

Sol-gel Si_{nc}/SiO₂ as active material for light emitters in an all integrated optical sensing scheme

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Abstract

Silicon nanostructures embedded in a silicon oxide matrix (nanocomposite) have been reported to be a reliable option to obtain silicon-based light sources. The technological process starts with the synthesis of a substoichiometric silicon oxide, followed by thermal treatment at high temperatures, to segregate the exceeded silicon into nanostructures. A variety of techniques has been used to achieve the synthesis, sol-gel being one of the simplest and inexpensive ones. In the present work we report on the synthesis of bulk substoichiometric silicon oxides by sol-gel technology and the subsequent thermal treatments. The precursor material is obtained by the combined hydrolysis and condensation reactions of an innocuous silicon alkoxide, hexaethoxydisilane (or hexamethoxydisilane), which is dissolved in ethanol and further diluted in acidic water. After gelation and cure, the material is annealed at different temperatures. Structural and optical properties are studied by FT-IR, XRD and PL techniques. As-synthesized material is luminescent and brittle. After annealing, a low density of silicon nanocrystals is detected. If oxidation (elimination of oxygen vacancies) is avoided during annealing, a highly luminescent material is obtained, with a luminescent spectrum picking at about 550 nm.

Keywords: Silicon nanostructure, silicon oxide, sol-gel, optical properties, silicon alkoxide

Introduction

The known advantages of the optical sensing are significantly improved when this approach is used in an integration scheme. An ideal all integrated optical sensing system should, in principle, integrate the optical source, the light guiding structures (waveguides), the sensing region, the light detector and the processing electronics. Furthermore, it should be fabricated in a unique technological process and preferably with the same basic materials. Microelectronic technology has given rise to significant advances in this direction. However, such an ideal integrated sensing system has not been produced so far. One of the main difficulties has been associated with the development of an efficient silicon-based light source. As it is known, silicon is an indirect band gap semiconductor and, consequently, the efficiency of radiative recombination is low in this material. This situation began to change at the beginning of the 90's, with the discovery of a photoluminescence radiation, visible with the naked eye, in porous silicon [1]. This

phenomenon was related to quantum confinement effect in silicon nanostructures (nanocrystals or nanoclusters, Si_{nc} here after) embedded in a silicon oxide matrix (Si_{nc}/SiO₂). In the last few years the development of silicon-based optoelectronics has received a decisive improvement with the fabrication of the first Si_{nc}/SiO₂-based light emitting diodes (LEDs) [2-4] and the observation of light amplification in Si_{nc} [5], opening a route towards a silicon injection laser.

Si_{nc} embedded in a SiO₂ matrix may be obtained through a variety of techniques such as implantation of Si in thermal SiO₂, co-sputtering, chemical vapor deposition, laser ablation, etc.

The use of sol-gel technology to obtain pre-ceramic materials that are subsequently annealed at high temperature in an inert atmosphere is a very simple and inexpensive approach. It promises obtaining such a nanocomposite material with adequate structural and optical properties for the development of light sources. Moreover, the versatility of this technology allows achieving bulk structures of

any required shape. Several papers may be found in the scientific literature over the last years, which report on the synthesis of this material by sol-gel as bulk samples [6] as well as thin films [7]. However, the difficulties this route has raised are far from being solved. Contradictions, the use of hazardous precursor chemicals and the report of high sensitivity of the material properties to even little technological parameter variations are some of the insufficiencies of most of these published works. Moreover, the absence of information about important aspects such as the low values of density of nanostructures, the absolute intensity of the luminescent radiation and the lost of physical integrity during drying, cure and annealing is a common fact in these papers.

We are engaged in a systematic effort to synthesize, by sol-gel technology, substoichiometric silicon oxides suitable for the development of silicon-based light sources in an all integrated sensing scheme. The preliminary results related to bulk samples are reported here.

The starting material was obtained by the combined hydrolysis and condensation reactions of two different innocuous silicon alkoxides, hexaethoxydisilane and hexamethoxydisilane, which have a silicon-silicon bond in their respective structural units. Pyrolyzed bulk samples were studied by FT-IR, XRD and PL techniques.

