

Porosity-induced gain of luminescence in CdSe

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2004 Semicond. Sci. Technol. 19 L121

(<http://iopscience.iop.org/0268-1242/19/12/L04>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 147.96.14.16

This content was downloaded on 10/10/2013 at 16:11

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Porosity-induced gain of luminescence in CdSe

E Monaico¹, V V Ursaki^{1,2}, A Urbietia³, P Fernández³,
J Piqueras³, R W Boyd⁴ and I M Tiginyanu^{1,2}

¹ National Center for Materials Study and Testing, Technical University of Moldova,
MD-2004 Chisinau, Moldova

² Laboratory of Low-Dimensional Semiconductor Structures, Institute of Applied Physics,
Academy of Sciences of Moldova, MD-2028 Chisinau, Moldova

³ Departamento de Física de Materiales, Facultad de Ciencias Físicas,
Universidad Complutense de Madrid, 28040 Madrid, Spain

⁴ Institute of Optics, University of Rochester, Rochester, NY 14627, USA

Received 26 August 2004, in final form 27 September 2004

Published 3 November 2004

Online at stacks.iop.org/SST/19/L121

doi:10.1088/0268-1242/19/12/L04

Abstract

Porous CdSe layers have been produced by anodic etching of crystalline substrates in a HCl solution. Anodization under *in situ* UV illumination resulted in the formation of uniformly distributed parallel pores with a diameter of 30 nm, stretching perpendicularly to the initial surface. At the same time, pronounced nonuniformities in the spatial distribution of pores were evidenced in samples subjected to anodic etching in the dark. Gain of luminescence was observed in some porous regions and attributed to the formation of ring microcavities for light in the porous network.

More than a decade ago porosity emerged as an effective tool for controlling properties of semiconductor materials. Besides porous Si, III–V semiconductors in the porous form were extensively studied [1]. Porosity-enhanced phenomena such as optical second harmonic generation and Terahertz emission have been reported [2–4]. One of the most intriguing observations is the porosity-induced increase of cathodoluminescence (CL) intensity in GaP [5]. In spite of the huge surface inherent to porous matrix, gallium phosphide in the porous form shows CL intensity one order of magnitude higher than that of bulk crystals under the same excitation conditions [5]. On the other hand, relatively little attention has previously been paid to the study of porosity-induced changes in the properties of II–VI compounds. The effect of photoetching on photoluminescence (PL) of n-CdSe was studied many years ago [6], but the authors claimed the formation of etch pits rather than pores. Formation of porous network which extends more than 100 μm below the initial surface was recently reported in p-Cd_{1-x}Zn_xTe by Ern  et al [7, 8]. Besides, Zenia et al subjected p-ZnTe crystals to electrochemical etching and observed the formation of needle-like structures exhibiting a blueshift of the excitonic

transition energies [9]. In this work, results on electrochemical pore etching in n-CdSe single crystals are presented. The luminescence of the samples was studied by CL in the scanning electron microscope (SEM) and by PL techniques. We show that optically homogeneous porous layers exhibit less luminescence intensity than bulk CdSe. At the same time considerable gain of luminescence was evidenced in some optically inhomogeneous areas of porous structures.

Wurtzite-phase n-CdSe single crystals were grown by chemical transport techniques using iodine as transport agent. Electrochemical etching was carried out in aqueous solution of HCl at room temperature under potentiostatic conditions as described elsewhere [10]. To reach uniform nucleation of pores, the samples were *in situ* illuminated by focusing the radiation of a 200 W Xe lamp on the CdSe surface (0.15 cm²) exposed to electrolyte. The morphology and chemical composition microanalysis of etched samples were studied using a TESCAN scanning electron microscope (SEM) equipped with an Oxford Instruments INCA Energy EDX system. PL was excited by the 514 nm line of an Ar⁺ SpectraPhysics laser and analysed through a double spectrometer. The resolution was better than 0.5 meV. The

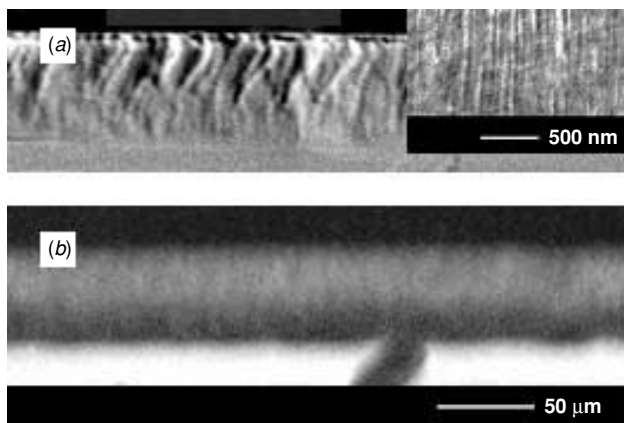


Figure 1. SEM (a) and CL (b) images taken in cross-section from a porous CdSe sample fabricated under *in situ* UV illumination. The inset shows the morphology of the porous layer near the interface with the substrate.

samples were mounted on the cold station of a LTS-22-C-330 cryogenic system. Cross-sectional CL images of the anodized samples were recorded in a Hitachi S2500 SEM at 90 K with an accelerating voltage of 20 kV, by using a Hamamatsu R928 photomultiplier.

