

Si-nanocrystals/SiO₂ thin films obtained by pyrolysis of sol–gel precursors

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Abstract

Polymer pyrolysis to nanoceramics is employed for the production of photo-luminescent thin film samples, consisting of Si-nanocrystals dispersed in silica matrix. Thin films were deposited on Si wafer by spin-coating technique from a triethoxysilane-derived sol–gel solution. This is a fast process and a low cost technique. Samples were annealed at different temperatures between 600 °C and 1300 °C, under N₂ gas atmosphere. Structural evolution and luminescence from Si-ncs vs. temperature were investigated by FT-IR absorption spectroscopy and photo-luminescence. Absorption spectrum of As-Prep sample shows several vibrational bands due to Si–H, C–H_x, and Si–O–Si structural units, without any appreciable luminescence. Silica phase segregation and intense PL (790 nm) due to Si-ncs were observed on annealing at $T > 1000$ °C.

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1. Introduction

During the last years, the research on Si-based light emitting systems has increased due to the high luminescence efficiency, optical gain, stability and robustness of silicon nanocrystals (Si-ncs) embedded in amorphous silicon oxide films [1–3]. Non-stoichiometric amorphous silicon oxide layers may be obtained by different techniques (PECVD, ion implantation, sputtering, etc.) and successively annealed at high temperature to induce nucleation of Si nano-aggregates following the reaction:



In addition to these techniques, sol–gel spin-coating (SSC) technique can be suited to deposit silica-based oxides (e.g., SiO_x) [4] and oxycarbides (e.g.: SiOC) [5] films. By controlling the reaction conditions, spin-coating cycle conditions, the annealing temperature and the dwelling time, one can obtain nano-aggregates, and/or crystalline phases of different size and

concentration, embedded in the silica matrix. In the past, few groups tried to use sol–gel technique in combination with other techniques such as Si-ion implantation [6] or pulverized porous silicon [7] to obtain the Si-ncs embedded in the silica matrix. Recently, Jia et al. [8] were able to obtain the deposition of thin film of different metal oxides using spin-coating technique and quoted the strength of this technique. Previously, Soraru et al. [9] succeeded in obtaining Si-ncs/SiO₂ nano-composites as bulk samples by using polymer pyrolysis technique. However, till now this technique was not exploited to fabricate Si-ncs/SiO₂ thin films although they could have a great potential as far as fast processing and cost effectiveness are concerned. In this work, we definitively demonstrate the success of polymer pyrolysis in combination with spin-coating technique to produce Si-ncs/SiO₂ thin films displaying intense photo-luminescence.

2. Experimental

2.1. Sample preparation

Triethoxysilane (TREOS) (ABCR, 99%) was dissolved in ethanol (TREOS/EtOH=0.5) and was hydrolyzed with acidic

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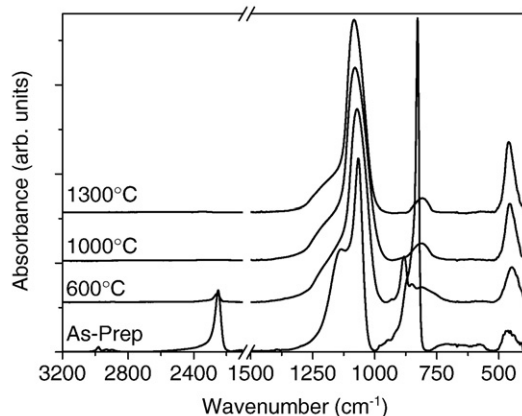


Fig. 1. FT-IR absorption spectra of the samples As-Prep, and annealed at 600, 1000, and 1300 °C in the range between 3200 and 400 cm^{-1} .

water (pH 5 by HCl) ($\text{H}_2\text{O}/\text{TREOS}=2$). To promote a slow hydrolysis rate and avoid phase separation the water was added drop by drop in the solution and the whole reaction process was performed in an ice bath. The solution was kept under fast stirring for 60 min. The sol was then transferred into plastic test tubes which were still kept in ice bath to avoid gelation. The deposition of film on n-type crystalline Si (001) wafer (thickness — 800 nm) was carried out using spin-coating technique with the max RPM (revolutions per minute) of 3000 for 15 s. To stabilize the thin film, the sample was kept at 80 °C and then the thermal treatment was performed under controlled N_2 atmosphere at fixed temperature with 1 h dwell time in the temperature range between 600 and 1300 °C. This pyrolysis treatment first converted the initial siloxane film into an inorganic silica-based film and then (for temperature higher than 1100 °C) promoted the precipitation of nanocrystalline Si in a SiO_2 matrix.

2.2. Characterization techniques

The different samples were spectroscopically investigated at room temperature by means of Fourier transform infrared (FT-IR) absorption spectroscopy and photo-luminescence (PL).

FT-IR absorption measurements were carried out in transmission mode at room temperature in the spectral range between 4000 and 400 cm^{-1} using a JASCO spectrometer (mod. FT/IR-660 plus) equipped with a ceramic source, a KBr beam splitter and a tri-glycine-sulphate (TGS) detector. The measurements were performed under vacuum conditions with a resolution of 4 cm^{-1} . The number of scans for each spectrum being automatically chosen and averaged in order to ensure an optimal signal-to-noise ratio.

