Feature Article

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1 Introduction

1.1 Photoluminescent silicon nanostructures

In the early 90’s, the first reports that showed that nanostructured silicon exhibits a drastic increase in luminescence efficiency were greeted with great interest. Many properties of materials (physical, chemical, optical, magnetic, electronic, etc.) are modified when their size is reduced to below a critical size, usually less than 100 nanometers [1]. In the case of indirect bandgap semiconductors such as Silicon, quantum confinement is the main effect that induces important changes in the electronic structure of these materials, since the charge carriers are essentially ‘confined’ in atomic-like energy potentials rather than a continuous band structure. This effect can be observed while the nanoparticle size is of the order of the De Broglie wavelength, which is about 5 nm for silicon. The variation of the nanoparticles’ size has an impact on the light efficiency and the emission wavelength. Due to the reduction in size, the bandgap of Si nanostructures increases involving a blue shift in photoluminescence spectra. The changes in electronic bandgap structure result in an increasing probability of carrier recombination in Si nanoparticles and, therefore, an increasing luminescence efficiency.

Since the discovery of the quantum confinement effect in semiconductor nanocrystals, a great effort worldwide has been devoted to the development of new techniques for the synthesis of Si nanoparticles to study and optimize their optical properties. In general, these works can be classified in two principal
groups according to the type of luminescent zero-dimensional structures, i.e. porous materials and silicon nanocrystals (Si-nc) embedded in a Si oxide matrix [2].

Both types of luminescent silicon structures were developed simultaneously and the first two reports on photoluminescence of Si nanostructures appeared in 1990. First, Takagi et al. [3] reported the synthesis of Si nanocrystals embedded in a Si oxide matrix by means of microwave plasma decomposition of polysilane and hydrogen in a resonant cavity, followed by annealing at 60 °C. The post-deposition treatment was used to tune the size of nanoparticles, depending on the annealing time. Si nanocrystals embedded in silicon oxide were observed to emit light in the red spectral region. A blue shift from 1.4 to 1.6 eV was observed for nanocrystal size decreasing from 5 to 3 nm.

At the same time, Canham [4] described the synthesis of porous silicon structures by anodization of Si wafers at low current densities in HF-based solutions. The porosity of Si samples was varied between 70 and 80% by tuning the exposure time to the HF solution. These nanostructures were observed to emit light in the red region, with a blue shift from 1.4 to 1.6 eV and increasing intensity when increasing the exposure time from 1 to 6 hours.

After the first publications on photoluminescent silicon, many techniques were proposed for the synthesis of Si nanostructures, such as ion implantation [5–10], evaporation [11–13], sputtering [14–16], laser ablation [17–24], PECVD [25–27], laser-assisted gas-phase pyrolysis [28], anodization [4, 29] etc. The main challenges related with the synthesis of “interesting” Si nanostructures so far are the non-uniform size distribution, the low density of nanoparticles, the relatively low photoluminescence efficiency, and the limited control of the size distribution. Moreover, electroluminescence of Si-nc, needed for their real optoelectronic applications, is limited by the presence of insulating Si oxide matrix in which nanoclusters are usually embedded. In this Feature Article, we will focus on the use of pulsed laser deposition for the synthesis of photoluminescent silicon nanostructures, highlighting recent work and describing perspectives for future studies.

1.2 Pulsed laser ablation for synthesis of Si nanostructures

Pulsed laser deposition (PLD), also referred to as laser ablation, is a technique of physical vapor deposition (PVD) based on the ablation of material from a target due to the laser-matter interaction. It is an extremely flexible technique for the deposition of thin films with varied structural and optical properties and controlled stoichiometry, i.e. chemical composition. Since it is not highly scalable, it is used mainly for basic research rather than industrial applications. Laser ablation is a perfectly appropriate technique for the deposition of both mentioned types of nanostructured Silicon structures, i.e. porous films and nanocrystals embedded in an oxide matrix.

