Comparative SEM and Cathodoluminescence Microanalysis of Porous GaP Structures

M.A. Stevens-Kalceff,[1] S. Langa,[2] I.M. Tiginyanu,[2] J. Carstensen,[3] M. Christophersen,[3] and H. Föll[3]
[1]Department of Applied Physics, University of Technology, Sydney, Australia
[2]Laboratory of Low-Dimensional Semiconductor Structures, Technical University of Moldova, Chisinau, Moldova
[3]Materials Science Department, Christian-Albrechts University, Kiel, Germany

ABSTRACT

Electron microscopy and cathodoluminescence (CL) microanalysis were used for a comparative study of porous layers fabricated by electrochemical etching of n-GaP substrates in a sulfuric acid solution. Both the CL and morphology of porous layers were found to depend upon the anodic current density. At high current density (100 mA/cm^2) anodization leads to the formation of so-called current-line oriented pores and an increase in the CL intensity. We observed self-induced voltage oscillations giving rise to a synchronous modulation of the diameter of pores and CL intensity. When the current density decreased to values as low as 1 mA/cm^2 the pores began to grow along <111> crystallographic directions and the CL intensity was observed to be lower than that of bulk GaP.

INTRODUCTION

Porosity is an effective tool for engineering basic parameters of semiconductor materials [1]. Compared with porous Si, III-V materials have a number of important advantages related to the possibility of changing the chemical composition and further extending the fields of applications of porous structures using properties specific to acentricity. In particular, porous III-V compounds were found to exhibit Fröhlich-type surface-related vibrations with porosity-tunable frequencies and efficient optical second harmonic generation [2-5]. The enhanced nonlinear optical response and intense luminescence reported for porous III-V compounds may enable the development of a fully integrated light source and frequency converter sub-system.

So far, most experiments investigating emission characteristics of porous III-V materials have been restricted to photoluminescence (PL). The PL of porous GaP, GaAs and InP at energies above the band gap of the bulk material has been attributed to quantum size effects [6-10]. Furthermore, a porosity-induced intensification of the near-band-edge emission was observed in gallium phosphide [11]. However, no correlation between luminescence properties and morphology features of porous III-V material has been reported yet.

In this work, we study the morphology and CL characteristics of porous layers obtained by electrochemical dissolution of n-GaP substrates. We report, for the first time, drastic modification in both morphology and CL intensity of porous gallium phosphide layers with changing anodization conditions. Self-induced voltage oscillations were observed during anodic etching at high current density and their impact on pore morphology and CL intensity was evidenced. The results of the CL microanalysis indicate the possibility of controlling the spatial distribution of emission in porous GaP.

EXPERIMENTAL

(100)-oriented n-GaP wafers cut from Czochralsky-grown S-doped ingots were used in this work. The free electron concentration in the as-grown substrates was 5 x 10^{17} cm^{-3} at 300 K. The anodization was carried out in a double-room electrochemical cell. A four electrode configuration was used: a Pt reference electrode in the electrolyte, a Pt reference electrode on the sample, a Pt counter electrode and a Pt working electrode. The electrodes were connected to a Keithley 236 Source Measure Unit.

The anodic etching was carried out in 0.5 M H_2SO_4 aqueous electrolyte in galvanostatical regime. The electrolyte was pumped in a continuous mode through both rooms of the electrochemical cell with the help of a peristaltic pump. The temperature was kept constant at T = 23 ^{o}C with the help of Julabo F25 thermostat. The area of the sample exposed to the electrolyte was 0.12 cm^2.

The CL experiments were performed in a Scanning Electron Microscope (SEM) equipped with *Oxford Instruments* MonoCL2 cathodoluminescence imaging and spectral analysis system, and cryogenic specimen stages. CL and SEM images were taken from the same sample areas for comparison. The CL was excited with a continuous electron beam at normal incidence, and measured using a retractable parabolic mirror collector. CL spectra were collected over the wavelength range 250-900 nm using a *Hamamatsu* R943-02 high sensitivity photomultiplier with a 1200 line/mm grating, blazed at 550 nm. The CL spectra were collected over a range of beam energies (E_b = 15-30 keV) and beam currents (I_b = 0.25-100 nA) and typically from ~7000 μm^2 regions to reduce electron beam induced effects. The spectra were converted from wavelength to energy space, and corrected for total instrument response.

