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# Cathodoluminescence from nanocrystalline silicon films and porous silicon

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**Abstract.** Luminescence emission of nanocrystalline silicon films has been studied by cathodoluminescence (CL) in the scanning electron microscope. As-deposited films show a dominant band at 400 nm as well as a band centered at about 650 nm. CL spectra of porous silicon samples also show emission at 400 nm. Spectral changes induced by annealing and implantation treatments of the films suggest that the presence of nanocrystals is the origin of the observed CL.

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The study of luminescence properties of silicon nanostructures, as porous silicon (PS) and silicon nanocrystalline films, is a subject of increasing activity due to their potential applications in Si-based optoelectronic devices. Photoluminescence (PL) is the most widely used technique, as compared with other luminescence techniques, to investigate the emission properties of these materials (for a review relative to PS see [1]). On the contrary cathodoluminescence (CL), which is often used to characterize many different semiconducting materials, has not been frequently applied to silicon nanostructures. Some reasons for this situation in the case of PS are the weak CL signal and its lack of stability during electron irradiation. CL spectra of oxidized PS present usually higher emission in the blue-green region than PL spectra, which has been attributed by different authors, see for example [2, 3], to recombinations in $SiO_2$ giving rise to blue-green emission. Mitsui et al. [4] observed a CL band in PS at 420 nm which seems to arise from the interface region between the porous layer and the Si substrate and they do not attribute it to an oxide layer covering the PS. As-prepared PS normally shows PL bands in the region 600–700 nm but also green-blue PL is present in oxidized PS. The origin of the blue PL of PS is a subject of discussion and it has been explained not only by recombination in the oxide layer but by mechanisms involving the presence of nanocrystals. Tsybeskov et al. [5] and Qin et al. [6] attribute the blue band to states at the surface of the nanocrystals or the interface between the Si nanocrystals and the oxide. On the other side Mimura et al. [7] conclude that the blue PL in oxidized PS originates from a quantum confinement state. The existence of blue luminescence in nanocrystalline Si films indicates that this emisssion is not necessarily related to the presence of oxides. In particular, nanocrystalline silicon films have been found [8] to show PL bands in violet and blue regions, which is interpreted by quantum size effects. Kanemitsu [9] studied the PL of surface-oxidized Si crystallites and concluded that a red band arises from recombination processes in the surface states while a blue-green emission is caused by the band-edge emission from the core state of the crystallite. The previous reports on visible luminescence from nanocrystalline Si films refer mainly to PL studies. In the present work the CL technique in the scanning electron microscope (SEM) is used to study the luminescence of low-pressure chemical vapor deposited (LPCVD) Si films and of PS samples. From the above-mentioned results it was expected that both kinds of samples present emission in the blue-green range under electron excitation, which would enable us to compare the corresponding luminescence bands and to study the suitability of CL to the characterization of nanocrystal properties.

## 1 Experimental method

Silicon polycrystalline films with a thickness of about 2 μm were obtained by low-pressure chemical vapor deposition (LPCVD) on silicon at a temperature of 570 °C and a pressure of 0.4 Torr. Some of the films were implanted with boron ions with an energy of 100 keV and doses in the range $1\times10^{13}$–$1\times10^{15}$ cm$^{-2}$. As-deposited films were annealed at 650 °C for 60 min in nitrogen atmosphere. Porous samples were prepared by electrochemical anodization of p-type (100) Si wafers in a HF:ethanol solution with current densities of 25 mA/cm$^2$ for 10 min. The structure of the films was investigated by X-ray diffraction techniques. Luminescence measurements in the visible range were performed by CL in a Hitachi S2500 scanning electron microscope at temperatures between 77 and 300 K with beam accelerating voltages between 15 and 25 kV. PL measurements were performed with a CD 900 spectrometer system from Edinburgh Instruments

with an R 928 photomultiplier in a Peltier-cooled housing. The samples were cooled in a closed-cycle helium cryostat working in the range 10–300 K. The excitation source was a 450 W Xe lamp. CL and PL signals were found to decrease with increasing temperature. Since spectra appear better resolved at low temperatures, the CL and PL spectra presented here were recorded at 77 K and 10 K respectively.

