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Influence of implantation parameters on the depth distribution of emitting Si-nc

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ABSTRACT

The photoluminescence (PL) spectra of silicon nanocrystals (Si-nc) produced by Si^+ implantation in SiO_2 are modulated by interference effects associated with the thickness of the SiO_2 layer and the depth where the Si-nc are situated. A model based on the Fresnel equation is used to determine the depth profile of emitting centers corresponding to the best fit between the calculated and measured integrated emission intensity of Si-nc for several thicknesses of SiO_2 [1]. A parametric study has been performed for a range of implantation energy and excess Si concentration. The emitter depth profiles obtained with an excitation at 405 nm have greater amplitude and are generally wider than those pumped at 488 nm; this has been attributed to the excitation of larger band gap Si-nc. The shape of the emitter depth profiles generally agrees with those of implanted Si^+, Si-nc and extinction coefficient. However, measurements performed using the 405 nm laser suggest that the emitter depth profiles produced with the large ion fluence of 1×10^{17} cm^{-2} are deeper, a possible consequence of the strong damage incurred during implantation. Finally, when the local excess Si concentration exceeds the threshold required for the formation of large Si-nc ($\sim 7 \times 10^{21}$ cm^{-3}), saturation and, probably a decrease in emitter density is observed.

1. Introduction

The integration of optoelectronic components on an all Si matrix would simplify the design and manufacture of integrated devices. This emerging technology requires the development of light source such as a silicon laser. One of the most promising processes is the synthesis of silicon nanostructures [2] such as silicon nanocrystals (Si-nc) [3]. The implantation of Si ions in a matrix of SiO_2 followed by annealing at ~1100 °C under nitrogen produces Si-nc of size close to the exciton diameter. This Si-nc can emit an intense photoluminescence (PL) light with wavelength ranging from 650 nm to 1 μm by photoexcitation [4,5].

Measurements indicate that the PL intensity increases with the excess Si concentration up to 25% and decreases for higher concentrations. The Si-nc size also increases for greater local excess Si concentration [5], with crystalline defects appearing in large Si-nc [6]. Even though such defects could be responsible for the observed decrease in luminescence intensity, to our knowledge no satisfactorily explanation has yet been proposed. The determination of the emitter depth profile could certainly shed new light on the effects of Si implantation, such as the implanted Si atom concentration and induced damage, on the Si-nc luminescence intensity. In this respect, ion implantation offers an additional control for Si-nc production by adjusting the depth distribution of excess Si.

In 2004, Elliman's group [7] demonstrated that the luminescence spectrum of Si-nc contained in a SiO_2 layer of thickness in the micron range is modulated because of optical interference effect. This spectral modulation is due to the spatial distribution of both the laser pump intensity and the light emitters in the layer [1,8,9]. More recently, our group has shown that such effects are also observed for a layer thickness as small as 100 nm [1]. A model based on the solving of the Fresnel equation is used to determine the depth profile of emitting centers corresponding to the best fit between the calculated and measured integrated emission intensity of Si-nc for several thicknesses of SiO_2 [1].

In this paper, we present a direct comparison of the shape of the emitter depth profile to those of implanted Si^+, Si-nc and extinction coefficient *k*. Implantation parameters such as implantation energy, which produces deeper and wider Si ion distribution, and ion fluence, that increases the defect concentration, have been varied. Their influence on the luminescence intensity and the emitters depth profile is used to obtain valuable information on the Si-nc luminescence mechanism.

2. Experimental

The samples consist of amorphous fused silica and films of amorphous SiO_2 thermally grown on a Si(1 0 0) substrate with thickness varying between 108 and 985 nm. One mm thick amorphous fused quartz lamellas were used as reference. The samples were implanted with 50 keV Si^+ ions at fluences ranging from

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5×10^{16} to 1×10^{17} Si^+/cm^2. Other samples were implanted with 100 or 150 keV Si^+ at fluences of 8×10^{16} and 1.1×10^{17} Si^+/cm^2, respectively, providing similar excess Si concentrations at the mean implantation depth. The implanted samples were annealed at 1100 °C during 1 h under an atmosphere of nitrogen (N_2) and passivated at 500 °C during 30, 60 and 270 mn in a forming gas of 5% H_2 + 95% N_2 for samples implanted at 50, 100 and 150 keV, respectively. PL measurements were performed using either the 488 nm Ar laser line or a 405 nm laser diode at incidence angles of 30°, 45°, and 70°. The Si-nc signal was collected normal to the sample surface. The laser pump intensities were kept below 2 W/cm^2 to avoid any damaging effect [10].

The depth profiles of the complex refractive indexes were determined by SE measurements in the 370–950 nm range, using the Bruggeman effective medium approximation (BEMA) and the multisample analysis detailed in Ref. [11]. In this BEMA approach, the SiO_2 matrix is described from a Cauchy sublayer, whereas the contribution of Si-nc to the dielectric properties is modelized from a Tauc–Lorentz oscillator [12]. The region where the Si-nc are located is depicted from stacked layers of ~8 nm thickness, which mix gradually the SiO_2 and Si-nc sublayers by following a Gaussian shape distribution. The data were recorded using a conventional Variable Angle Spectroscopic Ellipsometer (VASE – Woollam), spanning the 270–1000 nm range by step of 5 nm, for incident angles of 65°, 70° and 75°, with a 6 nm depth resolution [13]. In order to reduce the number of free parameters, the SE analysis is carried out simultaneously on samples having different oxide thicknesses, but implanted and annealed in the same conditions. Typically, a set of only 15 parameters, constrained to fluctuate within a range of +/− 20% during the fitting procedure, can reproduce the SE data collected in seven different samples for each incident angles (namely 21 measurements). Such a fit provides a global mean square error, MSE (see Ref. [13] for a complete definition of MSE), lower than 1 between the calculated and the measured absorption coefficients determined over the whole detection range. The Si depth profiles were simulated by means of SRIM-2008 [14], corrected to account for both swelling and sputtering effects.