Experimental

To prepare the *sol* solution, the hexaethoxydisilane ($C_{12}H_{30}O_6Si_2$; Hex) precursor (the procedure with the hexamethoxydisilane was analogous) was dissolved in ethanol (EtOH/Hex 2/1 in volume) and further diluted in acidic water (pH= 5; H_2O /Hex 2/1 in volume). The solution was maintained in an ice bath and stirred for 60 minutes. The drying (condensation) process took place in two stages. Initially the sol was dried in a furnace at 80 °C for 48 hours and then it was left to cure at room temperature for a week until a translucent and quite brittle solid is obtained.

The resulting bulk material was annealed in a N_2 atmosphere for one hour at temperatures in the range 1000-1150 °C. Two different annealing processes were employed. In the first one (named "rapid"), the samples were introduced with the furnace at 750 °C, then the temperature was raised (≈ 5 °C/min) until the final annealing temperature and decreased after annealing at the same rate, until 750 °C, when the samples were removed from the furnace. In the second annealing process (named "slow"), the samples were introduced at room

temperature, then it was raised (≈ 5 °C/min) until the final annealing temperature and decreased after annealing, at the same rate, until room temperature again.

As-obtained and annealed samples were analyzed by FT-IR using a Bruker spectrophotometer, model TENSOR27 (Bruker Optics GmbH, Germany), including an attenuated total reflectance module (ATR), in the range 500 - 4500 cm^{-1} with a resolution of 2 cm^{-1} .

Some of the samples were reduced to powder and analyzed by XRD in a XPERT diffractometer (PANalytical B.V., The Netherlands), using the $K\alpha$ -Cu line ($\lambda = 1.5419$ Å), in the range $20^\circ < 2\theta < 100^\circ$.

PL (photoluminescence) spectra were obtained in the range 450 - 850 nm by means of an Ocean Optics QE65000 spectrometer. For excitation, the 325 nm line of a 30 mW He-Cd laser was used and the luminescent radiation was collected by a silica 500 μm core optical fiber, with an open end placed very close to the laser spot in the sample surface. The laser beam was focused on sample surface by a quartz lens. It was eliminated from collected luminescent radiation by an adequate interferential filter.

Results and discussion

The structural basic unit of hexaethoxydisilane is shown in figure 1. It contains six hydrolysable ethoxy groups (EtO-), which, during hydrolysis are substituted by -OH groups and ethanol is produced as a side component.

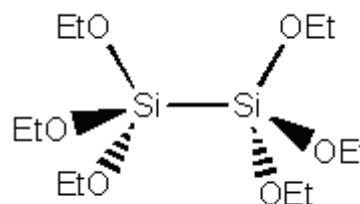


Fig.1. Structural basic unit of hexaethoxydisilane.

Condensation reaction of the hydrolysed monomer leads to the formation of the silicon oxide network, where Si-Si bonds are still present. These are responsible for the formation of Si_{nc} during annealing. By using hexamethoxydisilane, the process is analogous except that the hydrolysable moiety is a methoxy group (MetO-) and methanol is produced during the hydrolysis reaction.

Two set of samples were studied in our experiments. Set 1 corresponds to

hexaethoxydisilane as precursor and rapid annealing in the temperature range 1000-1150 °C. Set 2 was obtained with hexamethoxydisilane and the samples were annealed at 1150 °C by a slow annealing process.

Figure 2 is a confocal image (not real colors) under a 405 nm radiation, of a typical sample of set 1, annealed at 1150 °C. The sample is formed by a central reddish luminescent core, probably containing substoichiometric silicon oxide and silicon nanostructures, surrounded by a non-luminescent transparent colorless coating.

