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Abstract
The luminescence of porous InP prepared by electrochemical etching is
investigated by cathodoluminescence (CL) in a scanning electron
microscope (SEM). Anodization causes a strong reduction of CL intensity
as well as a blue spectral shift. Additional blue shift and enhancement of CL
intensity is observed in samples cracked in vacuum by the effect of the SEM
electron beam, which is explained by the reduction of the influence of
surface states on the recombination mechanism. The relationship
of the CL spatial distribution with the multilayer porous structure is
described.

1. Introduction

In addition to the intense activity over the last few years in
the study of the properties and applications of porous silicon,
other porous semiconductors have also been investigated.
In particular, porous III–V semiconductors with different
morphologies have been produced by electrochemical etching
(for a review see [1]), and their optical properties, such as
luminescence, Raman scattering and optical second harmonic
generation, have been investigated. Photoluminescence (PL)
has sometimes been used to study porous III–V materials such
as GaP, GaAs or InP, and the existence of emission at above
band gap energies is explained by quantum size effects in the
nanocrystalline structure [2–7]. Cathodoluminescence (CL)
in the scanning electron microscope (SEM), which enables
spatially resolved luminescence studies, has been used to
correlate morphology and luminescence properties in GaP, InP
[8, 9] and GaSb [10]. It was found in the case of InP that the
CL efficiency decreases with an increase of porosity, which
suggests that energy states at the surface of porous InP could
contribute to non-radiative recombination processes. In the
present work, CL in a SEM is used to investigate the spatial
and spectral distribution of luminescence emission in InP
porous layers with different porous morphologies. It has been
observed that porous layers cracked under the vacuum of the
SEM exhibit higher luminescence intensity than the original
porous samples, which is explained by the reduction of non-
radiative recombination centres at the new surface produced
after the cracking.

2. Experimental details

The wafers used in this work were (100) n-type Si doped InP,
with a donor concentration of about 10^{18} cm^{-3}. The anodic
etching was carried out in an aqueous electrolyte of HCl in
a potentiostatic regime. The anodization was carried out in
an electrochemical double cell using a configuration with four
electrodes: a Pt reference electrode in the electrolyte, a Pt
sense electrode on the sample, a Pt counter electrode and a Pt
working electrode, as described in [11]. The electrodes were
connected to a Gill AC potentiostat, the anodic etching being
performed in the dark. As previously described [9], a change
in the anodic current density or in the applied voltage with time
considerably modifies the degree of porosity. In particular, the
high porosity layers exhibit pores oriented perpendicular to
the initial surfaces [9]. In this way alternating layers with
different degrees of porosity can be easily fabricated. Two
series of samples, labelled A and B, have been produced in this
work. During the anodization process of series A samples, the
applied voltage was switched several times between 4 and 6 V,
and the thicknesses of the obtained porous layers (starting from
the top layer) were approximately 14, 15, 14, 20 and 14 μm,
respectively. The samples of series B were fabricated at a
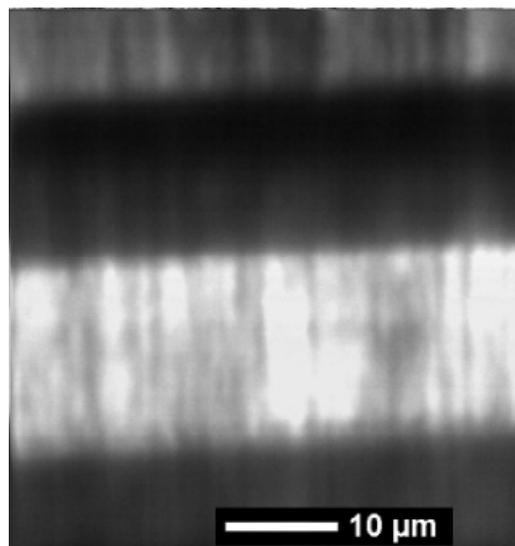voltage of 5 V, accompanied by periodically applied short
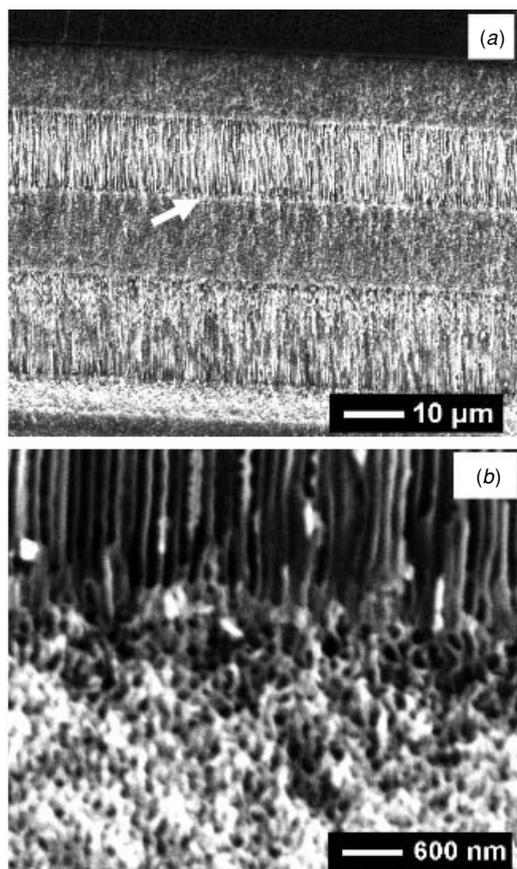
Figure 1. SEM images of the series A porous layers fabricated by switching the applied voltage several times between 4 and 6 V: (*a*) distribution of the layers and (*b*) details showing two kinds of pores in the area marked with an arrow in (*a*). The substrate is the dark area in the upper part of the image.

