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Time-correlated single-photon counting study of multiple photoluminescence lifetime components of silicon nanoclusters

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ABSTRACT

We report time-resolved photoluminescence measurements of thin films of silica containing silicon nanoclusters (Si NCs), produced by PECVD and annealed at temperatures between 700 °C and 1150 °C. While the near infrared emission of Si NCs has long been studied, visible light emission has only recently attracted interest due to its very short decay times and its recently-reported redshift with decreasing NCs size. We analyse the PL decay dynamics in the range 450–700 nm with picosecond time resolution using Time Correlated Single Photon Counting. In the resultant multi-exponential decays two dominant components can clearly be distinguished: a very short component, in the range of hundreds of picoseconds, and a nanosecond component. In this wavelength range we do not detect the microsecond component generally associated with excitonic recombination. We associate the nanosecond component to defect relaxation: it decreases in intensity in the sample annealed at higher temperature, suggesting that the contribution from defects decreases with increasing temperature. The origin of the very fast PL component (ps time region) is also discussed. We show that it is consistent with the Auger recombination times of multiple excitons. Further work needs to be done in order to assess the contribution of the Auger-controlled recombinations to the defect-assisted mechanism of photoluminescence.

1. Introduction

Thin films containing silicon nanoclusters embedded in a SiO_2 matrix are the subject of particular interest because of the possibility of increasing luminescence efficiency at room temperature by controlling the size of silicon structures at the nanometre scale. In the quantum confinement regime indirect bandgap semiconductor nanoclusters undergo significant changes of their band structures with important consequences for emission [1,2]. Enhanced quantum yield, and an increase in both oscillator strength and radiative recombination probability are strong stimuli for that area of research that aims ot produce optical emission from silicon.

Nanometre-sized silicon structures can emit a very large range of wavelengths, from blue up to the NIR, with peak emission closely related to the average size of clusters. Most work is focused on the red/orange region, in which emission has generally been attributed to quantum confinement and excitonic recombination inside the nanoclusters. However, a less efficient blue–green band can also be observed, which does not show a clear dependence on particle size. Relatively few studies have addressed the spectral characteristics of this band [3], and there is a general lack in the literature of studies that integrate the analysis of spectral characteristics with those of carrier dynamics in this range. As a result, the origin of the blue luminescence from silicon nanoclusters remains in dispute and different interpretations have been advanced, including luminescent defects, surface states, or direct optical transitions in silicon nanoclusters. Difficulties in finding an agreement over the microscopic origin are also enhanced by the strong dependence on the synthesis techniques and growth conditions of the nanoclusters.

Since the decay dynamics of the blue band are characteristically nanoseconds or shorter it is common to indicate it as "Fast Band" in opposition to the well-studied red band, known as the "Slow Band", which decays on the microsecond timescale. The purpose of this work is to study the nature of the blue/green emission from silicon nanoclusters by means of Photoluminescence (PL) and Time Resolved PL (TRPL) carried out on samples grown by PECVD and annealed at different temperatures.

Annealing is necessary to form Si nanocrystals with diameters of a few nm and to control precipitation, growth and crystallization of the clusters in oxide from a Si-rich layer. The optical properties arising both from the effect of confinement and the

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presence of defects are affected significantly by the annealing temperature. Depending on the main mechanism of photoluminescence, different effects are observable. It is well known that the intensity the emission band peaked between 800 nm and 900 nm increases with increasing annealing temperature and undergoes a redshift. Higher emission efficiency at higher annealing temperatures (T_a) is associated with a higher degree of crystallization of NC aggregates: crystalline Si-NCs have a higher quantum yield due to the reduction in number of non radiative recombination centres [4,5] The redshift is a consequence of the growth of bigger NCs [6,7].

On the other hand, a strong decrease of PL in the visible range with increasing T_a has been observed. Here a model that takes into account only quantum confinement or just defects may not exhaustively describe the observed behaviour. The complete transition from amorphous to crystalline minimizes effects arising from surface states present in materials with strong structural disorder, and affects the blue/green band decisively. However, in addition to the lifetime component associated with interface defects, a further contribution of the order of hundreds of picoseconds is observed showing a different dependence on annealing temperature and, consequently, on cluster crystallinity. We compare our results in light of very recent studies [8] in which picosecond lifetimes are associated with phononless radiative recombination of hot carriers generated under high photon flux.

