



# Optical properties of nanocrystalline silicon thin films produced by size-selected cluster beam deposition

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## Abstract

Molecular beams of size-selected silicon clusters were used to grow nanocrystalline thin films. This technique allows the control of both average size and size dispersion of Si nanocrystals, and is then very useful to provide model materials for the study of the luminescence in silicon. We report results obtained by high-resolution electron microscopy, Raman spectrometry and photoluminescence spectroscopy. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

It is well established that photoluminescence (PL) in porous silicon needs interconnected columnar crystalline silicon nanostructures, with diameters in the range 2–5 nm, and that the quantum confinement model is the most reliable theory to explain the so-called S-band PL [1]. Nevertheless, some authors argued about other possible effects for light emission such as amorphous hydrogenated silicon, siloxene molecules, defects or surface states [1]. Although the preparation of porous silicon has

been optimized over the past few years, it is still a very complex material to characterize. Hence, it may be difficult to identify the different origins of the luminescence and to obtain a quantitative agreement with the theory, even though a qualitative agreement is generally found. In this article, we describe a preparation technique of nanocrystalline silicon films, based on the cluster beam deposition, which could be used as a model for a better understanding of nanocrystalline silicon properties. The main advantages of the technique are: (i) particle formation independent of any substrate influence and without chemical or thermal treatment, (ii) knowledge of both mean size and size dispersion in the cluster beam by time-of-flight mass spectrometry.

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## 2. Experimental setup

The silicon clusters are formed by CO<sub>2</sub>-laser-induced pyrolysis of SiH<sub>4</sub> in a gas flow reactor [2]. They are extracted through a conical nozzle, and after being skimmed, they pass through a low-pressure differential chamber (Fig. 1). Finally, the cluster beam reaches the time-of-flight mass spectrometer (TOFMS), where the particles are ionized in a Wiley–McLaren-type ion source by the radiation of an ArF excimer laser ( $\lambda = 193$  nm). Since the CO<sub>2</sub> laser is operated in a pulsed mode, the source generates a cluster pulse, which becomes broadened as a result of the size-dependent velocity of the free clusters. Because the cluster sizes are naturally separated, it is possible to narrow the size distribution by introducing a rotating chopper wheel into the cluster beam [3]. As the CO<sub>2</sub> laser and the chopper wheel are synchronized, one can adjust the delay between the laser shot and the moment when the clusters pass through the chopper wheel slit. Hence, it is possible to select a portion with the chosen average size from the whole cluster distribution. In any case, the size-selected beam is analyzed by TOFMS and verified during and after the deposition, which is performed by introducing a substrate into the size-selected beam. In this article, we present results obtained on

nanocrystalline silicon films grown by depositing clusters of different average sizes.

High-resolution electron microscopy (HREM) was performed at 400 keV on a sample deposited without size selection at very low coverage on commercial holey carbon films. The thin films deposited on CaF<sub>2</sub> or LiF substrates were characterized by optical techniques, such as Raman and resonance Raman spectrometry, and PL spectroscopy. The PL experiments were performed on silicon clusters with mean diameters of 2.47, 3.65, 3.92, 4.95 and 6.37 nm. The size dispersion is about 1.5 nm (FWHM) for both smallest and largest mean sizes, and about 1 nm in the other cases. These samples, now referred to as A to E, are summarized in Table 1. The PL spectra were recorded either with continuous (Ar<sup>+</sup>, Kr<sup>+</sup>) or pulsed (Nd : YAG) lasers. Using the 266 nm radiation of the quadrupled Nd : YAG laser, the absolute value  $\eta$  of the PL efficiency was measured. It was obtained by ratioing the PL signals from the Si samples and the very efficient Rhodamine 6G dye ( $\eta \approx 1$ ), taken as a reference [4]. The Raman scattering experiments were carried out on two films, labeled F and G in Table 1, grown on LiF substrates which do not exhibit any signal that would mask the weak signal from the very thin Si layers. The Raman spectra were recorded using a conventional spectrometer

