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Photoluminescence properties of Nd-doped silicon oxide thin films containing silicon nanoparticles

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ABSTRACT

Neodymium-doped silicon-rich silicon oxide thin films SiO_x:Nd ($1 \leq x \leq 2$) were deposited by thermal co-evaporation of SiO and SiO_2 and annealed at temperatures up to 1200 °C. Due to the phase separation process induced by annealing treatments, amorphous silicon nanoparticles (aSi-np) are obtained. For annealing temperatures equal to or above 1000 °C, silicon nanocrystals (Si-nc) embedded in a SiO_2 matrix are obtained. Photoluminescence (PL) properties of the SiO_x:Nd thin films were studied as a function of the silicon excess, the annealing temperature and the Nd content. For annealed samples, Nd-related PL peaks at 920 nm, 1100 nm and 1400 nm are observed. It is shown that, despite the efficient energy transfer between Si-nc and Nd^{3+} ions, the highest luminescence intensity is obtained for samples containing aSi-np. Moreover, the concentration quenching effect occurs for higher concentration values in samples containing aSi-np, compared to that containing Si-nc. These results show that Si-nc are not necessary to indirectly excite Nd^{3+} ions and that samples annealed at temperatures lower than 800 °C are of potential interest for applications because of a lower thermal budget compared to that required for samples containing Si-nc.

1. Introduction

Silicon-based materials doped with rare earth (RE) ions have attracted considerable attention because of their potential use in optoelectronics [1]. Indeed the use of RE ions can give rise to light emissions at wavelengths from the far-infrared to the ultraviolet spectral range. The light emission from the RE ions generally arises from intrashell transitions of 4f electrons which are, in first order, electric dipole forbidden. Hence, a resonant excitation of the RE ions leads to a weak luminescence efficiency. However, an indirect excitation mechanism can lead to a strong increase in the excitation efficiency of the optically active ions. Energy transfer processes from the matrix to the ions can induce an indirect excitation of RE ions. For example, Er^{3+} ions can emit sharp luminescence at 1.54 μm, which is the commonly used wavelength for optical communications. Er^{3+} ions can be efficiently excited through electron–hole pairs recombination or by impact of energetic carriers in crystalline silicon [2,3]. The Er sensitization has also been widely studied in Si-rich SiO_2 layers. In silica containing Si-nc, the Er-related photoluminescence is strongly improved by an efficient energy transfer process from Si-nc to Er^{3+} ions [4–7]. The Er^{3+} ions can then be indirectly excited by Si-nc which have an absorption cross section of several orders of magnitude higher than that of direct Er excitation. Moreover, the temperature quenching due to energy back-transfer to silicon is strongly reduced because of the higher bandgap of the nanocrystals. Similarly to the case of erbium, Nd^{3+} ions present several technologically important luminescent bands including the $^4F_{3/2} \rightarrow {}^4I_{11/2}$, $^4F_{3/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ 4f-shell transitions which are, respectively, the basis of 1.05 μm Nd lasers, a second lasing transition at 900 nm, and a 1.3–1.4 μm band in the second fiber transparency window. Such bands have been observed in silicon oxide alloys prepared by plasma-enhanced chemical vapor deposition [8], sputtering [9,10] or evaporation [11]. In the previous work we have demonstrated that Nd^{3+} ions are also efficiently indirectly excited via Si-nc [12]. In silicon suboxide thin films, the crystalline silicon clusters, which act as sensitizers for RE ions, are generated by annealing post-treatments above 1000 °C, which involves the demixtion of the SiO_x film following the reaction $SiO_x \rightarrow Si + SiO_2$. This annealing treatment is a severe drawback for applications because of the high thermal budget and because of the impossibility to anneal some devices. Recent results have shown that the existence of Si-nc is not necessary to obtain high Er-related PL efficiency. It has been proposed that amorphous silicon clusters in SiO_x films can also act as efficient sensitizers for Er^{3+} ions [13–15].

In this paper, we present a study of Nd-doped SiO_x alloys. Films with different oxygen contents ($1 \leq x \leq 2$) were prepared by co-evaporation of SiO and SiO_2 and were annealed at temperatures

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up to 1200 °C. In order to obtain the highest luminescence yield, the influences of the stoichiometry, the annealing treatment and the Nd content were studied. It is demonstrated that samples annealed at temperatures lower or equal to 800 °C are more efficient than samples annealed at 1100 °C and containing Si-nc. The results are discussed in relation with the Si excess, the concentration quenching and the energy coupling.

2. Experimental details

The films were prepared by co-evaporation of SiO powder from a thermal cell and of SiO_2 powder from an electron beam gun in a high-vacuum chamber with a base pressure equal to 10^{-8} Torr. The prepared samples had the compositions SiO, $SiO_{1.3}$, $SiO_{1.5}$, and SiO_2. The deposition rate equal to 0.1 nm/s was controlled by a quartz microbalance system. The thickness of the films was equal to 200 nm. The Nd evaporation was performed from an effusion cell and the Nd content was also controlled by a quartz microbalance system. The temperature of the effusion cell, around 1200 °C, is precisely controlled to maintain a constant evaporation rate of Nd during the deposition of the film. Change in the Nd content is obtained by varying the temperature of the effusion cell while the deposition rate of the matrix is maintained constant. The Nd concentration, defined by $C_{Nd} = [Nd]/[Si]$, was varied from 0.05 to 2 at%. The silicon substrates were maintained at 100 °C during the deposition. The samples were then annealed under vacuum in a classical oven for temperatures less than 1000 °C and under a nitrogen flow in a rapid thermal furnace at higher temperatures. For annealing treatments less than (respectively higher than) 1000 °C, the annealing rate is 10 °C/min (respectively. 800 °C/min) and the duration of the treatment at the desired temperature is equal to 1 min (respectively 5 min).