The principle of laser ablation is shown in Fig. 1. A pulsed laser is focused on a target, solid or liquid, placed in a vacuum chamber. The laser energy focused on the target material locally creates a plasma, the so-called ablation plume. This plasma is directional and expands perpendicularly to the target. The
propagating ablated species are then collected on a substrate placed in front and at a given distance from the target. The deposition can be performed under varied gas pressures, which allows to control the energy of the species impinging on the substrate, as well as the chemical composition (typically using a reactive gas).

This short review describes the possibilities offered by laser ablation for the synthesis of luminescent Si nanostructures, i.e. silicon porous films and Si nanocrystals embedded in a Si oxide matrix. Section 2 gives a description of synthesis of Si porous films by laser ablation in inert gas atmosphere. Photoluminescence and structural properties of such nanomaterials are also discussed. Section 3 is devoted to the synthesis of Si nanocrystals embedded in a Si oxide matrix by reactive laser ablation. Various aspects, such as the formation mechanisms of Si nanocrystals as well as their photoluminescence properties are illustrated. We end with a brief conclusion and a discussion of perspectives for the use of Si nanostructures in optoelectronic devices.

2 Porous silicon

2.1 Photoluminescence

Laser ablation, or PLD in an inert gas atmosphere (e.g. using helium or argon) has been shown to be effective for the synthesis of photoluminescent silicon porous films. There is now a fairly extensive literature on the synthesis of Si nanostructured films [20, 22, 30–38]. Here we focus on two important contributions on the synthesis of Si porous films, which report extensive investigations on the influence of different deposition conditions on the photoluminescence properties of Si nanostructures.

Fig. 2 a) size distribution and b) photoluminescence spectra as a function of laser fluence [30].

Fig. 3 Normalized PL spectra of Si nanoclusters obtained at a fluence of 3 J/cm². (a) Pure He gas (4 Torr) and (b) mixture of He (3.5 Torr) and H₂ (0.5 Torr). Spectrum 1 (solid curve) was measured just after preparation, and spectrum 2 (dashed curve) after several months of exposure to ambient air [30].
Patrone et al. described the synthesis of Si nanoclusters by laser ablation under 4 Torr helium pressure and a laser density (fluence) varying from 1 to 3.9 J/cm$^2$ [30, 33]. Surface analysis by atomic force microscopy (AFM) showed that the morphology of the deposited films is nanostructured and demonstrated that the variation of laser fluence from 1 to 3.9 J/cm$^2$ results in an increase of the size of nanoclustered grains at the surface from $\sim$1 to $\sim$3 nm. Figure 2 shows the size distribution of Si nanoclusters as a function of laser fluence [33, 39]. The films made of nanoparticle grains were found to be luminescent at 3.5, 2.0, 1.8 and 1.7 eV for films deposited at 1.0, 1.4, 3.0 and 3.9 J/cm$^2$, respectively (Fig. 2b) [30]. The authors also studied the influence of sample oxidation during exposure to air. They observed a significant blue shift of the photoluminescence spectra after several months of exposure to ambient air (Fig. 3) [30]. This shift was described in terms of the oxidation and, consequently, the reduction in size of the Si nanocrystals.

Another important contribution to the synthesis of silicon porous films by laser ablation in inert gases was reported by Kabashin et al., who described the correlation between photoluminescence properties and morphology of Si nanostructured films [40]. To synthesize Si porous films, a Si target is ablated under helium pressure varying between 1 and 8 Torr. Under these conditions, the photoluminescence peak was observed to undergo a red shift from 2.15 to 1.6 eV with increasing helium pressure (Fig. 4) [40]. The maximum intensity was observed at 2 Torr of He pressure. For pressures higher than 2 Torr, no variation in the position of the PL peak was observed.

These studies clearly demonstrated that PLD allows to synthesize silicon nanostructured films, which exhibit PL in the red and infra-red region and that the position of PL peaks can be controlled by varying simple experimental parameters, such as the laser fluence on the target and the background gas pressure.

2.2 Structural properties of porous silicon films synthesized by laser ablation

In the work reported by Patrone et al. [33], the PL signal of nanostructured silicon films is interpreted in terms of the presence of Si nanoclusters because of the quantum confinement. Many experimental and theoretical studies were performed to demonstrate that laser ablation results in the synthesis of nanoparticles already present in the propagating plasma plume [20, 31, 41–44]. However, to the best of our knowledge, to date there are no convincing demonstrations of the mechanisms governing nanoparticle formation in the plasma plume. Moreover, the phenomenon of coalescence and agglomeration of such nanoclusters impinging on the substrate favors the formation of porous films, which in turn would exclude the possibility of the presence of individual nanoparticles in films.