## 2 Results and discussion

The deposition temperature corresponds to the condition for the formation of an amorphous film and X-ray diffraction reveals the presence of an amorphous structure. This observation agrees with previous results [10] reporting the absence of diffraction lines for LPCVD layers deposited at the same temperature used here. However, crystallites with sizes between 3 and 10 nm were observed in the layers by transmission electron microscopy [10, 11]. The CL spectra of as-deposited films show emisssion in the range 350–700 nm with bands centered at about 400, 480–500, and 670 nm (Fig. 1). The CL signal was stable under an electron beam to enable prolonged observations and to record reproducible spectra. The spectra have been found to be reproducible also after extended storage in air. Annealing at 650 °C caused the decrease of the CL intensity without variation of the spectral shape. X-ray spectra of the annealed samples showed the presence of a crystalline phase with an estimated average grain size of 16 nm. The CL intensity decrease with increasing the crystallite size indicates that emission is related to the nanocrystalline character of the samples. In the case of the as-deposited films luminescence would be due to the small nanocrystals rather than to the amorphous matrix. In [8] and [12] PL was observed in nanocrystalline films but no emission was detected under the same conditions in amorphous samples.

Implantation of as-deposited films causes a relative increase of the blue CL band (Fig. 2) which is more intense in the sample implanted with the low dose of $10^{13}\,\mathrm{cm}^{-2}$. The resulting spectrum is similar to the PL spectrum of the nanocrystalline films of [8] which was explained by quantum confinement effects. The mechanism causing the increase of

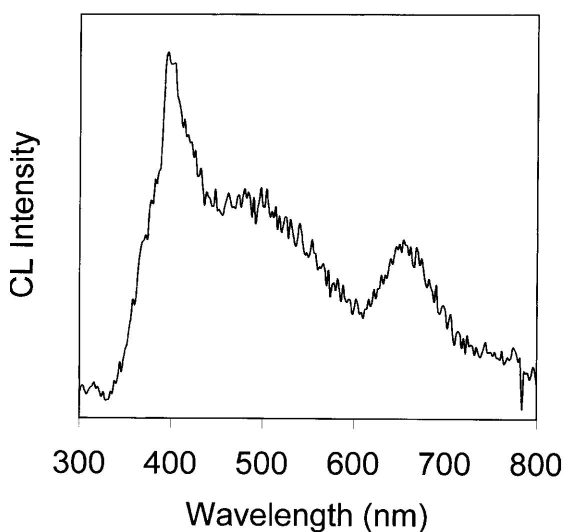


**Fig. 1.** Cathodoluminescence spectrum of as-deposited film at 77 K

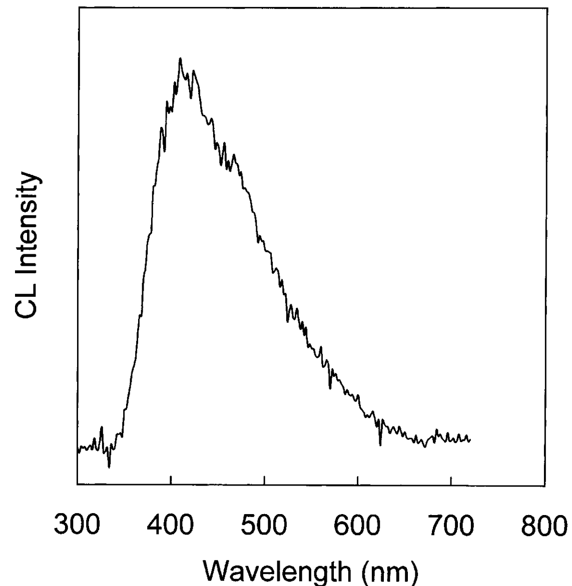


**Fig. 2.** Cathodoluminescence spectrum, at 77 K, of a film after implantation with a dose of $10^{13}\,\mathrm{cm}^{-2}$ of boron ions

the blue band by implantation can be related to the changes in crystallinity. Implantation with $10^{13}\,\mathrm{cm}^{-2}$ influences the average crystallite size which was estimated from X-ray pattern to be 8 nm and showed textures along ⟨111⟩ and ⟨220⟩ directions. In the layers implanted with a dose of $10^{14}\,\mathrm{cm}^{-2}$, X-ray spectra show that the average size of the crystallites with the mentioned preferred orientation increased, while new textures were detected with estimated crystallite size of 8 nm. The increase of the average size relative to the $10^{13}\,\mathrm{cm}^{-2}$ implantation would lead to the reduction of the emission related to quantum size effects. On the other hand the generation of non-radiative recombination centers during implantation modifies the emission properties, which is apparent from the decrease of CL intensity by increasing implantation dose.

