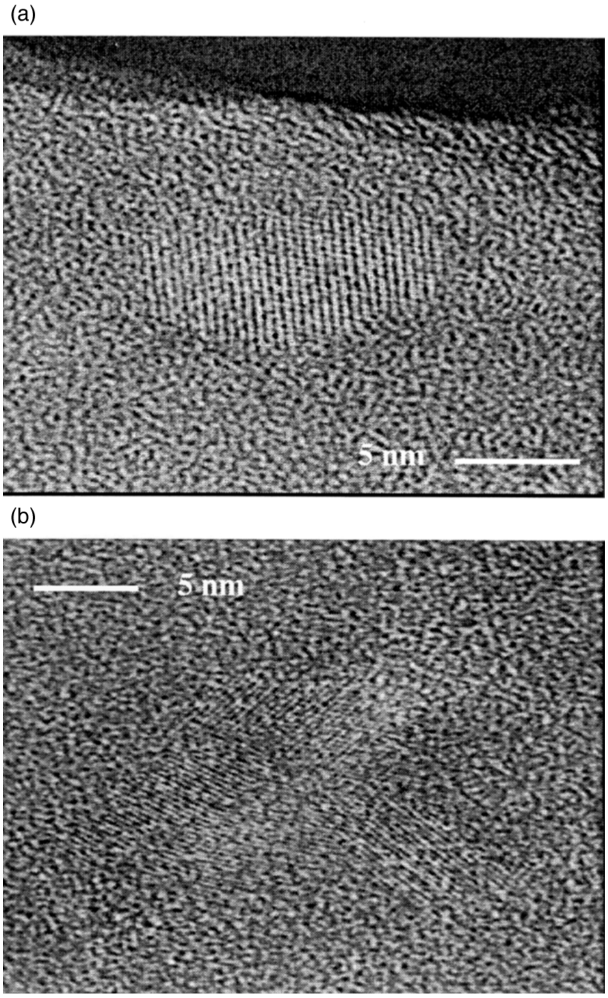

Fig. 6 HRTEM images of Si nanocrystals in densified samples pre-heat-treated at 500 °C (a) and 700 °C (b).

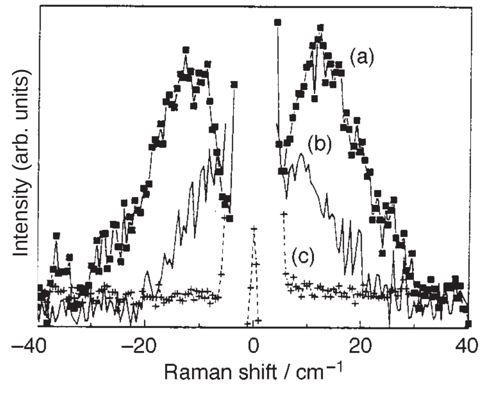

Fig. 7 LOFIRS spectra of densified samples pre-heat-treated at 500 °C (a), 700 °C (b) and 1000 °C (c).

and 700 °C can be understood by the presence of particles having average diameters close to 12 nm and 18 nm respectively.

The sizes estimated by LOFIRS are twice as large as those estimated by TEM (see Table 1). However data derived from either one of the two techniques depend upon very rough assumptions (spherical particles, gaussian distribution, *etc.*) and only a qualitative estimation can be expected. Anyway both techniques indicate clearly that the size of the particles keeps on growing when the samples are heated to higher and higher temperatures, reaching average diameters larger than 20 nm for the gel pre-heat-treated at 1000 °C.

Luminescence experiments were carried out on the samples observed by LOFIRS. No luminescence in the visible range could be observed for any of them. In order to understand these data, we wish to report first on preliminary results on another sample prepared according to the procedure described in the first part of the paper. In this case, the material precursor was an equi-molar mixture of triethoxysilane and tetraethoxysilane. The main idea behind this choice was to change the size of the particles by changing the amount of Si–H bonds present in the gel. In fact the main difference between this and the other samples was the presence of remaining Si–OH bonds in the 'mixed precursors' sample even in its densified form as indicated by IR spectroscopy. This technique was also used to check the disappearance of Si–H bonds in all samples under study. It confirmed the absence of Si–OH bonds in the samples prepared with triethoxysilane alone as the precursor. The difference between the two sets of samples could be expected. Hydrophilic gels are obtained when tetraethoxysilane is used as the precursor and the presence of remaining Si–OH bonds in the materials thus obtained, even after a high densification procedure is applied.[26] On the other hand triethoxysilane leads to hydrophobic gels and the further procedure under vacuum used to prepare the samples in our experiments prevents the generation of new Si–OH bonds during heat treatment. The most important result to be reported on the 'mixed precursor' sample is the existence of a very broad luminescence in the visible range. This result points toward a luminescence in relationship with specific surface states in the prepared sample. The procedure developed in this work allows the monitoring of remaining Si–OH or Si–H bonds. It also includes a heat treatment allowing the surface to relax and therefore the number of defects to be reduced. In contrast work reported in the literature clearly indicates that most Si containing materials which present large visible luminescence are usually obtained by aggressive methods based upon breaking initially large particles (etching,[5] ultrasonic breaking[3]). These methods clearly lead to materials with a large number of defects. Other techniques such as CVD are known to lead to materials containing a non negligible amount of Si–H or Si–OH remaining bonds. Luminescence in these materials was shown to increase upon water immersion and thus upon increase of surface Si–OH bonds.[4] Our experimental observation points also towards a visible luminescence linked to defects in the Si crystallite containing materials. It indeed confirms that the absence of Si–OH bonds and the minimisation of surface defects leads to non-luminescent materials while luminescent materials are obtained in the presence of remaining Si–OH bonds. Further investigations are in progress first to get more information on the 'mixed precursor' material and second to obtain a better control of the Si crystallite sizes to help in obtaining a better insight in the eventual role of the size particles in the luminescence properties in the visible range.

4. Conclusion

Si crystallites embedded in a silica matrix were prepared by the sol–gel route using triethoxysilane as the precursor. The formation of silicon during thermal degradation of the gel was monitored by X-ray diffraction, Raman and ^{29}Si NMR experiments. Silicon results from the decomposition of SiH_4 above 400 °C and its crystallisation occurred at about 650 °C. TEM and LOFIRS experiments showed that the sizes of the crystallites ranged from 5 to 20 nm in diameter. They depended upon the heat treatment of the materials and increased with the temperature of this treatment. No luminescence in the visible range was observed in these materials which did not contain any residual Si–OH or Si–H bonds. In contrast a similar material prepared from mixed precursors, *i.e.* triethoxysilane and tetraethoxysilane, presented a broad luminescence in the visible range. This material was shown to contain residual

Si–OH bonds. Therefore we conclude that the visible luminescence is rather related to surface states or defects in this new family of materials.

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