In the work of Kabashin et al. [40], the structural properties of Si films as a function of helium pressure were investigated using scanning electron microscopy (SEM). Figure 5 shows the variation of Si
film structure from dense to very porous film for helium pressure of 1, 2, 4 and 8 Torr. A quantitative analysis of film structure was performed by X-ray reflectometry (XRR), so as to measure film porosity. The critical angle $\theta_c$, determined by the phenomenon of total external reflection, was used to calculate the porosity of deposited films. The porosity as a function of helium pressure was found to vary between 10 and 95% for pressures varying from 0.2 to 10 Torr (Fig. 6). The observed correlation between the position of the PL peak and film porosity is an important contribution for the control of luminescence properties of nanostructured silicon films synthesized by laser ablation.

Our group contributed to the understanding of the dependence of the structural properties of semiconductor films on intrinsic laser ablation parameters [45]. We investigated the influence of the kinetic energy of the ablated germanium species, in flight toward a substrate through an inert gas atmosphere, on the characteristics of Ge films deposited on the substrate. Using time and space resolved plasma emission spectroscopy [46, 47], we correlated the plasma expansion dynamics (kinetic energy of deposition)
with the density of the Ge films. The density was estimated using XRR measurements as a function of pressure and substrate-to-target distance. Figure 7 shows the density of Ge films as a function of the kinetic energy of ablated species. The graph demonstrates that the density increases from 0.4 to 4.9 g/cm\(^3\) when the kinetic energy per atom increases from 0.2 to 70 eV and tends to the bulk density indicated by the dashed line at 5.32 g/cm\(^3\). With the kinetic energy being controlled via pressure and substrate-to-target distance variations, this ‘universal curve’ shows that the kinetic energy of ablated species is a relevant parameter that controls film density. This result demonstrates clearly the main advantage of PLD, namely the possibility to tune the kinetic energy of ablated species in a very wide range and, consequently, to control film porosity. A similar behavior is expected for the correlation between the kinetic energy of ablated species and structural properties of silicon films.

The expansion of the neutral Ge species ejected from the target was investigated by time-of-flight (TOF) emission spectroscopy, using the experimental setup described in Ref. [47]. Using TOF spectroscopy, we measured the spatial position of the plasma front as a function of time (time of flight) for various He pressures. For each distance, the TOF of the ablated species increases significantly with pressure, which indicates that the kinetic energy is smaller at higher pressures. The kinetic energy of the plasma front was then estimated using \(E = \frac{mv^2}{2}\).

To summarize the section on semiconductor porous films synthesized by laser ablation, the shown examples clearly demonstrate that laser ablation is an appropriate and flexible technique allowing the deposition of porous silicon films with the possibility of controlling the PL properties. The flexibility of PLD is determined by the possibility of a wide-range variation of the kinetic energy of the ablated species. The correlation between the kinetic energy of the ablated species and the structural properties of the deposited films represents, in our view, an important contribution in the context of controlling the structural and therefore luminescence properties of porous silicon synthesized by PLD.

