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We report the results of a study of the growth of pores in *n*-CdSe single crystals using anodic etching techniques. Upon anodization in dark, a nonuniform distribution of pores was produced. However, anodic dissolution of the material under *in situ* UV illumination proves to result in uniform distribution of pores stretching perpendicularly to the initial surface of the specimen. The porous structures exhibit less luminescence than the bulk samples. These results pave the way for cost-effective manufacturing of CdSe-based semiconductor nanotemplates for nanofabrication. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1864240]

Over the past several years, artificially introduced porosity has been shown to result in spectacular modification of the optoelectronic properties of III-V semiconductor compounds. In particular, dramatic surface effects, efficient optical phonon engineering, induced birefringence, and strongly enhanced nonlinear optical phenomena such as optical second-harmonic generation and terahertz emission have been demonstrated.[1–5] Recently, nonlithographic growth of two-dimensional single crystals of pores with diameters of 100 nm was realized on *n*-InP.[6] On the other hand, little attention has been paid to the study of porosity-induced changes in the properties of II-VI compounds. In particular, 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.[7] The effect of photoetching on photoluminescence (PL) of *n*-CdSe was studied many years ago by Garuthara *et al.*, who claimed the formation of etch pits.[8] No data on electrochemical growth of pores in *n*-type II-VI compounds have yet been reported. In this work, we present the results of our study of pore growth in *n*-CdSe single crystals subjected to anodic etching. The production of uniformly distributed, parallel pores is demonstrated. Porous CdSe structures are found to exhibit less luminescence intensity than the bulk material.

Wurtzite-phase *n*-CdSe single crystals were grown by chemical transport techniques using iodine as the transport agent. The concentration of free electrons in bulk material was 3×10^{17} cm^{-3} at 300 K, while the density of dislocations did not exceed 5×10^5 cm^{-2}. Samples with dimensions $5 \times 5 \times 2$ mm^3 were used. Electrochemical etching was carried out in 5% HCl aqueous solution at room temperature under potentiostatic conditions as described elsewhere.[6] To reach uniform nucleation of pores, the samples were *in situ* illuminated by focusing the UV radiation of a 200 W Xe lamp onto the CdSe surface (0.15 cm^2) exposed to electrolyte. The morphology and the chemical composition microanalysis of etched samples were studied using a TESCAN scanning electron microscope (SEM) equipped with an Oxford Instruments INCA energy dispersive x-ray (EDX) system. PL was excited by the 514 nm line of an Ar$^+$ SpectraPhysics laser and analyzed through a double spectrometer. The resolution was better than 0.5 meV. The samples were mounted on the cold station of a LTS-22-C-330 cryogenic system.

For anodization in dark, the etching process starts at surface imperfections. After this initial pitting of the surface, further etching proceeds in all directions radially away from the initial surface imperfection [Fig. 1(a)]. As a result, a po-
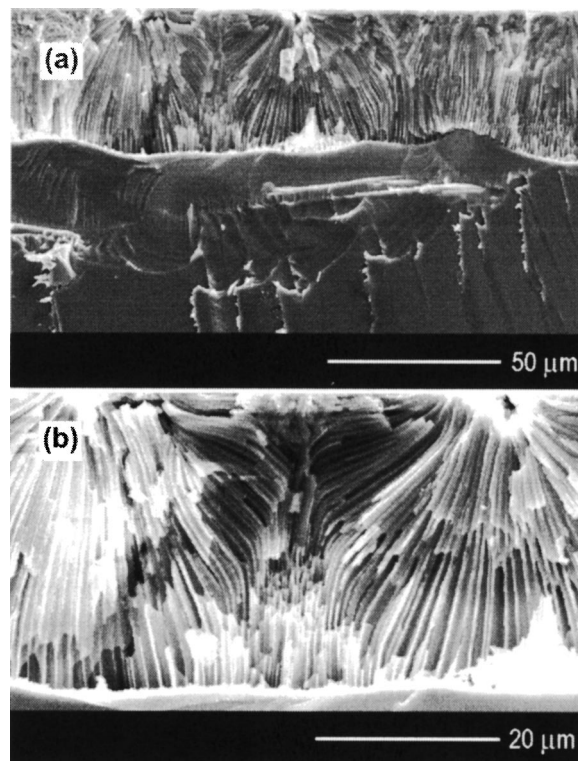

