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Short communication

Cathodoluminescence from mechanically cracked porous silicon

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Abstract

Cathodoluminescence of porous silicon after mechanical damage with a tip has been studied in the scanning electron microscope. Mechanical damage results in the exposure of new surfaces related to fracture and to small particles appearing over the porous silicon layer. The freshly generated surfaces caused an increase of several orders of magnitude in the luminescence efficiency.

Keywords: Cathodoluminescence; Porous silicon

Porous silicon (PS) layers obtained by anodization in hydrofluoric acid solutions are known to show visible luminescence under different kinds of excitations. The origin of this effect has been extensively investigated and many of the experimental results have been explained in the frame of a quantum confinement model [1,2]. In addition, surface effects, mainly related to the presence of oxides, play a key role in the luminescence behaviour of PS [2–4]. Most of the experimental work on the emission properties of PS has been performed by photoluminescence (PL) techniques. In contrast, cathodoluminescence (CL), which is a well established technique for characterising semiconductors, has been less frequently applied to PS. This is partly due to the usually weak and unstable CL signal under electron irradiation of PS. In addition, the spectra of the PL and CL emissions from PS usually differ with the CL signal showing a higher output in the blue-green spectral region. Blue-green CL bands in PS have been attributed in some cases [3,5] to the presence of oxides while other authors [6,7] did not observe a relationship between certain blue CL bands and the oxide layer. In any case, the influence of surface effects on PS luminescence is revealed in the degradation of luminescence during exposure to air or other atmospheres. This usually implies a blue shift of the spectrum. For this reason an analysis of the PS luminescence related to the crystallites would be more clearly performed in samples with a clean surface. In a previous work [8] we have generated new surfaces in PS during electron irradiation under vacuum in a scanning electron microscope (SEM). This treatment caused an increase of the CL signal up to about three orders of magnitude revealing that nanocrystals with fresh surfaces show an intense and stable CL emission peaked at ~ 720 nm. The method used to produce the new surfaces in PS was cracking of the samples by the thermal stresses induced during irradiation. Although we suggest that the presence of the new surfaces is caused by the strong luminescence observed, the effect of the electron irradiation could also be considered. In this work we generate the new surfaces in PS by mechanical cracking, without electron irradiation, and compare the resulting CL signal with that reported in [7].

Porous silicon samples were prepared by anodization of p-type (100) silicon wafers with a resistivity of 12 Ω·cm. The electrolyte used was an HF:ethanol solution mixture and the samples were etched at a current density of 25 mA cm^{-2} for times ranging from 1 to 60 min. CL measurements in the visible range were performed in an Hitachi S2500 SEM at 300 K with a beam accelerating voltage of 20 kV.

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The untreated PS samples had a flat surface when observed in the secondary electron (SE) mode of the SEM and showed a very weak CL signal, which decreased during the irradiation of the sample. Samples with new surfaces were prepared by mechanically damaging the surface of the porous layer with a steel tip or with a diamond microindenter. In order to reduce the formation of oxides in the damaged samples, they were introduced in the SEM chamber immediately after the mechanical treatment. Fig. 1 shows the SE and CL images of the same area after scratching with the steel tip. Fig. 1a shows that in the central part of the scratched area the porous layer is removed while cracks and parts of the layer separated from the substrate are observed in the surrounding region. Also many pieces of the porous layer appear scattered on the surface. In the corresponding CL image (Fig. 1b) it is observed that the undamaged PS surface practically does not show luminescence as compared with the strong emission of the fresh exposed regions in the cracks and in the scattered PS particles.