### 3 Si nanocrystals embedded in a Si oxide matrix

#### 3.1 Introduction

Among the nanocrystal-based systems, silicon nanocrystals embedded in a Si oxide matrix are considered as one of the most promising system since the growth method based on Si-rich oxide films allows to control nanocrystal size, size distribution, and density. To synthesize Si nanocrystals embedded in a silicon oxide matrix, Si-rich oxide films (SiO\(_x\), 0 < \(x\) < 2) are deposited. Then, an annealing treatment is performed at high temperature (usually above 1000 °C for one hour) under an inert gas so as to precipitate the excess Si in the Si-rich oxide films, thus forming Si nanocrystals in the SiO\(_2\) matrix. The Si nanocrystal size is directly controlled by the excess Si quantity in the Si-rich oxide films: the higher this excess, the larger is the resulting Si nanocrystal size. Therefore, the key issue in the synthesis...
of Si nanocrystals embedded in a SiO$_2$ matrix is the control of the excess Si in the Si-rich oxide films. Various techniques can be used for the synthesis of Si-rich silicon oxide films, including e.g. ion implantation [48], co-sputtering [11], or plasma enhanced chemical vapor deposition (PECVD) [49]. Ion implantation is a very common technique of synthesis of Si nanocrystals. Si atoms are directly implanted in thermally grown SiO$_2$ films. The excess Si quantity and its depth distribution are controlled by the ion dose and the ion energy, which determine respectively the size and the depth profile of Si nanocrystals.

Another widespread technique for synthesis of Si nanocrystals embedded in Si oxide is co-sputtering [14, 16]. The relative sputtering rates of Si and SiO$_2$ targets allow controlling the silicon sub-oxide composition. Finally, the third commonly used technique for synthesis of Si-nc in SiO$_2$ is PECVD, a technique which is widely used in industry. In PECVD, the stoichiometry of SiO$_x$ films is determined by the ratio of gas precursors (ultrapure SiH$_4$ and N$_2$O). This technique is considered as one of the most promising for the integration of Si nanocrystals in optoelectronics in real applications. For example, Si nanocrystals produced by PECVD combined with a photonic crystal provide a very bright electroluminescence [50]. Compared to ion implantation, where Si nanocrystals are situated at a fixed depth with a certain depth distribution, Si-nc synthesized by means of co-sputtering and PECVD are uniformly distributed within the whole film thickness.

An innovative approach has recently been developed in our group to synthesize, for the first time, Si rich-oxide films by means of reactive pulsed laser deposition (RPLD) combined with a post-deposition annealing treatment [51, 52]. In RPLD, the laser ablation of the Si target is carried out under a reactive gas background pressure, in this case oxygen. In contrast with conventional PLD in an inert gas pressure, the variation of oxygen pressure in the ablation process of the Si target enables the control of the oxidation degree of silicon-rich Si oxide films. The films were deposited using a KrF excimer laser for the ablation of a Si target under a very low oxygen pressure (0.03–1.5 mTorr). After deposition, the SiO$_x$ films are annealed at 1050 °C for 1 hour under inert gas flow. This is a crucial step for the formation of Si nanocrystals. During annealing, Si atoms diffuse in the films to form Si nanocrystals by precipitation.

### 3.2 Control of Si nanocrystal size

The size of Si nanocrystals formed during the annealing process is determined by the initial composition of Si-rich oxide films: Si nanocrystal size increases with increasing excess of Si in the sub-stoichiometric SiO$_x$ films.

Reactive PLD is a suitable technique for the accurate control of the composition of Si-rich oxide films by varying the background oxygen pressure during the ablation process. Indeed, the degree of oxidation of as-deposited SiO$_x$ films progressively increases with increasing background oxygen pressure, as shown by X-ray photoelectron spectroscopy (XPS) measurements in Fig. 8.

At low O$_2$ pressure (0.03 mTorr), the Si 2p spectrum indicates that the film mainly consists of non-oxidized Si (Si$^0$ peak at 99.3 eV). Spectral contributions at higher binding energy, resulting from silicon oxidation, gradually appear with increasing oxygen pressure. At the highest oxygen pressure used (1.5 mTorr), the films are found to be mainly composed of SiO$_2$ (Si$^{4+}$ peak at 103.3 eV). The Si 2p spectra demonstrate clearly the increasing oxidation of SiO$_x$ deposited films with increasing background oxygen pressure. Thus, we demonstrated that the accurate control of O$_2$ pressure in reactive laser ablation allows to synthesize SiO$_x$ films with varied chemical composition [52].