Figure 2. Panchromatic CL image of layers of a series A sample recorded at 77 K with the R-928 photomultiplier.
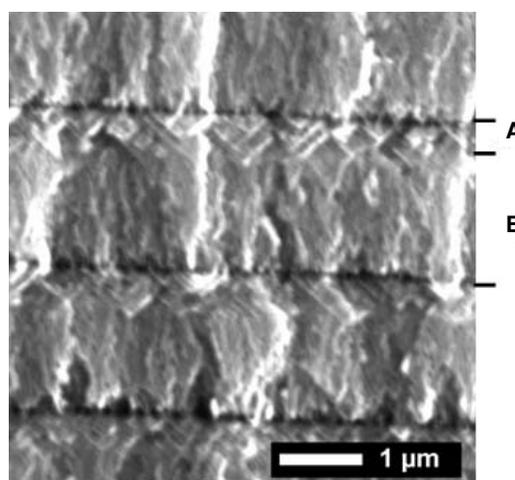
Figure 3. SEM image of the series B porous layers fabricated at 5 V followed by short pulses of 19 V. A layer with pores oriented along crystallographic directions is labelled A and a layer with random oriented pores is labelled B.

pulses of voltage as high as 19 V with a duration of 200 ms. At 5 V crystallographically oriented pores are formed, while at 19 V current-line oriented pores are formed. Current-line oriented pores grow perpendicularly to the initial surface. Random pores are usually related to crystallographically oriented pores or to transition regions from one kind of pore to another [12].

CL measurements were performed in a Hitachi S-2500 and a Leica 440 SEM at liquid nitrogen temperature with an accelerating voltage of 15 kV, using a Hamamatsu R-928 photomultiplier for detection in the visible range and in the near-infrared range up to about 850 nm (1.46 eV), and a ADC germanium detector for the infrared range of 800–1800 nm (1.55 eV–0.68 eV). For spectral measurements an Oriel 74100 monochromator was used.