PL measurements were carried out by using 488 nm emission line of an Ar^+ laser with nominal power of 10 mW, incident over a circular area of about $2.5 \times 10^{-3} \text{ cm}^2$ and a visible region spectrometer equipped with a CCD detector. PL spectra have been corrected for the spectral response of the optical setup.

3. Results and discussions

3.1. FT-IR absorption spectroscopy

FT-IR spectroscopy shows the gradual structural evolution of the as-prepared (As-Prep) sample undergoing thermal annealing. Typical FT-IR absorption spectra in the range between 3200 and 400 cm^{-1} for samples treated at different temperatures (As-Prep, 600 °C, 1000 °C and 1300 °C) are shown in Fig. 1. The spectrum of the As-Prep film is comparable to those reported in the literature for similar gel samples [10] and shows several vibrational bands centered around 3000 cm^{-1} (C–H vibration), 2250 (Si–H stretching), 830 (combination of Si–O–Si bending and Si– H_x bending vibration), 1080 (Si–O–Si asymmetric stretching mode) and 450 cm^{-1} (Si–O–Si rocking mode) [11,12]. For As-Prep sample, the observed asymmetric Si–H vibrational band is due to the presence of different structural units of $\text{HSi}-(\text{Si}_{3-n}\text{O}_n)$, $n=0-3$. The appearance of C– H_x band in the FT-IR spectrum for As-Prep film is due to the residual ethoxy moieties which were not hydrolyzed. The doublet structure of the Si–O–Si asymmetric stretching vibrations consists of two components centered around 1137 and 1066 cm^{-1} , which are related to two sub-sets of Si–O–Si units with different bridging angles [13]. The higher Si–O–Si asymmetric stretching is due to the cage structures with bridging angle between two silica units higher than 144°, whereas the lower frequency band is assigned to network structures with bridging angle lower than 144°.

Thermal treatment at 600 °C causes the drastic decrease in the intensity of both, combination of Si– CH_3 and Si–H rocking vibration band at about 830 cm^{-1} and Si–H stretching vibration band at 2250 cm^{-1} . Moreover, the C– H_x vibration band is no longer observable within the resolution limit. Finally, the doublet structure of asymmetric stretching Si–O–Si vibrations modifies into the single feature centered at about 1071 cm^{-1} , suggesting an evolution towards a cross-linked structure with bridging angle around 144°.

The absorption spectra of samples treated at temperature $T \geq 1000$ °C clearly show the complete disappearance of Si–H and C– H_x bands and suggests an evolution towards SiO_2

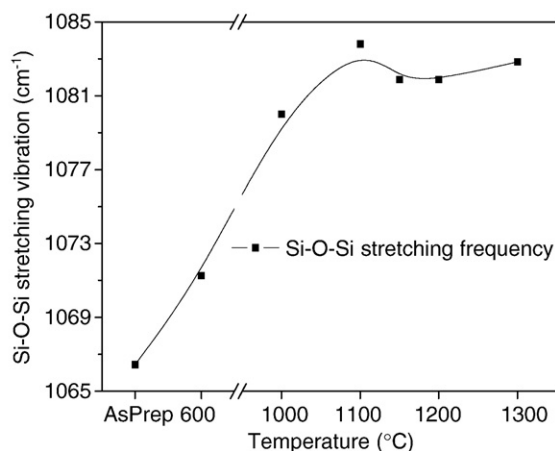


Fig. 2. Frequency shift of Si–O–Si asymmetric vibrational band with the annealing temperature.

structure. In fact, above 1000 °C the FT-IR spectra consist the vibrational bands at 455, 810, 1080 cm^{-1} , which are due to the Si–O–Si rocking, bending and asymmetric stretching modes, respectively. The decrease of the Si–O–Si asymmetric stretching bandwidth from 57 cm^{-1} to 47 cm^{-1} and the increase in peak frequency from 1071 cm^{-1} to 1082 cm^{-1} (shown in Fig. 2) for sample treated at 600 °C and 1300 °C, respectively, indicate the occurrence of a progressive structural rearrangement accompanying to the formation of an amorphous SiO_2 phase [14].

3.2. Photo-luminescence

Photo-luminescence (PL) spectra are reported in Fig. 3 for samples pyrolyzed in the range between 1000 °C and 1300 °C. All the data sets are normalized to the peak intensity. The As-Prep gel film does not show any relevant photo-luminescence (not shown in Fig. 3). Samples annealed at 1000 °C and 1100 °C show a PL band centered around 550–600 nm. This PL band could be attributed to recombination of carriers trapped on the pair of oxygen interstitial vacancy [15]. The generation of oxygen vacancy, in particular, could create a Si clusters. A new band starts appearing for the sample annealed at 1150 °C in addition to the band observed at around 550 nm. This band is centered at around 705 nm and shifts towards 790 nm and 860 nm with increasing the pyrolysis temperature for the sample annealed at 1200 and 1300 °C (Fig. 3). This PL band can be attributed to Si-nanocrystals luminescence. From Fig. 3, it is observed that the residual defects band at 550–600 nm is present up to 1150 °C. PL peak intensity evolution with the annealing temperature is reported in Fig. 4. As can be observed the intensity is low at 1150 °C then it increases of one order of magnitude at 1200 °C and finally it shifts down at 1300 °C. This kind of evolution is typically observed for Si-nanocrystalline systems [9,16]. It gives a clear indication on the matrix phase and quantum dots size evolution. At 1150 °C, non-radiative defect density into the matrix is still high thereby PL from Si-nanocrystals is suppressed but can be observed by an evolution of one peak around 705 nm. Non-radiative defects are annealed out at 1200 °C and as a consequence PL emission from Si-