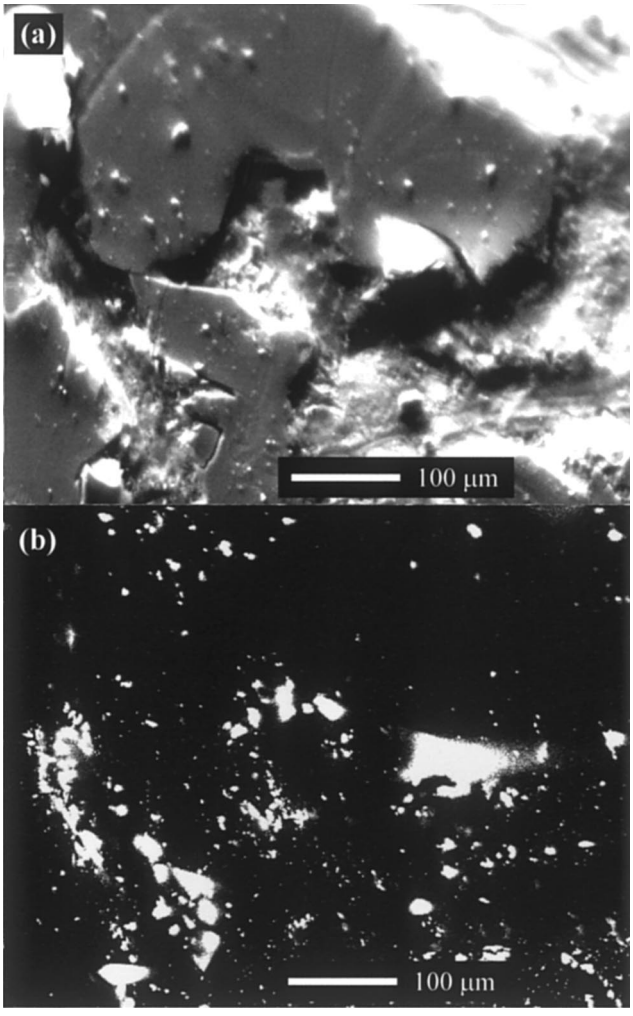

Fig. 1. PS sample mechanically damaged with a steel tip: (a) secondary electron mode and (b) CL mode.

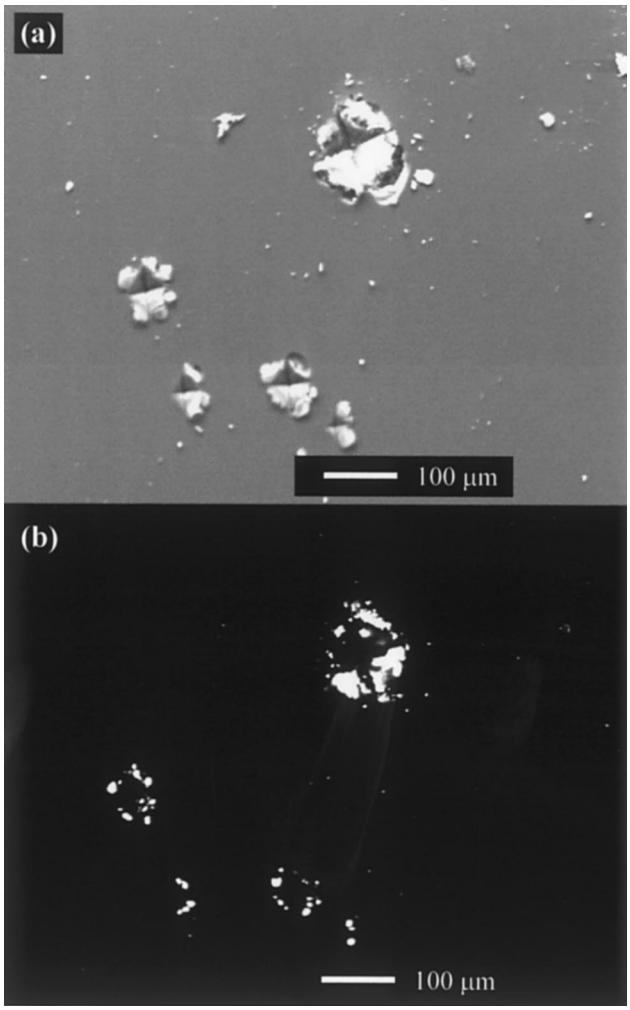

Fig. 2. Images of several indentations in a PS sample: (a) secondary electron mode and (b) CL mode.

Fig. 2 shows the effect of the indentations. Comparison of the SE and CL images reveals that the CL increase is not related to the indented area but to the debris appearing around the indent. This shows that the exposure of new surfaces of the material and not the direct effect of applying stress causes the emission enhancement. The SE image shows that there are not visible cracks in the surface, but only the indentation mark and the surrounding debris. However, stresses have been generated in the sample and after a slight electron irradiation in the SEM, which causes thermal stresses, the sample cracks along the diagonal of the square (Fig. 3) as in indentation processes of other materials. CL images show the appearance of crack-related emission.

As previously reported [8], electron irradiation of PS in the SEM can induce cracking of the sample associated with strong enhancement of light emission. To avoid this effect the deformed samples were observed in this work under electron beam excitations well below those capable of breaking the surface. The CL emission

