Photoluminescent Si and Ge nanoparticles by reactive PLD

Daria Riabinina, Christophe Durand, Mohamed Chaker, Federico Rosei

INRS-EMT, Université du Québec, 1650 Lionel-Boulet, C.P. 1020, Varennes (Qc), J3X 1S2, Canada

riabinina@emt.inrs.ca

Abstract. A novel approach, based on reactive laser ablation in oxygen, is proposed to synthesize Si and Ge nanoparticles embedded in SiO₂ and GeO₂, respectively. We observe a significant photoluminescence (PL) that strongly depends on the oxygen pressure. The size of nanoparticles, estimated from PL spectra, decreases with increasing oxygen pressure. The maximum PL was observed at an oxygen pressure of 0.8 mTorr for Si and 10 mTorr for Ge, corresponding to a size of 2.2 nm and 1.9 nm, respectively. We discuss the similarities and the differences between the PL properties and formation mechanisms of the Si/SiO₂ and Ge/GeO₂ systems.

1. Introduction

Zero-dimensional semiconductor nanostructures have recently attracted a great attention due to their remarkable optical properties [1,2]. In particular, significant photoluminescence properties have been reported for the indirect bandgap semiconductor nanostructures. The interest is focused on Si and Ge nanostructures due to their potential applications in widespread Si-based devices [3].

The most current techniques to synthesize photoluminescent Si or Ge nanoparticles are implantation and co-sputtering into a SiO₂ matrix. Although significant photoluminescence properties have been reported, the non-uniform size distribution, the low density of nanoparticles, the weak photoluminescent efficiency and the limited size control remain the main issues.

Pulsed Laser Deposition (PLD) is a versatile technique for the deposition of thin films and nanostructured materials. The variation of deposition kinetic energy yields significant changes in film structure [4]. For example, it has been demonstrated that PLD of semiconductors in an inert gas atmosphere allows to synthesize photoluminescent nanoparticles with controlled size [5,6,7].

In this paper, we report a novel and simple way to obtain photoluminescent nanoparticles by PLD in a reactive gas atmosphere (called reactive PLD). The laser ablation of Si and Ge targets is carried out in various oxygen background pressures in order to synthesize Si or Ge nanoparticles embedded in SiO₂ or GeO₂, respectively. The aim of this work is to describe the influence of oxygen background pressure on photoluminescent properties of Si and Ge nanoparticles.

2. Experimental details

SiOₓ and GeOₓ (0≤x≤2) films were deposited by reactive laser ablation in an oxygen background atmosphere (0.01 – 1.5 mTorr for SiOₓ films and 2 – 50 mTorr for GeOₓ films). A rotating target (Ge or Si wafers) was ablated using a pulsed excimer KrF laser (λ=248 nm) with a pulse duration of 17 ns and a repetition rate of 20 Hz. The laser density was set at 5 J/cm² and the substrate-target distance maintained at 40 mm. The thickness of the deposited films was ~200 nm. After deposition, SiOₓ films
were annealed for 1 h at 1050 °C in an inert gas atmosphere (N₂). The photoluminescence spectra of SiOₓ films were measured at room temperature, using a YAG laser (405 nm, 25 mW) as the excitation source, whereas photoluminescence spectra of GeOₓ films were measured at low temperature (5 K), using a Ar⁺ laser (458 nm, 46 mW).

3. Results

3.1. Silicon nanocrystals

Figure 1 shows the photoluminescence spectra of Si nanocrystals for several oxygen pressures (varied between 0.26 mTorr and 1.1 mTorr). In the insert, the PL spectra of the sample deposited under 0.68 mTorr of oxygen is shown as a function of excitation laser power (varied from 0.5 to 25 mW). We observe the variation of the shape of PL spectra. This behavior is typical of zero-dimensional semiconductor structures and can be associated to the distribution of excited carriers between energy levels in the quantum confined structure. Thus, we expect that PL spectra are due to the presence of Si nanoparticles in the sample.

![Photoluminescence spectra of Si nanocrystals as a function of oxygen pressure. All the PL spectra were normalized and the scaling factor is indicated in the figure. In the inset, PL spectrum of the sample deposited under 0.68 mTorr as a function of excitation power from 0.5 mW up to 25 mW.](image)

A strong photoluminescence signal is observed at 0.8 mTorr. The PL intensity increases with the oxygen pressure between 0.26 mTorr and 0.8 mTorr. We attribute this increase to the reduction of the nanocrystal size related to the increase of the oscillator strength and to the decrease of non-radiative Auger recombination processes [8,9]. A further increase of oxygen pressure (from 0.8 to 1.1 mTorr) results in a decrease of PL intensity. This effect could be explained by a low density of Si nanocrystals and/or by the low absorbance of excitation light for this sample.