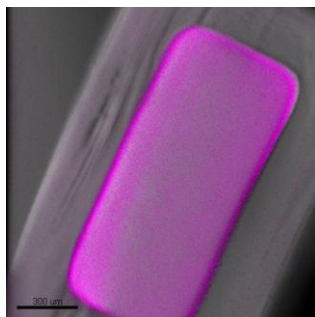


Fig.2. Confocal image (not real colors) of a typical sample of set 1, annealed at 1150 °C.

We consider that this zonal structure is the result of an oxidation process taking place during the rapid annealing. Indeed, in this case, the samples are introduced into the furnace reactor at 750 °C, with a simultaneous incorporation of atmospheric oxygen. When the oxidation temperature is reached, this oxygen has not been completely evacuated yet thus producing the complete oxidation of the external region of the sample. It is a defect-free non-luminescent stoichiometric silicon oxide, which constitutes the transparent colorless cover layer. The situation is different for samples of set 2 (not shown here for simplicity) since in this case they are introduced into the furnace at room temperature. Therefore, they exhibit a homogenous external appearance after annealing and no transparent non-luminescent regions are present. It should be pointed out that, for both sets, as-synthesized samples are quite brittle and may lose its physical integrity during cure and annealing. Therefore, great care must be taken, especially with thin samples, during these processes. However, this is not the case after annealing, when a ceramic mechanically stable material is obtained. Moreover, samples synthesized in different sol-gel processes with apparently identical experimental conditions, commonly show different opacity just after the synthesis. We believe that differences in the external appearance may be associated with undetectable differences in pH values or in other experimental conditions such as drying

temperature. However, no differences in structural and optical properties for as-synthesized and annealed samples were observed in these cases.

FT-IR spectra for as-synthesized and annealed samples show a very regular behavior irrespective of the alkoxide and annealing process used (set 1 or 2) or the annealing temperature. Figure 3 depicts four of such spectra corresponding to typical samples of set 1 and 2, before and after annealing at 1150 °C. For annealed samples, the spectral structure is typical of a silicon oxide with the two basic bands corresponding to bending and stretching of the Si-O bond (the rocking is out of the spectral range of the present spectra) situated, for set 2, at about 790 and 110 cm^{-1} respectively. For as-synthesized samples, however, some other bands are also present. Indeed, two bands associated with O-H bond in the Si-OH (stretching) and H-O-H environments at about 1625 and 3300 cm^{-1} , respectively for both sets are observed above the position of the stretching of Si-O. Below this position, two other bands are found. One is a very clear band for set 2, situated at around 945 cm^{-1} and associated with the bending of O-H in Si-OH (for set 1 a shoulder is observed at around the same position). The other band is a shoulder around 880 cm^{-1} for both sample sets, which we consider associated with a bond of some non-hydrolyzed ethyl or methyl group. After annealing, all of these bands disappear, as it is observed in figure 3.

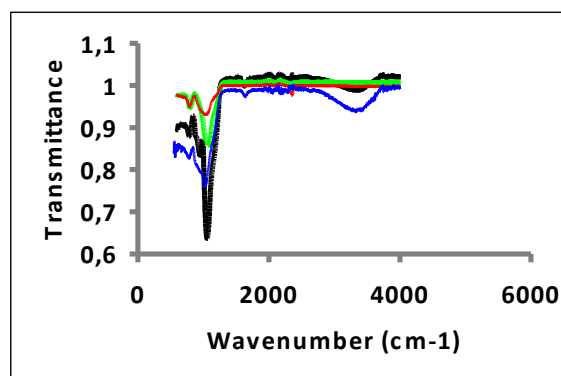


Fig.3. FT-IR spectra for set 1 as-synthesized (blue), set 1 annealed at 1150 °C (red), set 2 as-synthesized (black) and set 2 annealed at 1150 °C (green).