The average size of Si nanocrystals was estimated using X-ray diffraction (XRD). Assuming the absence of non-uniform strain, the broadening of the XRD peaks directly depends on nanocrystal size. If we assume that the Si nanocrystals are perfectly spherical, their average size can be estimated using Scherrer’s formula [53]. Figure 9a shows the evolution of Si(111) XRD peak as a function of background oxygen pressure. The error bars for Si nanocrystal size are determined by FWHM measurements (Fig. 9a). Figure 9b shows that Si nanocrystal size estimated using Scherrer’s formula decreases with
increasing oxygen pressure. Therefore, we conclude that RPLD may be used to control Si nanocrystal size, simply by tuning the background oxygen pressure during deposition.

Cross-sectional high resolution transmission electron microscopy (HRTEM) measurements of annealed samples allowed to observe individual Si nanocrystals in the oxide matrix. Figure 10 displays HRTEM images and size distribution histograms of annealed samples deposited at 1 and 0.15 mTorr, respectively. The average nanocrystal size is found to be 5.6 (±1.0) nm for 0.15 mTorr and 2.6 (±0.5) nm for 1 mTorr. These values are consistent with nanocrystal sizes obtained by XRD analysis. We note that the size distribution of Si nanocrystals embedded in an oxide matrix is narrow, compared to nanoparticles obtained by PLD in an inert gas.

Fig. 8  Si 2p XPS spectra of as-deposited films for oxygen pressures varied from 0.03 to 1.5 mTorr. All spectra were fitted with five peaks corresponding to silicon (Si⁰), sub-oxide (Si¹⁺, Si²⁺ and Si³⁺) and SiO₂ (Si⁴⁺) contributions [52]. To remove the native oxide, the surface was sputtered by a 4 keV Ar ion beam for 10 min (etch rate 5 Å/min) before performing XPS measurements.

Fig. 9  (a) (111) XRD spectra of Si nanocrystals as a function of oxygen pressure varied from 0.03 to 1.25 mTorr and (b) evolution of Si nanocrystal size as function of oxygen pressure [52].
3.3 Nucleation and growth of Si nanocrystals

To understand the formation process of Si nanocrystals in the oxide matrix, a correlation between the non-oxidized Si volume fraction $f_{Si^0}$ and the Si nanocrystal size previously measured by XRD $d^{XRD}$ was investigated [52].

The non-oxidized Si volume fraction is estimated from the concentration of non-oxidized Si $C_{Si^0}$ based on the $Si^0$ peak area measured on the Si 2p XPS region (Fig. 8) [52]. The correlation between $f_{Si^0}$ and $d^{XRD}$ is based on the following assumptions:

(i) The non-oxidized Si concentration $C_{Si^0}$ remains constant after the annealing treatment [54].

(ii) Amorphous clean-Si agglomerates and/or very small nanocrystals (not “seen” by XRD but detected by XPS) are not present in the sample, as confirmed by Raman spectroscopy and HRTEM images [52].

(iii) The nanocrystal size estimated by XRD is reduced by 0.4 nm, which corresponds to the thickness of the sub-oxide shell [54, 55], not detected in the $Si^0$ peak in XPS measurements.

Figure 11 displays the correlation between nanocrystal core size (obtained from XRD and HRTEM measurements) as a function of non-oxidized Si volume fraction (measured by XPS), recently reported by Riabinina and co-workers [52].

Riabinina et al. proposed a simple model for the distribution of nanocrystals in a Si oxide matrix. According to this model, the nanocrystals are assumed to be arranged in a simple cubic lattice configuration with distance $L$ between the centers of nanoparticles, as schematically shown in Fig. 12.

From this simple distribution model, the $Si^0$ volume fraction $f_{Si^0}$ may be directly related to the nanocrystal core size $d_{core}$ by:

$$
\frac{f_{Si^0}}{100} = \frac{4}{3} \pi \left( \frac{d_{core}}{2} \right)^3 \frac{L^3}{L'}. 
$$

(1)
Assuming that the distance between the nanocrystal centers is constant, the data from Fig. 11 were fitted using this model. In this case, the average size may be expressed as follows:

\[ d_{\text{ave}} = L(6f_{\text{Si}}/100\pi)^{1/3}. \]  

The best fit is obtained when the distance \( L \) between nanocrystal centers is equal to \((6.7 \pm 0.3) \text{ nm}\). The spatial distribution with fixed nuclei centers can occur when the diffusion process is completed. Additional measurements demonstrated that nanocrystal size stabilizes for annealing temperature and time superior to \(1050 \, ^\circ\text{C} \) and \(1\) h, respectively. According to nucleation and growth theory, energetic factors will drive some nanocrystals to grow, drawing mass from others, which shrink (Ostwald ripening). When their size reaches the critical size \( d^* \), the nanocrystals tend to grow, thus reducing the energy of the system.