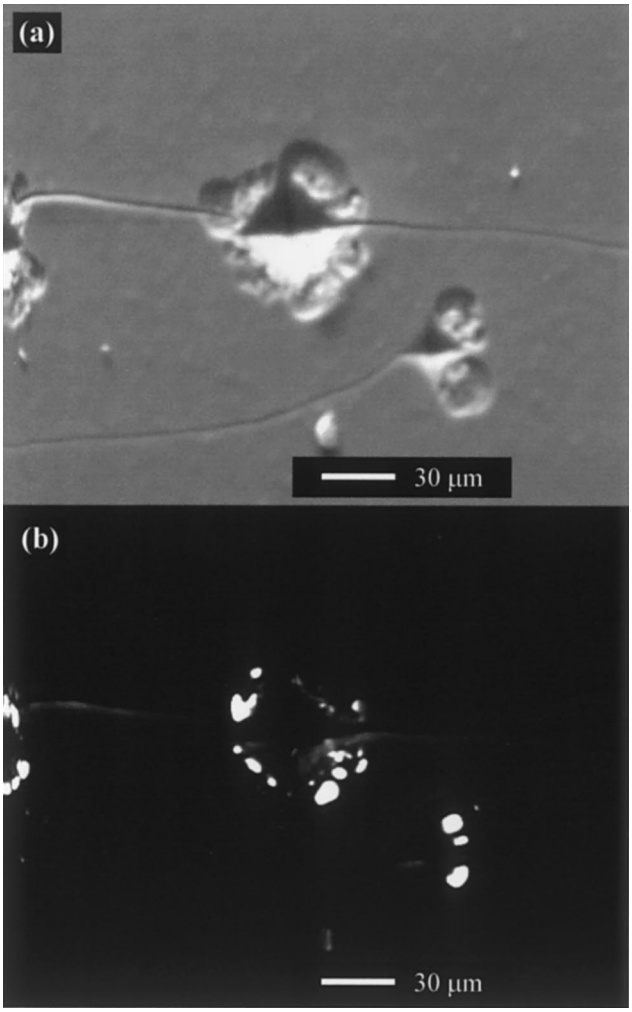

Fig. 3. Detail of an indentation, (a) in secondary electron mode and (b) CL mode.

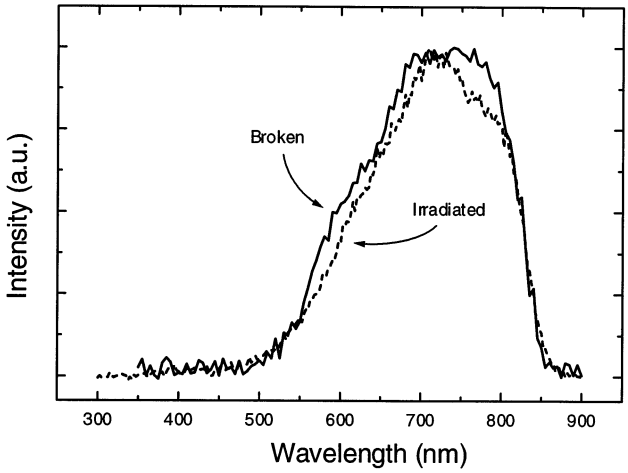

Fig. 4. CL spectra of the mechanically cracked PS (continuous line) and from the irradiated PS (dotted line).

observed in Figs. 2 and 3 is thus solely related to the mechanical damage of the sample and not to the electron beam damage.

Fig. 4 shows the CL spectrum of the mechanically damaged samples (continuous line). For comparison, the CL spectrum of a sample cracked by the effect of the electron beam is also shown (dotted line). Both spectra consist of an asymmetric broad band and are similar to those often reported in photoluminescence works on PS. The spectrum of the deformed sample peaks at 700 nm while in the irradiated PS the maximum appears at 720 nm. The difference can be explained by considering that the mechanical damage takes place in air while the cracking during irradiation takes place in the SEM vacuum. In fact we have observed that storing the irradiation damaged samples in air for a short time causes a blue shift of the CL spectra which become similar to those of the deformed samples.

The present results show that the mechanical treatment leading to cracks in the surface of PS causes a drastic increase in the luminescence intensity of the samples. This effect is due to the formation of fractured surfaces and the consequent exposure of new nanocrystals to the excitation beam. Such a mechanism is similar to the previously reported CL increase of PS when electron irradiation produces breaking of the samples by thermal stresses. It appears that electron irradiation without fracture of the PS layer alone does not cause the CL enhancement and the generation of new surfaces is necessary. It can be pointed out that stress induced surfaces may also develop in the course of other treatments frequently applied to PS such as rapid thermal oxidation or introduction into boiling water to restore quenched luminescence.

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References

[1] A.G. Cullis, L.T. Canham, Nature 353 (1991) 335.
[2] A.G. Cullis, L.T. Canham, P.D. Calcott, J. Appl. Phys. 82 (1997) 909.
[3] T. Suzuki, T. Sakai, L. Zhang, Y. Nishiyama, Appl. Phys. Lett. 215 (1995) 66.
[4] H. Mizuno, H. Koyama, N. Koshida, Appl. Phys. Lett. 69 (1996) 3779.

[5] A.G. Cullis, L.T. Canham, G.M. Williams, P.W. Smith, O.D. Doser, J. Appl. Phys. 75 (1994) 493.
[6] T. Mitsui, N. Yamamoto, K. Takemoto, O. Nittono, Jpn. J. Appl. Phys. 33 (1994) L342.
[7] J. Piqueras, B. Méndez, R. Plugaru, G. Craciun, J.A. García, A. Remón, Appl. Phys. A 68 (1999) 329.
[8] J. Rams, B. Méndez, G. Craciun, R. Plugaru, J. Piqueras, Appl. Phys. Lett. 74 (1999) 1728.