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Citation: Appl. Phys. Lett. **74**, 1728 (1999); doi: 10.1063/1.123669

View online: http://dx.doi.org/10.1063/1.123669

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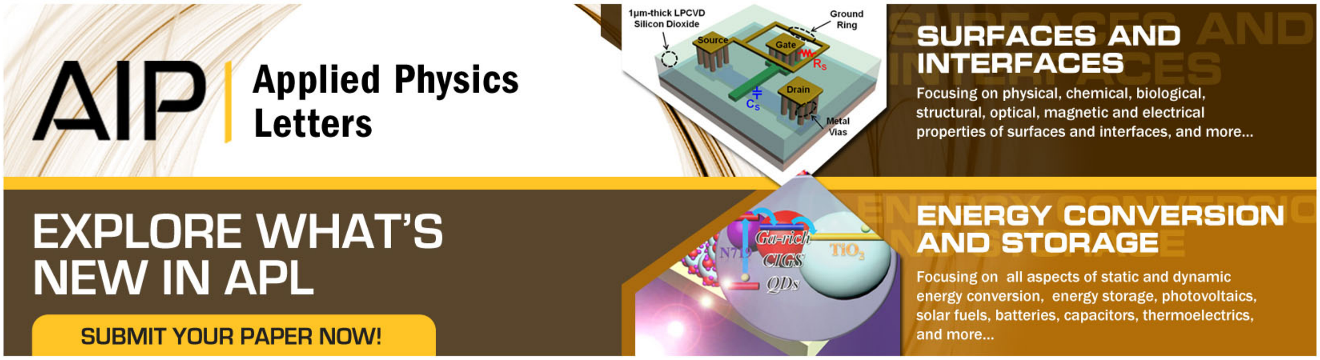

APPLIED PHYSICS LETTERS VOLUME 74, NUMBER 12 22 MARCH 1999

Cathodoluminescence enhancement in porous silicon cracked in vacuum

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(Received 27 October 1998; accepted for publication 26 January 1999)

An increase of the cathodoluminescence (CL) signal of porous silicon (PS) cracked in vacuum of up to three orders of magnitude has been achieved. Under high electron-beam currents, the samples cracked in interconnected pieces of tens of microns, exposing new surfaces to the electron beam. This treatment enhances the radiative intensity in PS associated with a broadband peaked at 720 nm, which is highly stable while the sample is kept in vacuum. Cross-sectional CL observations show that most of the light is generated in the top surface of the porous layer. The spectral depth dependence of the emitted light reveals a relatively weak blue emission in the region closer to the substrate. © *1999 American Institute of Physics.* [S0003-6951(99)02112-9]

The structure and properties of porous silicon have attracted the attention of many researchers since the discovery of its strong photoluminescence (PL).[1] The origin of the porous silicon (PS) luminescence has been extensively investigated and many of the experimental results have been explained in the frame of a quantum confinement model,[2] although the presence of oxides is known to influence the emission properties, e.g., Refs. 3 and 4. In spite of the general knowledge available on the mechanisms of PS luminescence, many questions remain unexplained, partially due to the strong dependence of the properties of the PS on the fabrication procedure and the stabilizing treatments (see Ref. 5 for a recent review on this matter). Most of the experimental work on PS emission has been performed by photoluminescence techniques. On the contrary, cathodoluminescence (CL), which is a well-established technique for characterizing semiconductors,[6] has been less frequently applied to PS. This is partly due to the weak CL signal and its poor stability often found during the electron irradiation of PS. The spectral distribution of the generated light strongly differs for CL and PL signals and, in general, a higher output of the CL signal in the blue spectral region has been described in the literature. Blue-green CL bands in oxidized PS have been attributed in some cases, e.g., Refs. 3 and 7, to the presence of oxides while other authors[8,9] did not observe a relation between blue CL and the oxide layer. Since some of the CL observations, including the lack of stability of the luminescence emission under electron irradiation, seem to be related to surface reactions, the use of clean surfaces of PS could enable the study of crystallite-related CL emission. In this work, PS samples have been cracked by the effect of the electron beam inside the chamber of a scanning electron microscope (SEM) and the CL of the fresh exposed surfaces has been investigated, revealing high radiative efficiency and a stable CL signal.