In order to detect the presence of silicon nanocrystals, samples of sets 1 and 2 annealed at 1150 °C were reduced to powder and analyzed by XRD technique. No evidence of diffraction picks was detected for set 1. However, for set 2 a little peak was observed at around $2\theta=28^\circ$ (see figure 4). To verify this assertion, a more fine register was accomplished around $2\theta=28^\circ$ and 47° , where

the presence of two much known diffraction peaks of cubic crystalline silicon take place. Figure 5 depicts such registers. Observe the two very little maxima at around $2\theta=28.3^\circ$ and 47.2° , which demonstrate unequivocally that silicon nanocrystals are present in our material. Its density, however, should be very low in accordance with the small intensity of these picks.

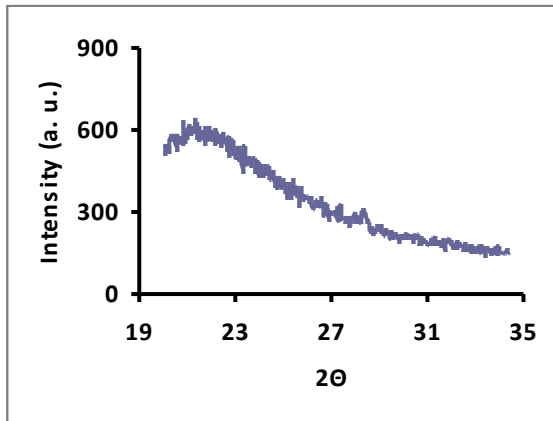


Fig.4. XRD spectrum for samples of set 2 annealed at 1150 °C.

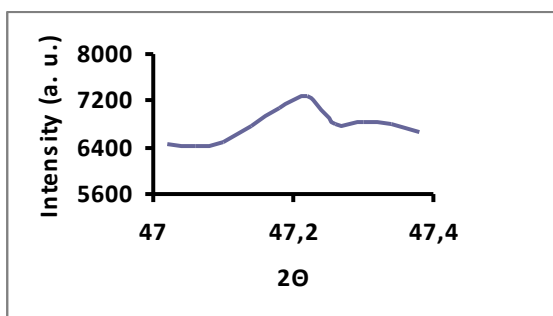
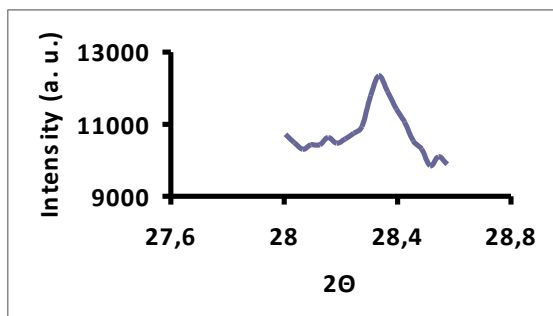


Fig.5. XRD spectra for samples of set 2 annealed at 1150 °.

The precedent results are correlated to the photoluminescence (PL) spectra. Figures 6 and 7 depict these spectra for samples of set 1 as-synthesized and annealed at different temperatures in the range 1000 °C – 1150 °C (rapid annealing) and samples of set 2 as-synthesized and annealed at 1150 °C (slow

annealing), respectively. According to these figures, some interesting remarks may be pointed out:

1- A high PL intensity is observed for as-synthesized samples and both sets, in contrast to previously published results [7], where no appreciable photoluminescence has been reported in this case. It suggests a low density of non-radiative recombination centres (defects) in our material even before annealing. This result could be of significant practical importance since losing the physical integrity during annealing at high temperatures may be, in our opinion, one of the most important drawbacks of sol-gel materials, especially in thin film configuration. The position of the PL bands (around 500 nm) indicates that they may be attributed to recombination in oxygen vacancies [8], which should be in high proportion in our material.

2- For samples of set 1 (rapid annealing), the photoluminescence intensity decreases significantly with the increase of the annealing temperature. This fact could be the result of an oxidation process taking place due to the presence of atmospheric oxygen in the reactor during the rapid annealing step, giving rise to a decrease of the oxygen vacancy density.