3. Results and discussion

Figure 1(*a*) shows the secondary electron (SE) image of the A sample in cross-section showing two kinds of porous layers produced by the change of anodic current density. In the high porosity layers, the pores are oriented perpendicular to the wafer surface while in the low porosity layers the pores have a more random orientation, as shown at higher magnification in figure 1(*b*). As previously reported [9], anodization causes

a strong reduction of the CL intensity of InP, which is more marked in high porosity layers. This is observed in the CL image of figure 2 which shows higher CL intensity in the layer with lower porosity. In the samples of series B the structure of the layer is inhomogeneous with a fringe of the layer composed by pores oriented along crystallographic directions [111] (figure 3) as a result of switching during the anodization process as described in [9], while the rest of the layer is formed by less oriented pores. CL images recorded with the R-928 photomultiplier (figure 4(*a*)) show dark fringes in the interface of the different porous layers. The images recorded with the germanium detector show that besides the dark layer interfaces, a bright layer appears which is related to the crystallographically oriented pores (figure 4(*b*)). This is shown in the CL images of figure 4 and reveals that radiative centres, in particular centres with infrared radiative transitions at energies below 1.46 eV, accumulate in the crystallographically oriented pores.
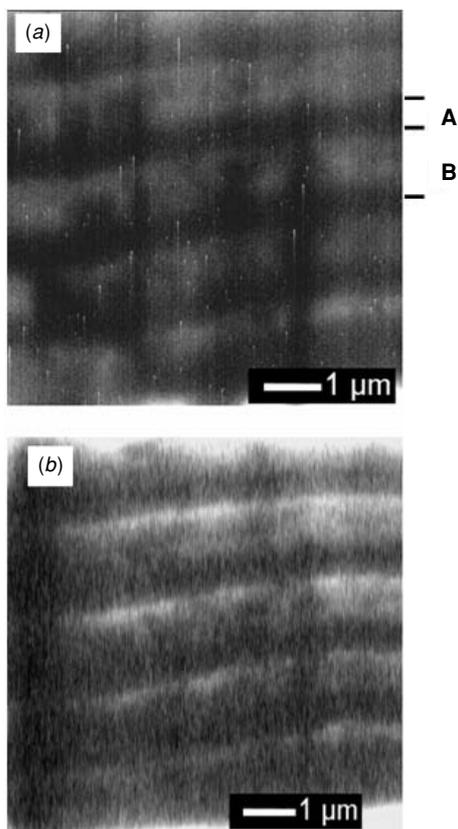
Figure 4. CL images of the sample with the pore structure shown in figure 3, recorded with (*a*) a photomultiplier and (*b*) a germanium detector. The dark and bright fringe in (*a*) labelled A and B, correspond approximately to the layers with pores oriented along crystallographic directions and random oriented pores, respectively.
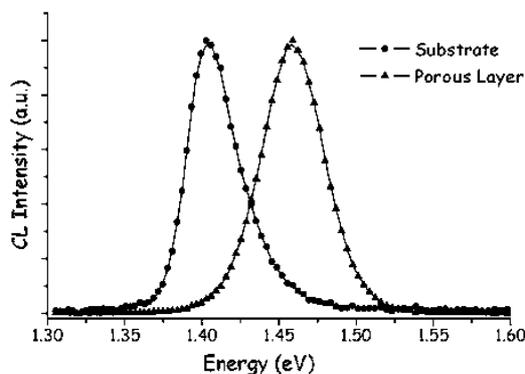
Figure 5. Comparison of the CL spectra recorded in the InP substrate and in a porous layer of a sample of series A. Spectra are recorded at 77 K and 20 kV.