Figure 1 illustrates SEM and panchromatic CL images taken in cross-section from a CdSe sample anodized under *in situ* illumination. The porous layer exhibits parallel pores with diameters of about 30 nm, the thickness of the walls being of the same order of magnitude (see inset in figure 1(a)). Since the dimensions of the entities of porous structure are much less than the wavelength of the electromagnetic radiation in the visible region of the spectrum, such porous layers are optically homogeneous. The composition of the porous skeleton corresponds to the stoichiometric one with the exception of a thin (about 3 μm) nucleation layer that actually shows no luminescence at all. The CL image clearly shows a porosity-induced decrease of the emission efficiency of CdSe, the level of the decrease being dependent upon the deepness of the porous region. As one can see from figure 1(b), the deeper the porous area, the lower the CL intensity. In this connection one may assume that the level of passivation of the internal surface of deep porous regions is lower than that inherent to shallow areas.

Figure 2 shows SEM and panchromatic CL images taken in cross-section from a CdSe sample anodized in the dark. The spatial distribution of the CL intensity along the porous layer proves to be highly nonuniform. Moreover, one can easily distinguish some porous areas exhibiting much more luminescence than the bulk CdSe. According to EDX microanalysis, the composition of the porous skeleton corresponds to that of CdSe in all areas.

The nonuniform distribution of CL intensity may be related to geometric effects. Indeed, due to nonuniform nucleation of pores at the initial surface, a porous domain forms around each etching pit. The pores grow in all possible directions radially away from the initial surface imperfection (figure 3). When neighbouring domains meet, the pores near the border separating the domains change their direction of growth and no pore intersection occurs. Due to space

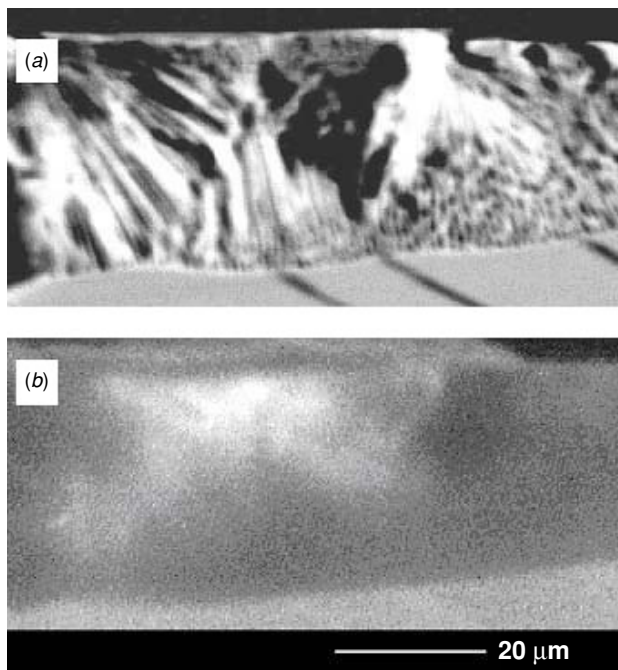


Figure 2. SEM (a) and CL (b) images taken in cross-section from a CdSe sample anodized in the dark.

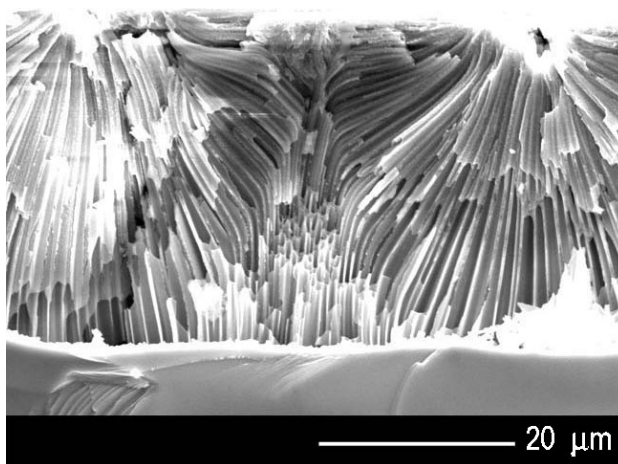


Figure 3. Development of porous structure in n-CdSe under anodization in the dark.

confinement, the density of pores in the emerging triangular-like regions between neighbouring domains prove to be higher than the density of pores outside the areas involved. Taking into account the transverse dimensions of pores and walls, one may expect the occurrence of especially strong scattering of light in such regions. As a result, closed loop paths can be formed through multiple light scattering. Actually, the architecture of the porous network may generate a huge amount of closed loop paths. Playing the role of ring microcavities for light, the loops involved may lead to the occurrence of lasing effect. Note that such an effect, called random laser action, was earlier observed in ZnO and GaN powders [11]. Besides, enhancement of photoluminescence was recently reported in CdSe pillars fabricated by the combination of electron beam lithography and electrochemical deposition [12].