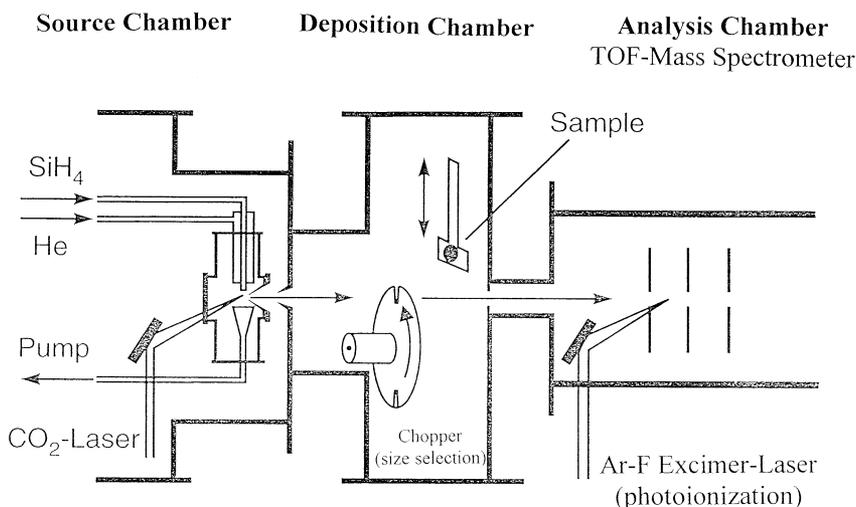


Fig. 1. Schematic view of the cluster source.

Table 1  
Size distributions and photoluminescence energy of the size-selected clusters

Sample	Average number of atoms/cluster	$\langle D \rangle$ /FWHM (nm)	PL energy (eV) (this work)	Exciton energy (eV) (Ref. [7])
A	395	2.47/1.5	—	
B	1220	3.65/1	1.76	1.75
C	1575	3.92/1	1.68	1.66
D	3175	4.95/1	1.49	1.51
E	6755	6.37/1	—	
F	2600	4.63/1.5	1.58	1.61
G	9070	7.03/1.5	—	

and the 488 nm wavelength of an Ar<sup>+</sup> laser as well as an UV-specified spectrometer and the 363.8 nm line of the same laser. All spectra were taken in the macro-configuration with a limited laser power on the nanocrystalline samples to prevent any annealing effects (5 mW, 500  $\mu$ m diameter spot).

### 3. Results

It is now well known that clusters deposited at low energy do not fragment or coalesce when they reach the substrate and form nanostructured films with low density [5]. These films can thus be seen as a random stacking of elementary building blocks, which correspond to the incident clusters, weakly connected and largely surrounded by vacuum. This is the reason why the structure and the properties of these cluster-assembled materials are closely related to those of the free clusters [5].

As an example, Fig. 2 shows a high-resolution electron micrograph of an isolated silicon particle. The particle of nearly spherical shape has a monocrystalline core of diamond cubic lattice type surrounded by a thin amorphous layer, which is probably silicon oxide. In the observed size range (2.5–10 nm), the particles show comparable structural characteristics and are almost completely free of planar lattice defects.

Using Raman spectrometry, we also verified that the average size of both free and deposited clusters was the same. According to the phonon correlation length model proposed by Richter et al. [6], it is possible to determine the size of nanometric