RESULTS AND DISCUSSION

Fig. 1 (a and c) shows SEM and panchromatic CL images in cross-section taken from a sample subjected to successive anodization steps at the current densities: j_1 = 100 mA/cm^2 for 30 min and j_2 = 1 mA/cm^2 for 240 min. Electrochemical etching at high anodic current density leads to the formation of the so-called current-line oriented pores which are quasi-uniformly distributed and grow inside the sample at nearly the same rate (Fig. 1a). A thorough analysis of the SEM image showed that the top porous layer exhibits weak horizontal trajectories related to the modulation of the diameters of the pores. Some of these trajectories (marked by arrows) are clearly seen in the enlarged portion presented in Fig. 1b. Somewhat surprisingly, the panchromatic CL image of the top porous layer shows similar horizontal lines (Fig. 1c) indicating a correlation between cathodoluminescence and morphology in porous GaP.

Fig. 1d illustrates the time dependence of the voltage applied to the sample during anodization. The applied voltage oscillates under the galvanostatic etching conditions employed. Although it is difficult to find a direct relation between peaks seen on the voltage/time diagram and horizontal trajectories in the SEM image, we believe that the self-induced voltage oscillations are responsible for the synchronous modulation of the pore diameters. Note that we observed a similar phenomenon when anodizing n-InP under galvanostatic anodic etching conditions.

The magnification used in Fig. 1a does not permit observation of the morphology of the second porous layer, produced at the current density of 1 mA/cm^2. At higher magnifications, however, the pores are oriented along specific crystallographic directions, in this case along

<111> directions (Fig. 2). As expected, in this case the rate of dissolution and the degree of porosity are relatively low. Note that preferential orientation of pores along <111> crystallographic directions was recently observed in (100)-oriented n-InP crystals when anodized at low current densities [12].

A subject of particular interest is the quite different impact of porosity upon CL efficiency at high and low anodic current densities. Anodization at high current densities (e.g. 100 mA/cm^2) sharply enhances the CL intensity, while etching at current densities as low as 1 mA/cm^2 quenches the luminescence. This is seen in Fig. 1c, and more clearly in Fig. 3, where the CL spectra of bulk GaP and porous layers produced at high and low current densities are illustrated. Although all the spectra are dominated by a band with the maximum at approximately 1.5 eV, they give further evidence that the top porous layer exhibits the most intense luminescence. The second layer produced at the current density 1 mA/cm^{2}is less luminescent than either the top porous layer or bulk GaP.

It is important to note that the situation changes drastically when the anodization current in the second layer is increased several times. In this case, the higher the degree of porosity the higher the intensity of luminescence (Fig. 4). This correspondence was also observed when measuring CL spectra.