The CL spectrum of the crystalline wafer anodized with $25\,\mathrm{mA/cm}^{-2}$ is shown in Fig. 3. The spectral features, as dominant blue-green emission and the positions of the different bands, appear similar in both kinds of samples, films and PS. The above-described results indicate that the CL from the films originates in the nanocrystals and the marked spectral analogy between films and porous samples suggests that also in PS the crystallites influence the blue emission, in particular the 400-nm band, observed in this work.

Electron excitation induces dominant blue-green emission in all samples, nanocrystalline films and porous silicon, studied here but differences in luminescent behavior are observed when photon excitation is used. The nanocrystalline films did not show measurable PL signal under laser or Xe lamp illumination. This is contrary to the observation of [8] in which films with higher luminescence efficiency were used and PL spectra could be obtained. The films used here have amorphous structure modified by the presence of crystallites whereas those of [8] consisted of a homogeneous distribution of small crystallites responsible for the blue emission. The high excitation density produced with the SEM electron beam enables us to record spectra in our nanocrystalline films and shows the capability of the CL technique to characterize nanocrystalline silicon.

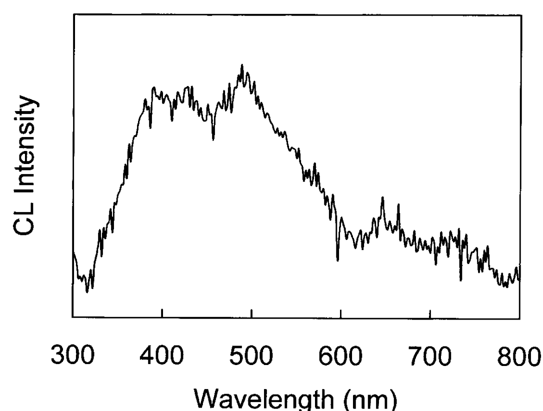


**Fig. 3.** Cathodoluminescence spectrum, at 77 K, of a porous sample

Figure 4 shows the PL spectrum of the porous sample whose CL spectrum is shown in Fig. 3. The CL emission at about 650 nm appears, with high intensity, as the only resolved band in the PL spectrum. The differences between CL and PL spectra of semiconductors are partly explained by the selective character of photon excitation and by the higher excitation energy of electrons. In this work, the often-reported 650-nm PL band is also observed in the CL spectra. It can be pointed out that the band appears in the CL spectra of PS and of nanocrystalline films suggesting that its origin is not only due to the presence of oxides. Suzuki et al. [3] report CL bands at 460 nm and 650 nm, not observed in the PL spectrum, which attribute to defects in $SiO_2$ covering the porous silicon. Cullis et al. [2] also reported different PL and CL spectra in highly oxidized porous silicon and concluded that only a CL band at 750 nm is related to the presence of nanocrystallites whereas other emissions at lower wavelengths are due to oxides. It is suggested that the silicon oxide CL emission at about 460 nm reported in highly oxidized porous silicon is not related to the 400-nm band of this work which, according to the present results, seems to be influenced by nanocrystallite size. In fact the 400-nm band of the nanocrystalline films appears to be stable whereas the same emission of the PS shifts with time to lower energies, which is probably due to the appearance of an oxide-related component. The 400-nm peak is close to the CL maximum observed in the porous samples of [4] and to the PL peak of the nanocrystalline films of [8], which were not attributed to oxide layers. However, the blue band has a complex character and oxide phases in the porous samples could contribute to the observed emission.

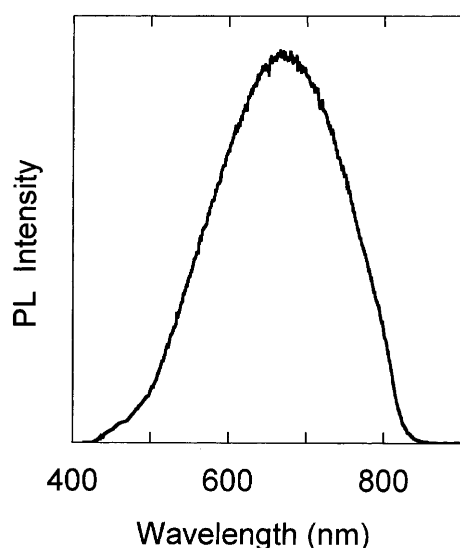


**Fig. 4.** Photoluminescence spectrum, at 10 K, of a porous sample

## 3 Summary

As-deposited nanocrystalline silicon films show CL emission with predominance of the blue band. Variations of CL spectra with annealing or ion implantation suggest that the presence of nanocrystals is the origin of the observed CL. Nanocrystalline films and PS samples present similar CL spectra in which a CL band at 400 nm is a common feature.

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