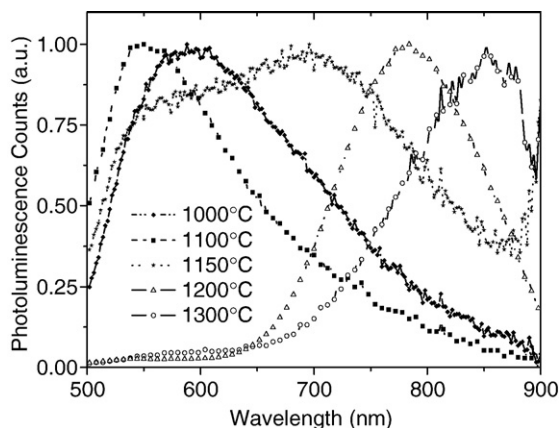


Fig. 3. Normalized PL spectrum for the all the samples (As-Prep and annealed at different temperatures) in the frequency range between 500 and 900 nm.

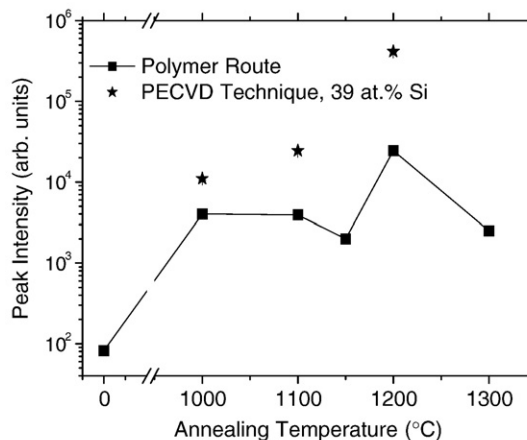


Fig. 4. PL peak intensity shown in logarithmic scale vs. annealing temperature. Fig. shows an increase of more than one order for 1200 °C annealed sample with respect to the 1150 °C annealed sample. In order to compare, PL intensity for the samples prepared by PECVD technique is also inserted.

nanocrystals is highly enhanced. Further increasing of the pyrolysis temperature leads to an the increase of the quantum dots size, in agreement with published results [17]. PL efficiency is reduced because of quantum confinement weakening. In Fig. 4, we also inserted the PL intensity of PECVD samples, annealed at different temperatures. Figure shows that PL intensity from polymer route samples follow the same trend as PECVD samples.

4. Conclusions

We have developed SiO_x thin film using sol–gel spin-coating technique. The successful growth of SiO_x film followed by annealing at higher temperature, through the so called “polymer pyrolysis route” to obtain Si-ncs could be an alternative technique to fabricate the Si-based optoelectronic devices. Many possibilities exist to vary the Si-ncs size and the quantity by changing the TREOS/EtOH, hydrolysis ratio ($\text{H}_2\text{O}/\text{EtOH}$) and the final pyrolysis temperature. Different techniques, FT-IR absorption, and photo-luminescence, have been utilized to assess the evolution of nanocrystalline structure.

FT-IR spectrum for As-Prep sample shows different vibrational bands related to Si–O, Si–H and C–H_x structural units. Thermal treatment at moderate temperate shows the disappearance of Si–H and C–H_x bands and simultaneously the shift in Si–O–Si asymmetric stretching band towards higher frequency. At temperature $T > 1000$ °C, the spectra look quite similar to amorphous silica ones, showing its characteristics vibrational bands at around 450, 805 and 1080 cm^{-1} related to the rocking, bending and asymmetric stretching vibrational bands, respectively. These results indicate the formation of the amorphous SiO_2 within the film.

The PL spectrum for 1000 °C annealed sample shows the asymmetric broad band (toward high wavelength) at around 590 nm which on annealing at 1150 °C shows two clear peaks at around 575 and 705 nm. Further increase in annealing

temperature shows extremely high PL band at around 790 nm, contribution attributed to the Si-ncs. The red shift in the PL position with increase in annealing temperature is clearly observed which indicates the increase in particle size.

In summary, spin-coating technique could be utilized to produce the high quality SiO_x films, showing intense photoluminescence (certainly, not better than those prepared by other physical and/or chemical vapour deposition technique) but by keeping the cost and time for fabrication much lower than the traditional techniques. These results are extremely promising and further research is needed to have better understanding on the intrinsic relationship between the optical properties of the films and parameters of polymer solution.

Acknowledgements

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