Porous silicon samples were prepared by anodization of *p*-type (100) silicon wafers with a resistivity of 12 Ω cm. The electrolyte used was a 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 two different SEM, a Hitachi S2500 at temperatures between 77 and 300 K with a beam accelerating voltage of 20 kV, and a Leica Stereoscan 440 at room temperature with voltages from 3 to 20 kV, and probe currents from 1 μA down to 1 nA. The photomultipler used was a Hamamatsu R928 with a spectral range of 185–900 nm, with low sensitivity above 850 nm.

At room temperature the samples showed a weak CL signal that decreased rapidly during the observation in the SEM. The electron-beam degradation of luminescence has been previously reported.[8,10,11] In our case, the signal degradation made impossible the acquisition of any spectra or CL image in any of the samples investigated. By decreasing the sample temperature the CL emission was enhanced, but also the resistivity of the porous layer increased, with the subsequent charging of the sample. Under these conditions, the sample cracks when high probe currents are used. This effect depends on the porosity of the sample, appearing rapidly in samples anodized for longer times while it is difficult to achieve after short anodization times. The resulting appearance of the sample can be observed in the lower part of Fig. 1(a). This structure is similar to the one described in Refs. 10, 12, and 13, and is commonly related to stress. In these cases the crack formation is supposed to arise from the capillary tensions due to the liquid–vapor interfaces that appear during the drying process of the porous material. In our case the only possible sources of stress are thermal or electrical discontinuities, the first being the most probable ones. After the breaking of the surface, the CL intensity increased up to three orders of magnitude as compared with the initial CL signal. The emitted light could be seen by the naked eye even at room temperature. CL images show that the emission arises from the cracked regions of the sample, as observed in

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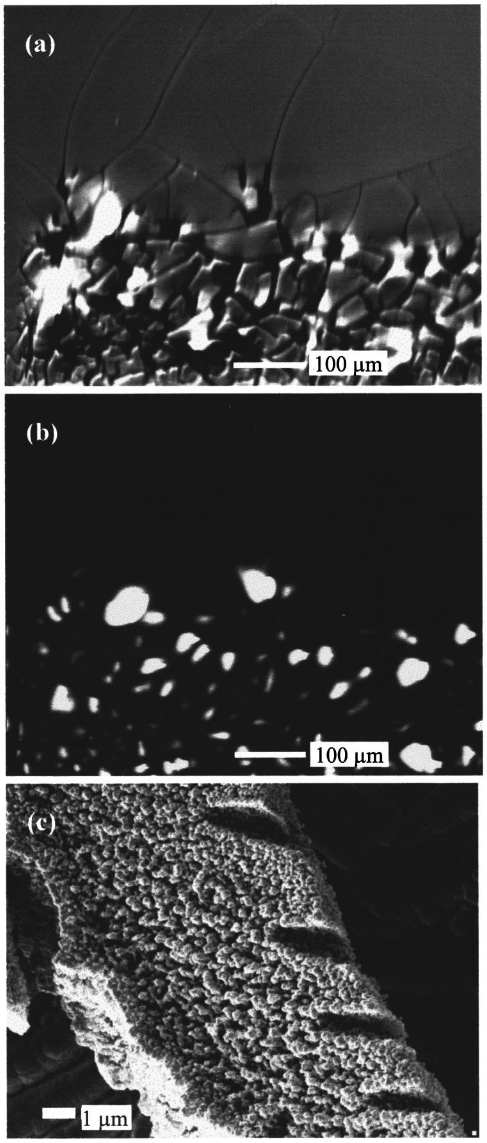

FIG. 1. PS sample with cracked and uncracked parts, in (a) secondary electron mode, (b) CL mode, (c) secondary electron mode of the broken part at higher magnification.