Observe that, because of the spectral position of maxima in PL spectra, the PL radiation may be associated with recombination by oxygen vacancies, for all annealing temperatures studied. By increasing the integration time until 20 sec, however, we detected a little PL band at around 780 nm for annealing temperature of 1150 °C (not shown in figure 6). This band can be attributed to luminescence of nanometre-sized silicon crystals embedded in silicon oxide matrix (quantum confinement effect in Si_{nc}) [9]. Its relative very low intensity correlates well with the low density of nanocrystals that was observed by XRD.

3- Unlike the samples of set 1 (figure 6), the samples of set 2 (slow annealing) exhibit a drastic increase in intensity of PL radiation (visible with naked eye as a bright spot) with the thermal treatment at 1150 °C. Indeed, as can be seen in figure 7 for two different annealed samples, the integration time was reduced to 0.1 sec (instead of 1 sec for as-synthesized ones) in order to avoid the saturation of the spectrometer. This fact allows concluding that non-radiative recombination centres (defects) are annealed out at this temperature. Moreover, the density of oxygen vacancies is not reduced during the slow annealing due to the absence of atmospheric oxygen into the reactor.

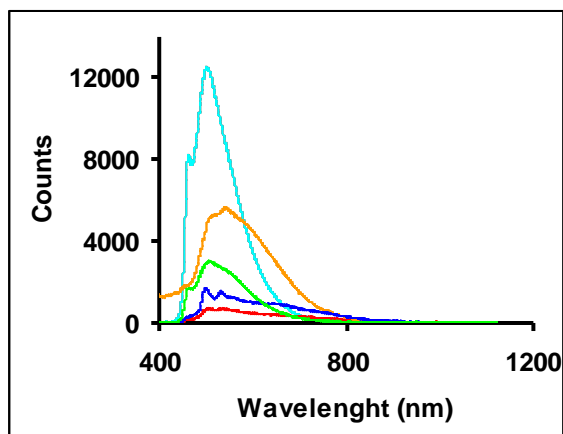


Fig.6. PL spectra for samples of set 1 as-synthesized (blue-green) and annealed at 1000 °C (orange), 1050 °C (blue), 1100 °C (green) and 1150 °C (red). The integration time in all cases was 1 sec.

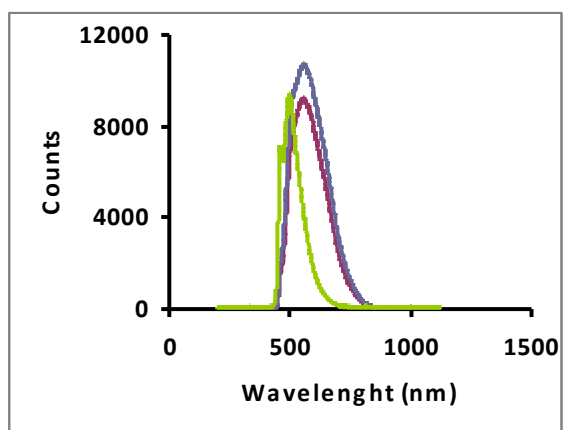


Fig.7. PL spectra for samples of set 2, as-synthesized (green, 1 sec of integration time) and annealed at 1150 °C (blue and red, 0.1 sec of integration time).

Conclusions

Two innocuous silicon alkoxides (hexaethoxydisilane and hexamethoxydisilane), have been used to synthesize substoichiometric silicon oxides suitable for silicon-based light sources, through a sol-gel route. As-synthesized samples exhibit a high photoluminescence radiation around a unique intensity value, irrespective of the alkoxide used in the synthesis. The corresponding spectra show a peak at around 500 nm, thus indicating an oxygen vacancy recombination mechanism. Annealing at high temperatures leads to very important material features. Firstly, the FTIR spectra show the typical bending and stretching bands of Si-O bonds for all of the samples studied. Secondly, a null or very low silicon

nanostructure density is detected by XRD in this case. This fact correlates with the observed null or very low PL radiation produced by quantum confinement effect in silicon nanostructures. Finally, a quite drastic increase of the PL radiation intensity is observed, if a reduction of oxygen vacancy density by oxidation is avoided during this process.

Acknowledgements

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