particles from the redshift of the phonon peak compared to the position observed for a bulk single crystal. Nevertheless, Raman spectra recorded with visible excitation exhibit a broad band that can be attributed to amorphous silicon, which could be due to clusters not fully crystallized. Since the more or less empirical treatment of such spectra may affect the exact characteristics of the crystallite peak, we performed resonant Raman scattering experiments to enhance the crystalline part signal to the detriment of the amorphous part signal. Under the resonance condition, which occurs when the excitation energy corresponds to a real electronic transition in the material, the Raman scattering cross section increases by several orders of magnitude. The selectivity between the crystalline and amorphous contributions is due to the sharp electronic transition in the crystalline part, which is spread in the amorphous material because of disorder effects. Thus, we used the 3.4 eV line of an Ar<sup>+</sup> laser, which is close to the first direct transition in silicon ( $\Gamma_{25'}-\Gamma_{15}$  at 3.37 eV). Both visible and UV Raman spectra are compared in Fig. 3, to illustrate the advantage of the resonance approach. From the peak shifts in the resonant Raman spectra, we deduced diameters of 4.8 and 7.3 nm for samples F and G, respectively, according to the phonon confinement model for spheres. These values are in a rather good agreement with the sizes of the free clusters determined by TOFMS.

As mentioned above, photoluminescence spectra were recorded with different kinds of lasers. However, the PL band positions, reported in Table 1,

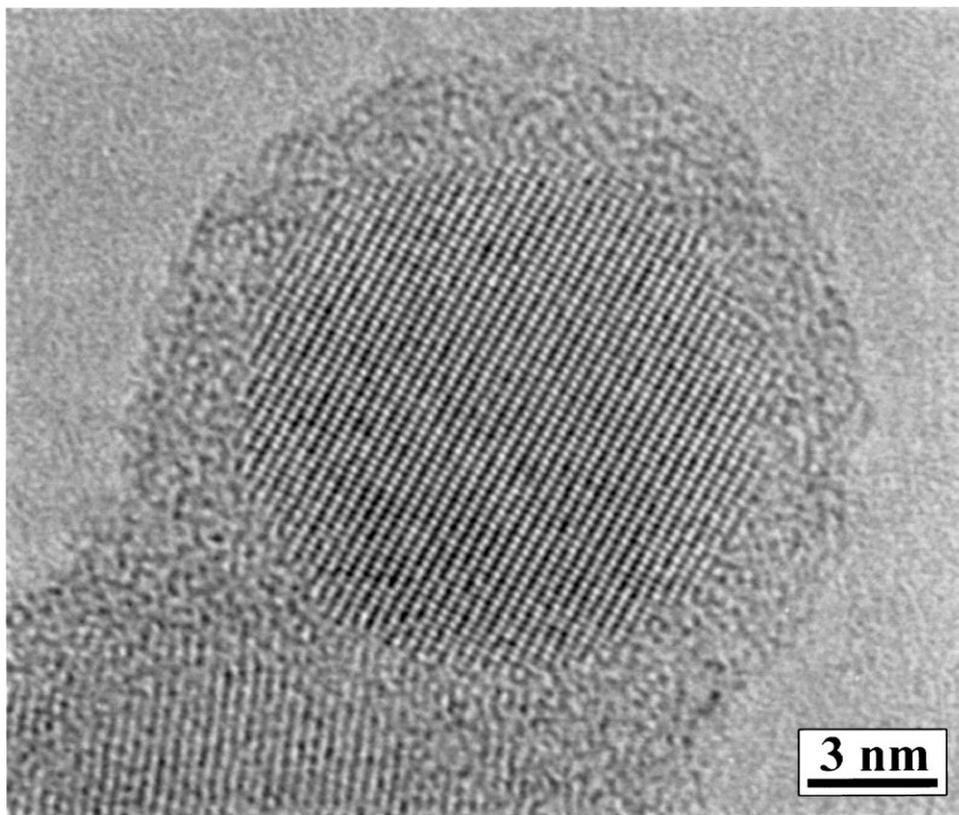


Fig. 2. HREM image of an isolated deposited cluster on top of another particle.

