Porosity-induced gain of luminescence in CdSe

LETTER TO THE EDITOR

Porosity-induced gain of luminescence in CdSe

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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$_x$Te by Erné
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 cm^2) 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
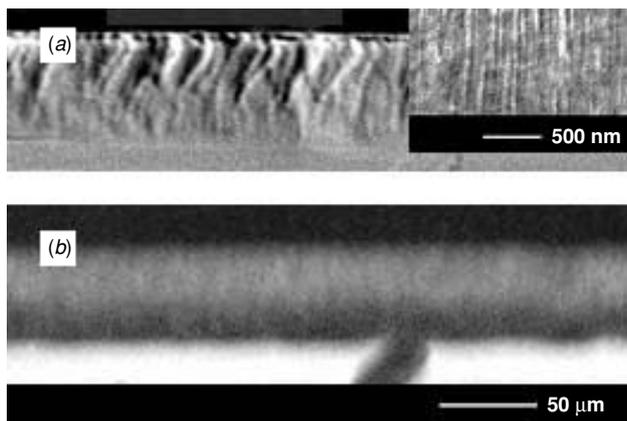spectrometer. The resolution was better than 0.5 meV. The

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
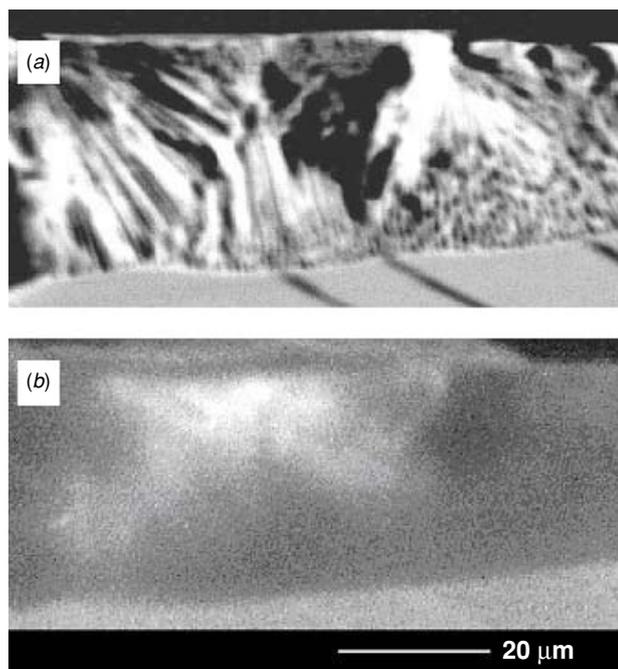

Figure 2. SEM (*a*) and CL (*b*) images taken in cross-section from a CdSe sample anodized in the dark.
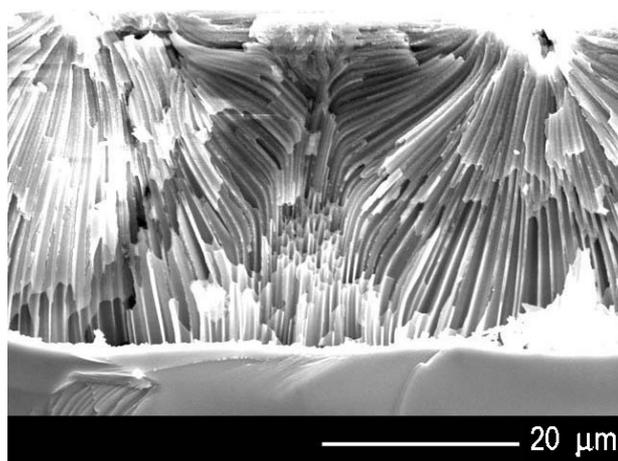

Figure 3. Development of porous structure in n-CdSe under anodization in the dark.

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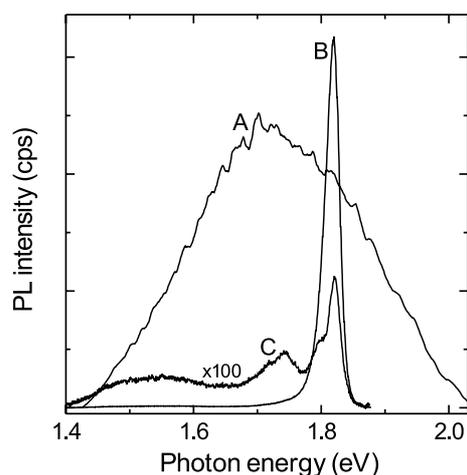
Figure 4. PL spectra of porous CdSe regions exhibiting strong scattering of light (curve A), bulk CdSe (curve B) and porous CdSe fabricated under *in situ* illumination (curve C). Excitation power density (W cm^{-2}): curve A, 10^3; curves B and C, 3×10^2.

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 $I_{PL} \sim (J_{ex})^5$. 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.

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