CL spectra recorded in the porous layers show a band peaked at about 1.46 eV, while the emission band of the bulk wafer peaks at 1.40 eV. No spectral differences were observed between high and low porosity layers. Figure 5 shows the normalized CL spectra of the substrate and of the porous layers. According to the spectra, the observations of figure 4 show that the crystallographic oriented pores have an enhanced emission in the low energy side of the band peaked at 1.46 eV. The spectra of the porous layers correspond to the upper surface of the porous sample. Due to the low luminescence intensity
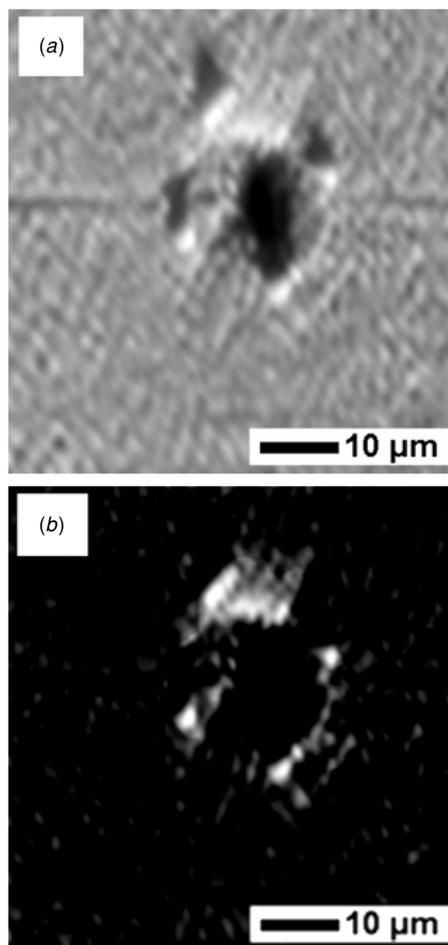

Figure 6. (*a*) SEM image of an area of the porous sample after electron irradiation induced cracking and (*b*) a CL image of the same area.

in the interior of the porous sample, no local CL spectra could be recorded in the cross-sectional region shown in figure 4.

A blue shift of the PL band of porous InP relative to that of bulk material has been previously reported by different authors. Liu and Duan [7, 13] and Fujikura *et al* [14] reported blue shifts of about 14 meV to 24 meV at temperatures above 150 K, due to quantum confinement, and a red shift of 30 meV at low temperatures, attributed to radiative recombination via the surface states. The blue shift of 50–60 meV observed in the present work also shows the existence of quantum confinement. The difference relative to the shift reported in the mentioned works would be due to the different anodization conditions and samples investigated, and also to the fact that PL and CL spectra of semiconductors often show differences due to the different excitation conditions.

Observation of porous layers in the SEM can cause cracking of the columnar structure in some samples. This effect has been previously reported in the case of porous silicon [15] and is favoured at low temperatures and high beam currents. Under these conditions the resistivity of the porous layer increases and stresses arise, most probably related to thermal discontinuities. When the porous sample cracks under the vacuum of the SEM, fresh surfaces are exposed for luminescence measurements. It was found in [15] that the
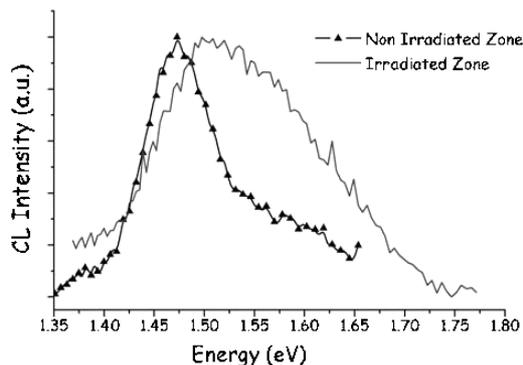
Figure 7. Comparison of CL spectra of a porous sample and of an area of the same sample containing electron irradiation induced cracks.

new surfaces present enhanced CL intensity emission and a blue spectral shift, which was interpreted as a reduction of the influence of surface states. A similar effect, which we suggest is explained in the same way, has been observed in this work. Figure 6(*a*) shows the SEM image of an area of sample A after local cracking induced during irradiation, and figure 6(*b*) shows the corresponding CL image, with enhanced emission in the cracked areas. The spectra of the high luminescent areas show a blue shift relative to the original porous layers, with a maximum at about 1.52 eV (figure 7).

4. Conclusions

In summary, InP porous layers present a reduced CL intensity and a spectral blue shift of about 60 meV relative to the bulk material, which is attributed to quantum confinement. The formation of fresh surfaces of porous InP under the vacuum of the SEM leads to a marked increase of the CL intensity and an additional blue shift of the emission, which is related to a reduced influence of surface states in the luminescence process. The degree of porosity influences the CL intensity

and spectra. Pores oriented along crystallographic directions show an enhanced infrared emission at energies below 1.46 eV, greater than for other less oriented pores with the same layer.

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