Fig. 1(b). The emission was found to be stable after repeated measurements on different days with the sample stored in the SEM chamber under vacuum.

High magnification secondary electron images of the irradiated area [Fig. 1(c)] show a complex topographic structure in the crack surfaces, with features of tens of nanometer size. Since these structures are not present in the nonirradiated parts of the sample, it appears that electron irradiation produces a high increase of the external surface area.

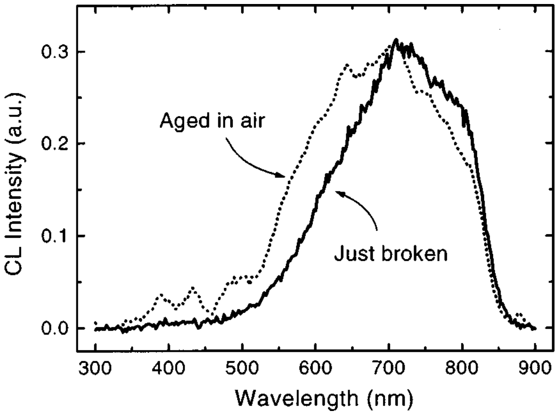

FIG. 2. Cathodoluminescence spectra of the (a) just broken porous silicon and (b) of the same zone after 60 days in air.

Figure 2 shows the CL spectrum recorded from a sample shortly after the appearance of cracks and the normalized spectrum of the same sample after 60 days storage in air. Both spectra were obtained with a 20 kV accelerating voltage and at room temperature. The spectrum of the as-broken sample consists of a broadband in the approximate range of 550–800 nm with its maximum at 720 nm. The emission goes beyond the photomultiplier detection range and extends into the near infrared up to about 1600 nm, as it has been measured with a cooled Ge detector. As stated above, the CL spectra of PS usually show emission in the blue-green spectral range whose origin, silicon nanocrystalline structures or oxides, is a subject of discussion. Cullis *et al.*[7] reported a CL spectrum in rapid thermal oxidized PS with a weak peak at 520 nm and a more intense broadband from 600 nm to about 800 nm (detector cutoff). By comparison with the spectra of oxides, they concluded that only the emission around 750 nm is characteristic of oxidized PS and could be attributed to recombination of quantum-confined carriers in the Si nanostructures. The present results, however, show that the CL emission of fresh exposed surfaces, which is not expected to be greatly influenced by the oxides but due to the presence of nanocrystalline silicon, extends in the 600–800 nm range. The CL spectra appear similar, or comparable, to the PL spectra of PS reported in the literature, e.g., Refs. 2, 14, 15, and 16. The spectrum of the aged sample, in Fig. 2, shows a shift to higher energies, similar to that reported by different authors for the case of PL.[5]

For cross-sectional CL measurements the samples anodized for longer times (30 and 60 min) were used. CL images in the visible range show an inhomogeneous intensity distribution as a function of depth with a higher intensity at the top of the porous layer (Fig. 3). Infrared CL images also showed, in general, an enhanced intensity from the top region. Representative CL spectra from the top and bottom of the porous layer are shown in Fig. 4. Both spectra show clear differences as the presence of a blue-resolved emission and a reduced signal in the bottom of the layer. Spectral variations of PS luminescence along the porous layer cross section have been previously reported. Matsuda *et al.*[17] reported PL observations in which the shorter-wavelength luminescence arises mainly from the near surface, which qualitatively agrees with the present CL results. Mitsui *et al.*[8] studied the CL from PS at different accelerating voltages of the beam to vary the excitation depth and concluded that a band at 420 nm arises from the interface between the porous layer and the unetched silicon. It is to be noticed that the 420 nm band reported in Ref. 12 was observed at 20 K and at beam voltages higher than 160 kV. In our samples the blue luminescence is observed at room temperature and with 20 kV excitation. This appears to be due, with the presence of the very intense 720 nm band, to the specific conditions of formation of fresh surfaces in the samples used in this work. The spectral variations along the cross section are related to structural