Some Si depth profiles were also measured by Rutherford backscattering spectrometry (RBS) (described in details elsewhere [15]) using a 350 keV $^4He^+$ ion beam incident at 20° (with respect to normal) and backscattered ^4He at 145° to the beam. The ^4He spectrum is deconvoluted into a depth profile with the SIMNRA computer code [16]. In order to obtain the depth profile of implanted Si, the concentration of the Si atoms of the SiO_2 matrix was subtracted from the depth profile measured by RBS. The depth resolution is around 15 nm and the precision of the Si concentration is estimated to 5×10^{20} cm^{-3}.

The model used to determine the emitter density profile assumes a four parameter super-Gaussian distribution of the form $A\ \exp\left[0.5 \times \left(\frac{(z-\mu)}{\sigma}\right)^N\right]$ where z is the depth in the SiO_2 layer, A is the amplitude, μ, the location of peak, σ, a measure of the width of the distribution and N, the exponent (2 for a Gaussian distribution); the exponent is constrained to be greater or equal to 2. This type of distribution is considered sufficiently general to represent a large swath of possible emitter density profiles using a limited number of parameters.

For each implantation condition, several samples are produced with different SiO_2 thicknesses (N samples). For each laser illumination wavelength, the integrated PL spectrum of each of these thicknesses is measured for three illumination angles, producing $3N$ data points for each ensemble.

Using the super-Gaussian emitter density distribution, the model generates an equivalent number of integrated PL data points. The model considers that the local (in depth) amplitude of PL emission is proportional to the product of the pump laser amplitude and emitter density. The local pump laser amplitude is calculated considering interference effects associated with the angle of incidence, the thickness of the SiO_2 layer, the depth distribution of the complex refractive index measured by spectroscopic ellipsometry (SE) and the reflection from the Si substrate. We assume that the emitted PL spectrum is independent of the depth location of the emitter and represented by the measured PL of a sample implanted in fused quartz (infinite SiO_2 thickness) with the same parameters; there are no interference effects associated with this sample. A minimization program (MPFIT) [17] determines the value of the four parameters of the super-Gaussian emitter density distribution that produces the smallest difference between the measured integrated PL and the values computed by the model for each sample set. The aim of this work is to compare the emitter density distribution for a range of implantation parameters and excitation wavelengths to determine trends in the distribution parameters. As such, we are less concerned with the exact form of the distribution but rather to use it as a basis of comparison with the other measured depth distributions. Essentially, not all Si-nc luminesce so we want to determine at what depth do Si-nc light up and advance a possible explanation.

3. Results and discussion

A comparison of the implanted Si^+ depth profile simulated with the computer code SRIM (corrected for sputtering and swelling) to those of the emitting centers (following excitation at 405 and 488 nm) and the extinction coefficient at wavelengths of 405 and 488 nm is shown in Fig. 1 for implantation energies of 50, 100, and 150 keV and similar excess Si concentration at the mean implantation depth. Implanted Si depth profiles measured by RBS are also plotted on this figure. As expected, the mean depth and the width of the implanted Si^+ depth distribution increase with energy. The agreement between the SRIM simulation and RBS measurement is very good indicating that the procedure used to account for sputtering and swelling effects is appropriate in this material. Also, this good agreement confirms that the implanted Si^+ ions do not diffuse to a long distance in the SiO_2 matrix. Both extinction coefficient profiles measured at 405 and 488 nm have a shape very similar to the implanted Si depth profiles indicating that SE is a reliable tool for the determination of the excess Si in substoichiometric SiO_x samples.

The depth profiles of the emitting centers have been normalized to the integral of the photoluminescence intensity obtained with the same pumping laser intensity, so that the y-axis gives an indication of the relative concentration of emitters. It is worth mentioning that the PL intensity is approximately four times greater when the samples are excited with the 405 nm laser while the extinction coefficient (the light absorption) is only ~three times larger. This discrepancy indicates that excitons produced with the 405 nm laser evolves more efficiently towards a radiative recombination.

The profiles of emitters obtained with an excitation at 488 nm are close to the implanted Si and extinction coefficient (k) profiles. Transmission electron microscopy (TEM) measurements indicate that the Si-nc size distribution is relatively uniform with an approximate mean diameter of 3 nm [5,18]. Also, the Si-nc depth distribution matches with the implanted Si depth profile. However, it cannot be excluded that Si-nc smaller than 2 nm are also present in the samples; these cannot be observed by TEM because of their small size. On the other hand, wider and larger emitter depth profiles are observed following an excitation of the samples implanted at energies of 50 and 100 keV with a 405 nm laser. The use of higher energy photons, 405 nm or 3 eV, allows the generation of excitons in Si-nc with larger band gap, thus increasing the number of