When such nanocrystals are formed, their center positions remain fixed. Therefore, the “constant \( L \)” model, described previously, can be attributed to the nucleation regime in which the nuclei centers are in stable positions. For \( f_{\text{Si}} > 50\% \), the simple cubic lattice configuration model is not valid. In fact, the volume fraction corresponding to the situation in which the nanocrystals are in contact (i.e. \( L = 0 \)) is equal to 52.4\%. Therefore, the increase by a factor of two of Si nanocrystal size for \( f_{\text{Si}} > 50\% \) can be explained by the coalescence of two or more nanocrystals.

In conclusion, in RPLD Si nanocrystals embedded in an oxide matrix are formed during the annealing treatment and are uniformly distributed in the oxide matrix with a constant average distance between the nuclei centers (for nanocrystals smaller than 6 nm).

### 3.4 Luminescence properties

In this sub-section, we describe the luminescence properties of silicon nanocrystals embedded in Si oxide synthesized by laser ablation. Photoluminescence measurements were carried out using a diode laser (405 nm, 25 mW) as a source of excitation and detected by a CCD camera in the region between 550 and 1100 nm. Photoluminescence was reported for samples containing Si nanocrystals with size varying from 1.9 to 6.4 nm. Figure 13 displays PL spectra of Si-nc as a function of nanocrystal size. The stars indicate samples whereby the size was determined from the existing correlation between the size and position of PL peaks [11]. The intensities of all PL spectra are normalized and the coefficients are shown in the figure. The PL intensity increases with decreasing nanocrystal size and reaches its maximum at
2.6 nm. This behavior is inherent to the quantum confinement effect characterized by an increasing intensity while the nanocrystal size decreases. For sizes inferior to 2.6 nm, the intensity decrease can be attributed to the low volume density of nanocrystals and/or low absorbance of the sample with composition close to silicon oxide. The position of the PL spectra maximum shifts from 740 nm (1.67 eV) to 920 nm (1.35 eV) while nanocrystal size is increasing from 1.9 nm to 6.4 nm. The possibility of controlling the PL peak position with respect to nanocrystal size is particularly exciting for future optoelectronic Si-based applications.

In the recent literature, numerous articles described the interpretation of the luminescence spectra of systems containing Si nanocrystals embedded in a Si oxide matrix. A large number of studies was performed on the influence of size and distribution [56, 57], of temperature [58, 59], of annealing time and temperature [58, 60] as well as specific parameters of the synthesis methods [61]. An exhaustive review of the literature on this subject exceeds the scope of this feature article. In this section, we will briefly mention the possible origins of PL in Si-nc systems. An example of the enhanced PL of hydrogen passivated samples will also be described.

Although a large number of studies are devoted to the theoretical or experimental studies of the origin of luminescence in Si-nc containing systems, the physical mechanisms of carrier recombination in such nanostructures are still not clear. Amongst these models, we note quantum confinement, spatial confinement, interface states, defects etc. In general, the PL spectra of all systems containing Si nanocrystals can be interpreted in terms of a combination of two or more of these phenomena. Quantum confinement is a targeted property in silicon nanocrystals, due to the possibility of tuning the emission wavelength in relation to nanocrystal size. Many models of quantum confinement were proposed, including first principles calculations [51, 62–66], DFT calculations [67], etc. All these models predict a blue shift in the bandgap structure of Si nanostructures while the confinement is increasing, and are in good agreement with experimental data. The second type of the origin of carrier recombination in Si nanocrystals is spatial confinement [68]. This mechanism decreases the probability of recombination of carriers on non-radiative sites and is not related to the electronic structure of the materials in this case. The position of PL spectra is thus not dependent on the size of the nanoparticles involved. Another source of luminescence is due to the presence of interface states between the Si nanocrystals and the surrounding oxide.
matrix [59, 69, 70]. The position of these spectral contributions is also not dependent on the Si-nc size. An important mechanism influencing the intensity and the shape of Si-nc embedded in Si oxide refers to the presence of Si dangling bonds. These bonds are generally present at the nanocrystal/oxide interface and play the role of non-radiative sites. An efficient way to reduce the influence of dangling bonds and to increase the PL intensity is the well-known hydrogen passivation method, which consists in sample annealing at 500 °C under partial hydrogen pressure [10, 71–73]. The efficiency of the method depends on passivation time, temperature and pressure [12, 74].