are found to be independent of the excitation wavelength and of whether the laser was operated in the continuous wave or pulsed mode. Furthermore, an intensity increase and a slight blueshift of the PL emission were observed upon cooling the samples down to  $\text{LN}_2$  temperature. No ageing effect was evidenced over several months. According to Table 1 and Fig. 4, it can be seen that the maximum of the PL curve shifts to the blue with decreasing cluster mean size. The values are also in a very good quantitative agreement with exciton energy calculations [3,7]. However, no PL signal could be detected from both smallest and largest clusters (above 6 nm). While the result from small clusters is surprising, the other one confirms the quantum confinement model as will be discussed in the next section. Furthermore, it can be noted that not only the PL energy is size

dependent, but also the PL intensity. We initially attributed this intensity variation to a difference in the layer thickness. In fact, the measured absolute values of the PL efficiency  $\eta$  are of 1%, 12% and 1.6% at room temperature for samples B, C and D, respectively.

#### 4. Discussion

Nanocrystalline silicon films, with controlled grain mean diameters and size dispersions, were prepared using the cluster beam deposition technique. These films can be modeled by a stacking of crystalline Si spheres surrounded by a thin amorphous layer, probably formed of silicon oxide. Hence, we assume that such materials are nearly ideal in the sense that they almost reproduce the

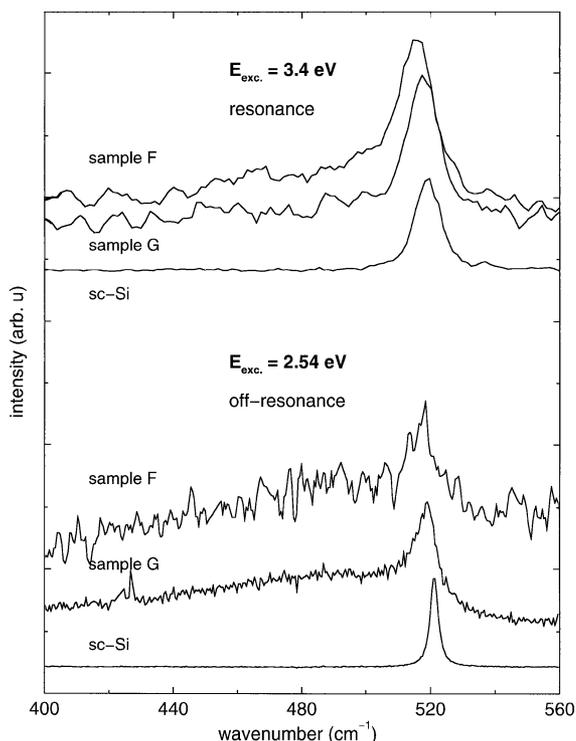


Fig. 3. Raman spectra and resonant Raman spectra of samples F and G.

theoretical case of a single particle with saturated surface bonds, placed into the vacuum. At least, for cluster diameters ranging from about 3.5 to 5 nm, this model is supported by the very good quantitative agreement between the experimental PL peak energies and the theoretical exciton energy calculated within a quantum confinement model. In other luminescent materials, the interconnected nanoparticles are not necessarily perfectly surrounded by a thin passivated surface and by vacuum. Hence, a simple explanation for the Stokes shift, that is observed in some cases between the PL emission and the optical absorption edge, can be proposed. Considering the deviation from the ideal theoretical case, the confinement volume seen by an exciton could be slightly larger than the apparent nanoparticle size. Similarly, the chemical nature and the thickness of the barrier between adjacent particles should greatly influence the confinement. Of

course, the discrepancy may also arise from the size-dependency of  $\eta$ , as much as the contribution of crystallites of about 4 nm in diameter should dominate the PL spectrum provided by a wide size distribution. Nevertheless, the quantum confinement model is sustained by the PL disappearance in large cluster-deposited films (samples E and G). Indeed, according to Cullis et al. [1], no confinement should occur in particles with a diameter larger than the Bohr radius of the bulk exciton, which is 5 nm in Si.