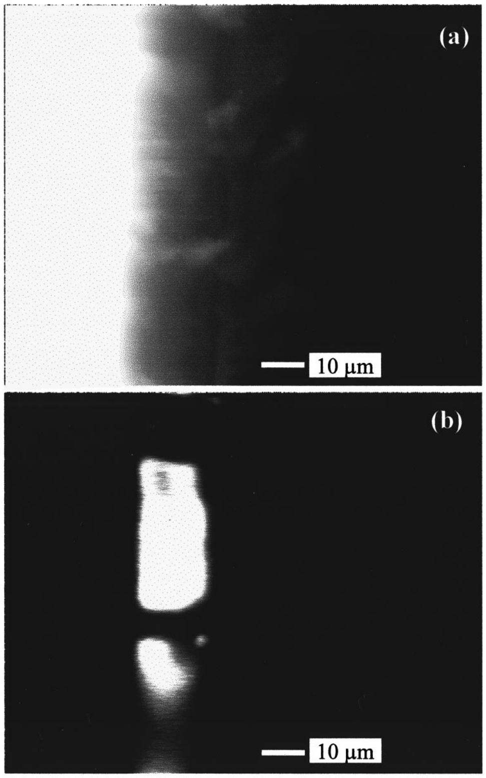

FIG. 3. SEM photograph of the cross section of a PS in (a) the secondary and in (b) the cathodoluminescence mode.

differences produced during the anodization process. The observation of our work and of Ref. 12 of enhanced blue emission at the layer bottom does not necessarily apply to any PS sample and, in fact, in Ref. 17 longer wavelengths were dominant at the bottom. The differences can be explained by considering that the in-depth size distribution of the nanocrystals strongly depends on the treatment, and does not always decrease or increase as a function of depth, as it has been observed in micro-Raman studies.[18]

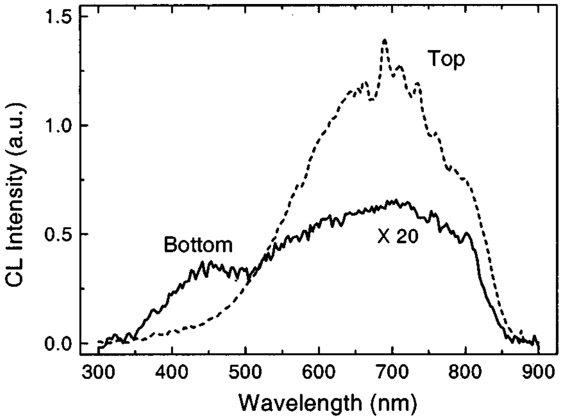

FIG. 4. CL spectra from the top and bottom of a cross section of a PS layer.

The observations presented here show that stress, and in particular, the subsequent cracking, has a marked effect on the optical properties of PS and has to be considered when applying treatment to this material. Stress may take place during rapid thermal oxidation (RTO) or when restoring the luminescence by introducing the PS sample in boiling water. In both cases it does appear to be a topographic structure similar to the one we create with irradiation. However, the effects might differ depending on the treatment, because our samples are transformed under vacuum and, therefore, oxides would not contribute to the observed luminescence.

In summary, the formation of new surfaces of PS under vacuum leads to an intense CL signal in the visible, with a peak at 720 nm, and near-infrared range. The luminescence signal is stable under vacuum even after prolonged electron irradiation and the spectral distribution is comparable to previously reported PL spectra of PS. The origin of the observed CL is attributed to the presence of nanocrystalline silicon. Cross-sectional CL measurements show, in samples cracked in vacuum, a blue luminescence band located preferently in the bottom part of the porous layer, near the undamaged silicon substrate.

This work was supported by the DGES (Project No. PB96-0639) and by the Scientific Cooperation Programme between Spain and Romania.

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