Figure 14 shows an example of the influence of hydrogen passivation on Si nanocrystals synthesized by reactive laser ablation. The intensity is observed to increase by a factor of two after annealing for one hour at 500 °C. This experiment demonstrates the high influence of this parameter on the intensity of PL spectra.

4 Conclusions and perspectives

We have described how PLD allows to synthesize both porous Si and embedded Si nanoparticles systems. The latter approach is generally preferred for optoelectronic applications because it allows a better control of nanocrystal size, size distribution and density. Recently, several promising applications based on Si nanocrystals embedded in Si oxide have been developed, such as electroluminescence properties for LED (Light Emitting Diode) [75, 76], erbium doping for devices operating at 1.54 µm and light gain for laser applications [77].

Despite numerous investigations on luminescence properties of Si nanocrystals, only a few groups have demonstrated electroluminescence arising from Si nanostructures. The difficulties in obtaining the electroluminescence are due to the carrier injection through the wide band gap oxide (in the case of Si-nc embedded in Si oxide). Nevertheless, electroluminescence has been obtained for Si nanocrystals synthesized by various techniques such as Si⁺ implantation [78], low-pressure chemical vapor deposition [79], co-evaporation [80], or PECVD [81]. The origin of electroluminescence is not yet well understood. Although quantum confinement is likely to be the dominant light emission mechanism, there are other possible origins of light emission, such as oxide’s defects or the monocrystalline silicon substrate [82]. Electroluminescence properties depend on the structural properties of the Si nanocrystals [83]. Generally, photoluminescence and electroluminescence spectra do not have similar shapes, due to differences in light emission mechanisms. For instance, Jambois et al. have shown that electroluminescence spectra are broader and sometimes differ significantly from PL spectra [80]. In their work, the electroluminescence spectrum is attributed to the quantum confinement in Si nanocrystals, based on the blue spectral shift with the bias voltage, as well as to defects in the SiO₂ matrix. To improve the carrier injection in the silicon oxide matrix, some authors have tried to replace silicon oxide by silicon nitride [84, 85]. Efficient light sources based on silicon nitride have been demonstrated. Also, an enhancement of light emission
from Si nanoclusters has been shown using a photonic crystal as top electrode [50]. Electroluminescence of Si nanostructures synthesized by PLD is reported for Si nanocrystallites synthesized in an inert background gas (porous silicon) [86]. Many other studies and developments based on PLD may be carried out to develop electroluminescent applications of Si nanostructures.

Another promising approach to the synthesis of luminescent Si nanocrystals consists in doping with Erbium. In this case, the presence of Si nanocrystals highly improves the Er luminescence efficiency at 1.54 µm [87, 88]. Doped Si nanocrystals are thus interesting for telecommunications applications. For example, an enhancement of Er\(^{3+}\) emission has been recently achieved combining doped Si nanocrystals and silicon-on-insulator photonic crystal waveguides [89]. Therefore, the synthesis of Er-doped Si nanocrystals by PLD represents a promising approach for electroluminescence applications.

Although PLD is presently not a viable technique for large scale industrial production, it remains a very flexible deposition technique, which allows varying a multitude of deposition parameters, yielding nanostructures with a very large spectrum of properties. Thus, PLD is an excellent tool for fundamental research and for the development of new materials for industrial applications, including the integration of Si in optoelectronics. The integration of Si-nc to the current Si-based technology remains a great challenge for future investigations.

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References

D. Riabinina et al.: Luminescent silicon nanostructures synthesized by laser ablation

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