2. Methods

Samples of thicknesses around 1 μm were grown on Si substrates by Plasma Enhanced Chemical Vapour Deposition (PECVD). Silane (SiH_4) and nitrous oxide (N_2O) were used as precursor gases. Absolute measurements of spectral reflectance were obtained by means of a Lambda 900 Perkin-Elmer double-channel spectrophotometer in the 350–800 nm range using a calibrated mirror as reflectivity reference. Photoluminescence spectra and decay traces were measured with an Edinburgh Instruments Lifespec TCSPC System. Excitation was provided by a diode laser emitting at 405 nm with a repetition rate of 20 MHz, pulse width of 66 ps and peak power of 110 mW. The emitted light was analysed by a computer-controlled monochromator with 1200 grooves/mm and 250–850 nm wavelength range. A Micro-Channel Plate red-sensitive photomultiplier in a cooled housing, (Hamamatsu Photonics R3809U–50), was used to detect light in the 450–750 nm spectral range with an Instrument Response Function (IRF) < 50 ps and an extremely low dark count rate, 10 cps. The measured fluorescence decay curve is the convolution of the IRF with the multiexponential decay acquired. We have measured the IRF by detecting the scattered excitation photons at 420 nm from a sample whose photoluminescence was negligible-a silicon wafer. Additional information on photoluminescence dynamics was obtained through a Hamamatsu streak camera system coupled with a 250 mm effective focal length spectrometer (overall time resolution of about 20 ps).

3. Results and discussion

3.1. PL spectroscopy

Fig. 1 shows the room-temperature photoluminescence spectra of samples annealed at 700 °C, 800 °C, 1100 °C, and 1150 °C. Spectra are broad and distorted, with several peaks that make it difficult to determine the peak emission and FWHM. Thin-film interference phenomena modulate and distort the shape of the

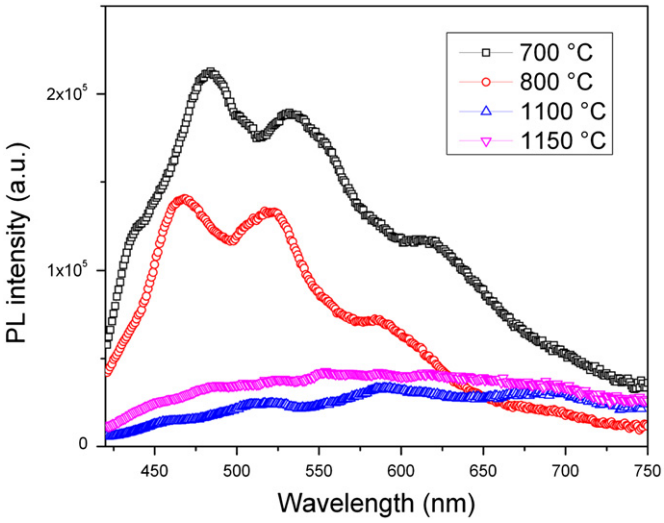

Fig. 1. PL spectra of Si NCs after annealing at 700 °C, 800 °C, 1100 °C and 1150 °C.

spectra of samples whose thickness and refractive index meet the condition for the formation of fringes [9]. Indeed, spectral reflectance measurements, not shown here, provide us with clear evidence over the entire range scanned (200–800) of the fringes due to interference between the optical reflection from substrate and the SRSO layer. Consecutive maxima and minima of interference fringes were found to be equally spaced (as function of photon energy), suggesting low optical dispersion in the whole spectral range investigated, as expected for high-quality SiO_2 films.

Only one sample, that one annealed at 1150 °C, appears to be less affected by interference. This sample suffered from cracking during the annealing treatment, which will change the conditions for interference.

We observed bright PL, visible to the naked eye, from the samples annealed at lower T_a, and a significant intensity decrease with increasing annealing temperature. The evolution of PL intensity is separated into two regimes: one for films annealed at 700 °C and 800 °C that emit strong PL, and the other for films annealed at 1100 °C and 1150 °C whose emission intensity decreases by a factor of 4. A similar blue PL band intensity decrease and redshift has been observed and attributed to the presence of defects and to band tail state transitions in confined amorphous Si NCs [10]. Such a decrease is due to structural changes during thermal treatment resulting in a reduction in defect concentration, different sizes of nanoclusters, cluster density, and crystallinity. By annealing substoichiometric Si oxide (SiO_x) layers at relatively low temperatures, Si nanoclusters are formed in the amorphous phase. Although the amorphous–crystalline transition temperature depends on different factors, above 1000 °C the silicon nanoclusters are largely crystalline [11].

For all samples the emission band extends from 1.7 to 2.7 eV: a range where optically active centres in the host matrix can emit. Indeed, PECVD favours the formation of defects, such as oxygen-deficiency centres (ODCs), E′ centres, and Nonbridging Oxygen Hole Centres (NBOHC), leading to luminescence bands in the blue/violet range [7,12–14]. It is therefore tempting to attribute the observed emission in this range to recombination via defects in the SiO_2 matrix, regardless of the synthesis technique [15-17]. When annealing does not reach a temperature sufficient for phase separation, the oxygen-deficient matrix is considered responsible for the observed photoluminescence. This is consistent with the strong PL decrease with increasing annealing temperature, which drastically reduces the oxygen deficiency centres. However, some studies have shown that the diffusion of silicon in the matrix and