Finally, at the opposite side of the size range (2.47 nm mean diameter), our finding is very different from other studies since the PL also disappears, even though this is in agreement with the decrease of PL quantum efficiency for particle diameters below 4 nm. At this time, we do not have any satisfying explanation for this behavior. Nevertheless, it should be mentioned that our films are grown by deposition of clusters in their ground state, which is not necessarily the case for other preparation techniques involving chemical or thermal treatments. It is possible that a specific phase occurs in small nanoclusters, since *ab initio* calculations for Si clusters containing a few tenths of atoms yield ground state structures corresponding to endohedrally self-doped fullerenes [8]. It has also been proposed that small clusters with diameters below 2 nm are amorphous, or appear amorphous [9]. Such structural changes would thus explain the PL disappearance. Further experiments are planned, in particular Raman studies on new samples deposited on substrates better suited than  $\text{CaF}_2$ .

## 5. Conclusion

We have shown that cluster-deposited films with controlled mean sizes and size dispersions can provide a model for Si-based luminescent materials. The agreement with the calculations may arise from the very specific structure of the cluster-deposited films. It is suggested that the discrepancy between the calculated band gap and the PL emission energy in more conventional materials may be due to the deviation from the ideal case of isolated nanocrystallites. For the future, it is planned to

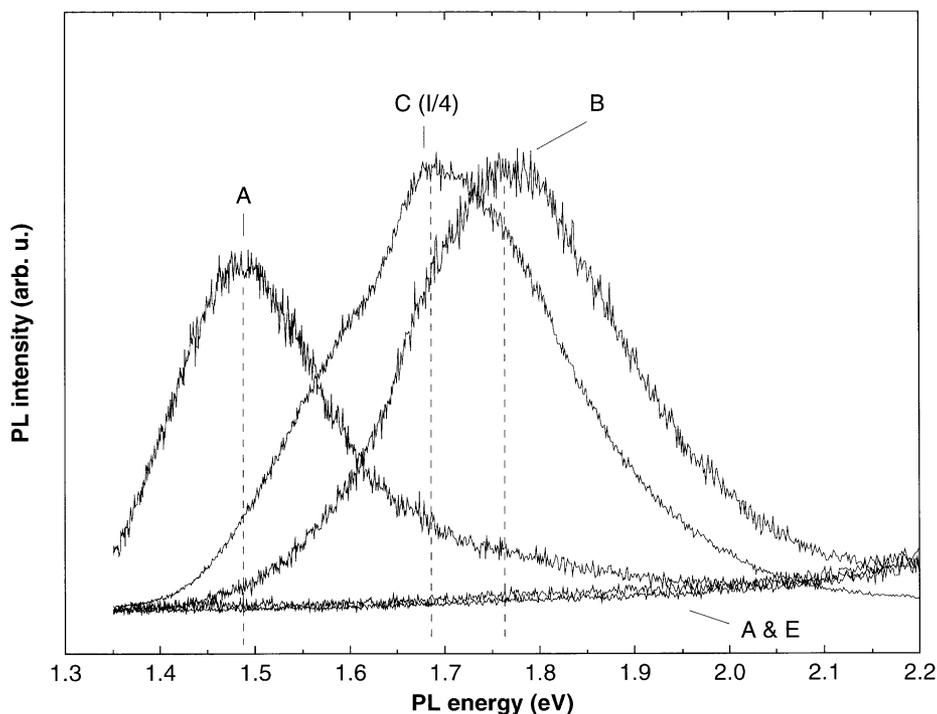


Fig. 4. PL spectra of samples A to E (CaF<sub>2</sub> substrates,  $\lambda_{\text{exc}} = 488$  nm).

investigate the PL emission of hydrogenated and oxidized free clusters (before deposition), as well as the influence of the size dispersion for a given mean size. IV–IV alloys will be also studied in order to engineer the band-gap while keeping the highest PL efficiency, since it is strongly size dependent.

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