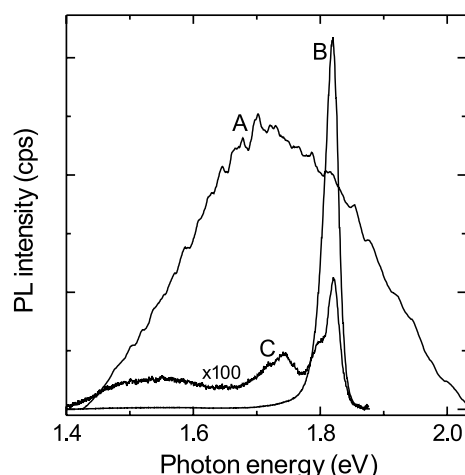


Figure 4. PL spectra of porous CdSe regions exhibiting strong scattering of light (curve A), bulk CdSe (curve B) and porous CdSe fabricated under *in situ* illumination (curve C). Excitation power density (W cm^{-2}): curve A, 10^3 ; curves B and C, 3×10^2 .

The PL spectrum of porous CdSe regions exhibiting strong scattering of light is illustrated in figure 4 (curve A). A threshold behaviour was observed, namely the PL was totally quenched at excitation power densities lower than 300 W cm^{-2} . Above 300 W cm^{-2} , the integrated emission intensity sharply increased with the excitation power density (J_{ex}), in accordance with the relation $I_{\text{PL}} \sim (J_{\text{ex}})^5$. It means that an increase of the excitation power density by a factor of 10 leads to an increase of the luminescence intensity by 5 orders of magnitude. We attribute this fascinating effect to the amplification of the emission in ring microcavities inherent to porous CdSe areas characterized by strong light scattering. The broadness of the spectral emission illustrated in figure 4 may be attributed to statistical size distribution of ring microcavities occurring in the porous network. For the purpose of comparison, figure 4 also shows PL spectra of as-grown (curve B) and porous CdSe fabricated under *in situ* illumination (curve C). The PL peak at 1.819 eV and the shoulder at 1.797 eV seem to be related to the radiative recombination of bound excitons, while the PL band at 1.74 eV corresponds to free carrier recombination via donor–acceptor pairs [13].

In conclusion, porous layers with transverse dimensions of pores and walls as low as 30 nm have been fabricated on

CdSe using photoelectrochemical etching techniques. Such porous layers show less luminescence intensity than bulk samples. Anodization of CdSe in the dark leads to the formation of porous layers exhibiting pronounced fluctuations in the spatial distribution of the density of pores. Gain of luminescence was observed in porous regions characterized by strong light scattering. The obtained results pave the way to the design and fabrication of random lasers based on semiconductor materials.

Acknowledgments

This work was supported by US Civilian Research and Development Foundation under grant nos ME2-2527 and MR2-995, MCYT under grant no MAT2003-00455 and Supreme Council for Research and Technological Development of Moldova under grant no 4-031P.

References

- [1] Föll H, Langa S, Carstensen J, Christophersen M and Tiginyanu I M 2003 *Adv. Mater.* **15** 183
- [2] Tiginyanu I M, Kravetsky I V, Monecke J, Cordts W, Marowsky G and Hartnagel H L 2000 *Appl. Phys. Lett.* **77** 2415
- [3] Tiginyanu I M, Kravetsky I V, Langa S, Marowsky G, Monecke J and Föll H 2003 *Phys. Status Solidi a* **197** 549
- [4] Reid M, Cravetschi I V, Fedosejevs R, Tiginyanu I M and Sirbu L 2004 *Appl. Phys. Lett.*
- [5] Stevens-Kalceff M A, Tiginyanu I M, Langa S, Föll H and Hartnagel H L 2001 *J. Appl. Phys.* **89** 2560
- [6] Garuthara R, Tomkiewicz M and Tenne R 1985 *Phys. Rev. B* **31** 7844
- [7] Ern  B H, Million A, Vigneron J, Mathieu C, Debiemme-Chouvy C and Etcheberry A 1999 *Electrochem. Solid-State Lett.* **2** 619
- [8] Ern  B H, Mathieu C, Vigneron J, Million A and Etcheberry A 2000 *J. Electrochem. Soc.* **147** 3759
- [9] Zenia F, Levy-Clement C, Triboulet R, K nenkamp R, Ernst K, Saad M and Lux-Steiner M C 1999 *Appl. Phys. Lett.* **75** 531
- [10] Langa S, Tiginyanu I M, Carstensen J, Christophersen M and F ll H 2003 *Appl. Phys. Lett.* **82** 278
- [11] Cao H, Zhao Y G, Ho S T, Seelig E W, Wang Q H and Chang R P H 1999 *Phys. Rev. Lett.* **82** 2278
- [12] Chen Y L, Chen C C, Jeng J C and Chen Y F 2004 *Appl. Phys. Lett.* **85** 1259
- [13] J ger-Waldau R, St cheli N, Braun M, Lux Steiner M, Bucher E, Tenne R, Flaisher H, Kerfin W, Braun R and Koschel W 1988 *J. Appl. Phys.* **64** 2601