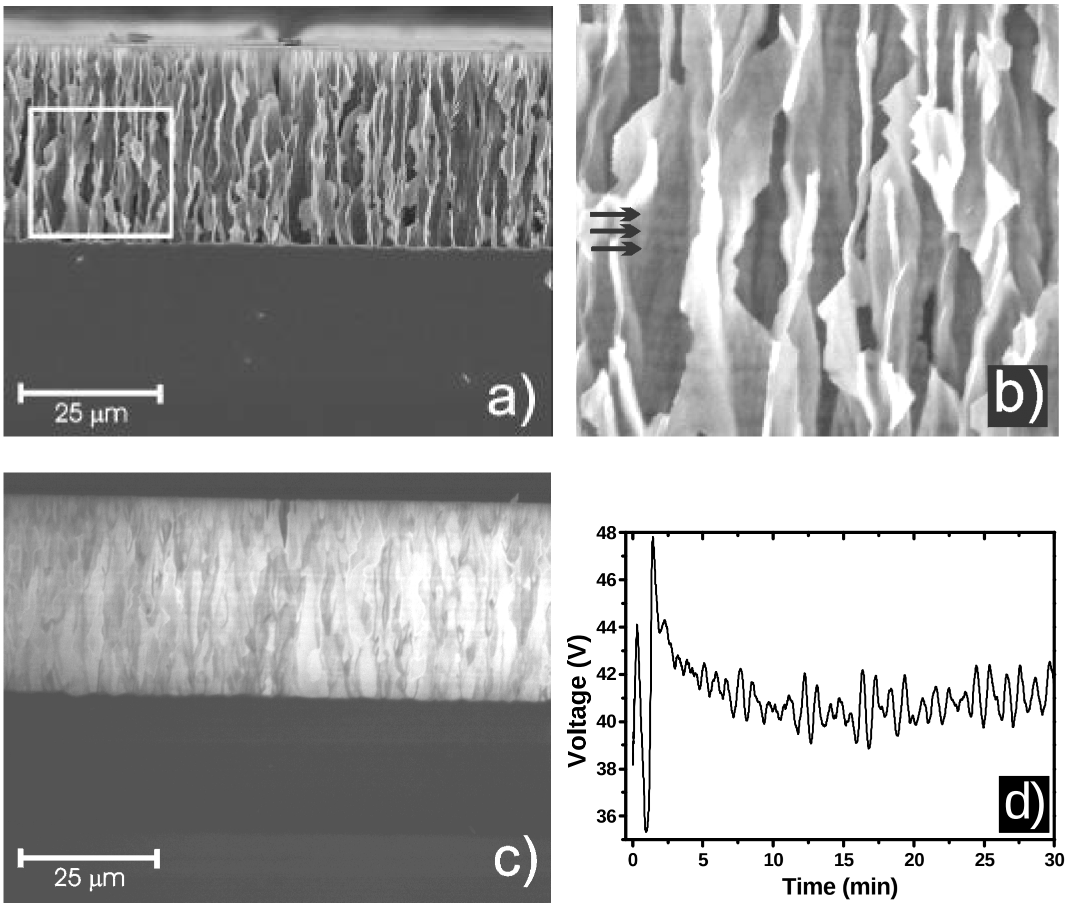

Figure 1. *(a, b) SEM and (c) panchromatic CL images in cross-section taken from a sample anodized galvanostatically at two current densities:* j_1 *= 100 mA/cm*^{2} *for 30 min and* j_2 *= 1 mA/cm*^{2} *for 240 min; (d) time dependence of the self-induced voltage oscillations.*

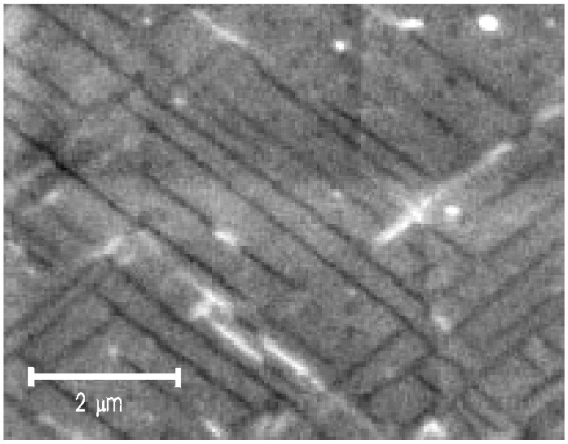

Figure 2. *SEM image in cross section taken from the porous layer produced at current density* $j_2 = 1$ *mA/cm*^{2} *for 240 min (see Fig. 1).*

Taking into the account the effect of H-passivation of pore walls in Si [13], the {112} planes in III-V compounds are exxpected to be the most stable against dissolution, i.e. most easily passivated set of planes enveloping <111> directions. We suggest that the crystallographically oriented pores obtained at the current density 1 mA/cm^2 expose {112} planes which are efficiently passivated in the electrolyte. On the other hand, under ambient conditions these planes seem to be characterized by poor passivation (or, in other words, the dangling bonds are not saturated). As a result, the non-radiative recombination of the free carriers via surface states becomes sufficiently strong to compete with the radiative recombination processes. This qualitatively explains the decrease in the luminescence intensity caused by anodic etching at the current density 1 mA/cm^2 (Fig. 3, curve 3).

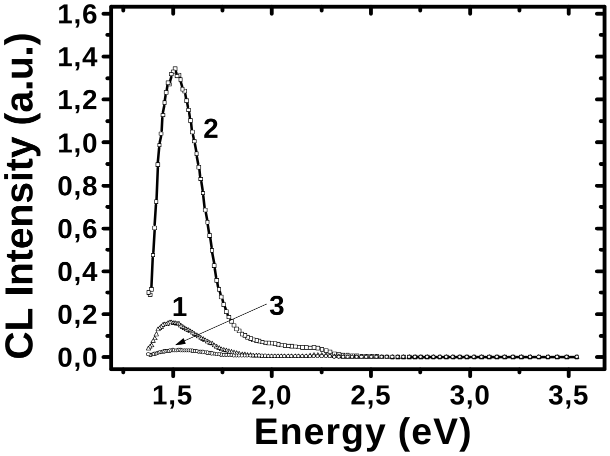

Figure 3. *CL spectra of bulk GaP (curve 1) and porous layers produced at current densities* $j_1 = 100$ *mA/cm*^{2} *(curve 2) and* $j_2 = 1$ *mA/cm*^{2} *(curve 3). The beam energy is 25 keV, beam current is 50 nA.*