The position of PL maximum (Fig. 1) depends on the oxygen pressure. The maximum shifts from 1.35 eV to 1.8 eV with increasing oxygen pressure. This variation is attributed to the nanoparticle size and to the size distribution. Using a model based on solution of Schrödinger equation for a zero-dimensional quantum structure with Gaussian distribution of size, we estimated the nanoparticle size variation from ~2 nm to ~6 nm for pressures varying between 1.1 and 0.26 mTorr.
3.2. Germanium nanoparticles

Figure 2 shows the photoluminescence spectra of films of Ge deposited by RPLD under various oxygen pressures. The PL intensity was normalized and the scaling factor is indicated in the figure. We observe a shift of the maximum of PL spectra from 1.05 eV to 1.18 eV when the oxygen pressure increases from 7.5 to 20 mTorr. We assume that our PL spectra (in near infrared region) are not due to the Ge oxide defects, since the PL of those features was observed in a blue spectral region (2.1–2.5 eV) [10,11]. As the PL spectra position undergoes an oxygen pressure dependent shift, we can attribute the PL spectra to the Ge nanoparticles, and the PL shift to the variation of their size.

The GeOx (0 ≤ x ≤ 2) film, deposited at room temperature without annealing, is a non-equilibrium system, and the size distribution cannot be described by a Gaussian. Therefore, the model used for Si nanocrystals is inappropriate in the case of Ge. To estimate the size of Ge nanoparticles, we compared our PL spectra to the photoluminescence from Ge nanocrystals embedded in SiO2 matrix, reported in literature [12]. According to the correlation model elaborated by Takeoka et al., we estimated the size of Ge nanoparticles to be equal to ~1.9 nm and ~1.7 nm for the samples deposited under 10 and 20 mTorr, respectively. In the case of 7.5 mTorr, we observe a constant photoluminescence from 1.05 eV to 0.8 eV. We attribute this shape of PL spectra to the wide nanoparticle size distribution with a lower limit at 2.3 nm.

As in ref. [12], a remarkable increase of photoluminescence intensity (by the factor of 20) was observed for the oxygen pressure of 10 mTorr, corresponding to the nanoparticle size of 2 nm. As for Si, we observe a variation of PL intensity as a function of oxygen pressure. The explanation of this effect is similar to the Si nanocrystal case.

4. Discussion

In this work, we discuss the growth of photoluminescent Si and Ge nanoparticles by reactive PLD. In both cases, we observe important variations of the position and of the shape of PL spectra as a function of oxygen pressure. We attribute the PL spectra of both systems to be due to the quantum confinement in semiconductors. We observe the changes in the shape, position and intensity of PL spectra, mainly controlled by the nanoparticle size. Photoluminescence of Si and Ge nanoparticles covers the near-infrared and red spectral region between 0.8 and 1.9 eV.

However, we note important differences in PL properties and in the formation of Si and Ge nanoparticle systems. First, the Si nanoparticles, formed after annealing at 1050°C, are crystalline, while non-annealed Ge nanoparticles are amorphous. Since the PL is present in both cases, the crystallinity of nanoparticles is not essential for PL properties. The key-factor determining the PL position is the quantum confinement, described by the solution of Schrödinger equation for zero-dimensional structures. However, many articles, reporting on hydrogenation effect in photoluminescence of Si nanocrystals, indicate that PL can significantly be decreased by the presence of defects on the nanoparticle/matrix interface and the disorder in the nanocrystalline structure of Si.
dots [13,14]. As we observe an important PL for Ge nanoparticles, clearly their amorphous nature does not cancel the photoluminescence properties. However, it is still possible that the disordered structure modifies the PL spectra.

The second point concerns the formation of nanoparticles. In the case of Si nanocrystals, the nanoparticles are formed by precipitation of Si atoms during annealing at 1050°C. In this system, the directional Si plasma expands in a very low oxygen pressure with a low probability of Si-Si collisions. In the meantime, the ablated Si species undergo enough collisions with the background oxygen atoms to be partially oxidized and to form uniformly dispersed Si in Si-oxide matrix. In contrast, Ge nanoparticles are present in the as-deposited samples. Ge oxidation occurs at much higher pressure than Si (by a factor of 10). In these conditions, the probability of Ge-Ge collisions significantly increases, which causes the formation of Ge nanoparticles in plasma plume. Therefore, two processes perfectly compete: the pressure is sufficiently low to avoid over-oxidation of Ge while remaining sufficiently high to allow the formation of Ge nanoclusters in the plasma.

5. Conclusion
In conclusion, we proposed a simple method of synthesis of strongly photoluminescent Si and Ge nanoparticles. We have shown that RPLD allows excellent control of the nanoparticle size by varying the oxygen background pressure. The size of Si nanocrystals varies between 2 and 6 nm for oxygen pressures between 1.1 mTorr to 0.26 mTorr. The Ge nanoparticle size changes from 1.7 to 2.3 nm for an oxygen pressure varying from 20 to 7.5 mTorr. We conclude that the formation of Si nanoparticles occurs during annealing by precipitation of Si atoms uniformly embedded in a Si-oxide matrix. In contrast to Si, we suggest that Ge nanoparticles, deposited at higher oxygen pressures, are formed in the plasma plume.

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