The structure of the films was analyzed by Fourier transform infrared (FTIR) absorption spectroscopy. The spectra were obtained with a resolution of 4 cm^{-1}. The contribution of an uncoated reference silicon substrate was subtracted from the experimental spectra.

For the steady-state PL experiments, the samples were excited by the 325 nm line of a 30 mW He–Cd laser. For the PL excitation (PLE) experiments, the samples were excited by an optical parametric oscillator (OPO) laser. The OPO laser pulse frequency and the duration were typically equal to 10 Hz and 5 ns, respectively. The PL signal was analyzed by a monochromator equipped with a 600 grooves/mm grating and by an InP/InGaAs photomultiplier tube cooled at 190 K, with a detection range of 600–1700 nm. For experiments using the OPO laser, the PL emission from the samples was obtained by integrating the time-dependent luminescence. The response of the detection systems was precisely calibrated with a tungsten wire calibration source.

3. Results and discussion

Infrared absorption spectroscopy is a very efficient technique to study the composition of silicon oxide films. The vibration energies of Si–O bonds are strongly dependent on the chemical environment, which renders possible determination of the composition. The infrared spectra, which are represented in Fig. 1 for as-deposited samples with different stoichiometries, present two absorption bands at 450 and 1000 cm^{-1} which are due to the rocking motion and the asymmetric stretching vibration in the Si–O–Si bonds, respectively. These vibrations are present in all the SiO_x films but their frequencies are dependent on the environment of Si atoms. Because of the strong electronegativity of the oxygen atom, these absorption frequencies are increasing functions of x. A linear relation between x and the frequency ν of the asymmetric stretching vibration is generally accepted in an homogeneous silicon oxide film [16]. In our group, such a relation was determined using reference samples: $x=(\nu-918)/81$ [17]. The composition values obtained using this formula are in good agreement with the expected values from the calibration of the deposition rates of the SiO and SiO_2 sources in the evaporator, so it can be supposed that the alloys are homogeneous.

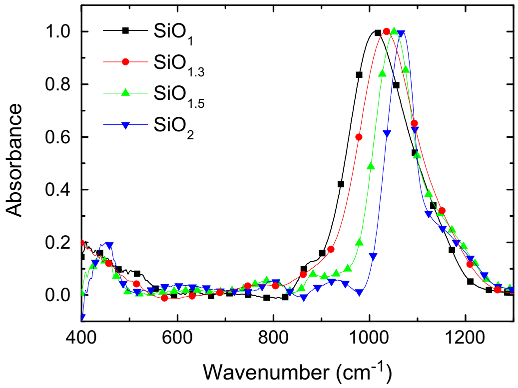

Fig. 1. Normalized infrared absorption spectra of SiO_x as-deposited samples with different x values.

The IR spectra were followed during the annealing treatments at temperatures up to 1200 °C. The evolution is similar for all the samples. As an example, Fig. 2 shows the IR spectra obtained for the SiO_1 sample. With annealing treatments, a shift in the asymmetric stretching vibration band is observed from 1010 cm^{-1} for the as-deposited film to 1075 cm^{-1} for the sample annealed at 1200 °C. In a homogeneous film, these absorption-band positions would correspond to $SiO_{1.1}$ and $SiO_{1.94}$ alloys, respectively. In fact, as no further oxidation of the films was observed neither during exposure to air nor during annealing treatments, it is concluded that a decomposition process occurs in the thermodynamically unstable SiO_x alloys with the appearance of amorphous Si-nanoparticles in a matrix which becomes richer and richer in oxygen. At temperatures higher than 1000 °C, there occurs crystallization of these aggregates to form Si nanocrystals [18].

Steady-state PL experiments have been performed at room temperature for Nd-doped SiO_x layers with Nd concentration equal to 1 at% as a function of annealing temperature. The excitation line was non-resonant with electronic levels of neodymium ions. Whatever the annealing temperature, no PL band was observed for pure SiO_2 samples. PL was only observed for silicon suboxide alloys. Fig. 3 shows the spectra for Nd-doped SiO_1 samples as-deposited and annealed at different temperatures up to 1200 °C. The as-deposited sample shows a broad band around 600 nm, which is attributed to the presence of defects in the SiO_x matrix, such as non-bridging oxygen hole centers [19,20]. The spectrum also presents the three Nd-related PL bands at 920 nm, 1100 nm and 1400 nm. After thermal treatment at 500 °C, the defects band is still observed and the Nd-related PL intensity strongly increases. For samples annealed at 700 °C, the defects band is shifted towards higher wavelengths and the PL-related intensity decreases. After annealing treatments at 1000 °C and 1100 °C, another PL band appears around 830 nm. This band is attributed to Si-nc which have appeared in the layers. For these samples annealed at high temperatures and containing Si-nc, the Nd-related PL is weak compared to that obtained for an annealing at 500 °C. Finally, at 1200 °C, no more PL peaks are observed.

The dependence of the Nd-related PL with annealing temperature suggests that different excitation mechanisms occur. As mentioned above, the phase separation process induces the