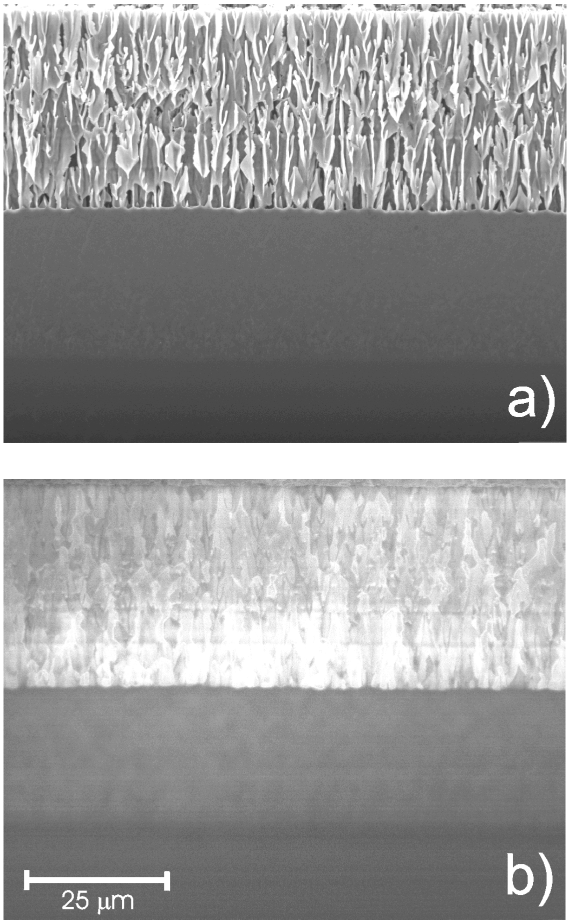

Figure 4. *(a) SEM and (b) panchromatic CL images in cross-section taken from a sample anodized galvanostatically at two current densities:* $j_1 = 100$ *mA/cm*^{2} *for 30 min and* $j_2 = 4$ *mA/cm*^{2} *for 240 min.*

In contrast, the pore walls at high anodic current densities exhibit weak passivation in the solution and efficient passivation under ambient conditions. The saturation of the dangling bonds, however, does not explain the relatively strong increase in the luminescence intensity induced by porosity. Note that electrochemical dissolution of n-type semiconductor materials is known to preferentially remove the dislocations and other lattice imperfections which may play the role of non-radiative recombination centers. Reduction in the density of non-radiative recombination centers accompanied by in-situ surface passivation may qualitatively explain the observed increase in CL intensity induced by porosity. In addition, in the porous form, GaP, being and indirect gap semiconductor, exhibits surface related vibrations [2] which can participate in the process of free-carrier radiative recombination and, consequently, increase its probability considerably.

CONCLUSIONS

Electrochemical etching of (100)-oriented n-GaP wafers in H_2SO_4-based solution at high current densities leads to the orientation of pores along the current lines. When the current density is switched down to 1 mA/cm^2, the pores start to grow along <111> crystallographic directions. The orientation of pores along definite crystallographic directions reflects the anisotropy of etching at low current density.

The impact of porosity upon the CL efficiency was found to depend on the anodic current density. Anodization at current densities as low as 1 mA/cm^2 quenches the luminescence. Porosity introduced at high current densities intensifies the CL, in spite of the huge surface inherent to anodized samples. We observed for the first time self-induced voltage oscillations during pore etching in n-GaP. The oscillations lead to a synchronous modulation of both the diameter of pores and CL intensity. The self-induced oscillations may be useful for three-dimensional microstructuring of n-GaP and therefore deserve further investigations.

ACKNOWLEDGMENT

M.A.S-K. gratefully acknowledges the support from the Australian Research Council, and technical support from UTS staff.

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