FIG. 1. SEM images taken in cross section from a CdSe sample anodized in dark: (a) general view and (b) development of the porous structure after neighboring domains meet.

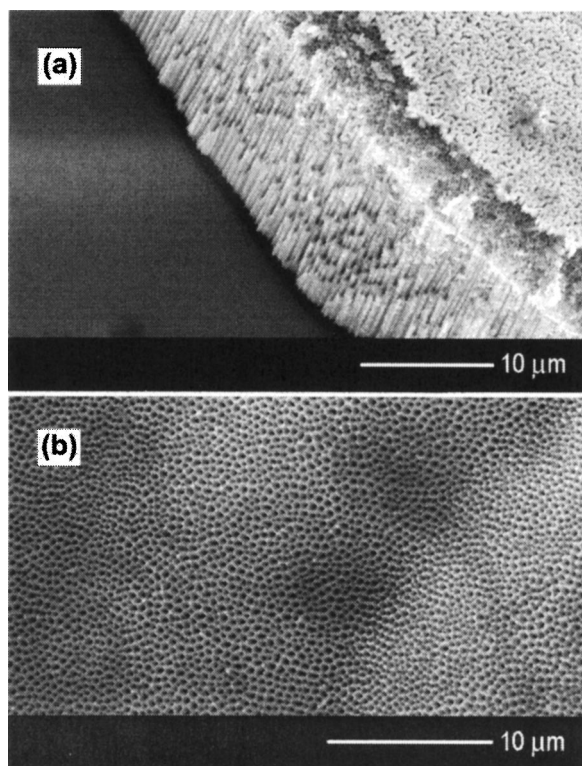[a)]Electronic mail: tiginyanu@mail.md

FIG. 2. SEM images taken from porous CdSe samples fabricated under *in situ* UV illumination: (a) general view and (b) top view after removal of the nucleation layer.

FIG. 3. PL spectra of as-grown CdSe measured under excitation power densities of 300 (curve 1) and 3 W/cm^2 (curve 2) as well as the spectrum of a photoelectrochemically etched sample (curve 3) measured under excitation power density of 300 W/cm^2.

rous domain forms around each etching pit. The pores obviously grow perpendicular to the equipotential lines of the electric field in the anodized specimen. When neighboring domains meet, the pores near the border separating the domains change their direction of growth and no pore intersection occurs [see Fig. 1(b)]. Due to space confinement, the density of pores in the emerging triangular-like regions between neighboring domains proves to be higher than the density of pores outside the areas involved. Thus both the direction of the growth of pores and their density show pronounced spatial fluctuation in this case. Note that the EDX analysis confirmed the stoichiometric composition of the porous CdSe skeleton in spite of its rather exotic morphology.

In situ UV illumination of the anodized samples allows one to reach much more uniform nucleation of pores. In this case one can easily distinguish a near-surface nucleation layer with a thickness of about 3 μm, followed by a porous layer with pores stretching perpendicular to the initial surface of the sample [Fig. 2(a)]. The chemical composition of the nucleation layer is not stoichiometric, the content of Se (about 70 at. %) being more than two times higher than that of Cd. This layer can be easily removed mechanically or by isotropic wet etching. Figure 2(b) shows the top surface of the porous layers after removal of the nucleation layer. Note a rather uniform distribution of pores, the lateral dimensions of both pores and walls being about 200 nm. According to the results of the EDX analysis, the composition of the porous skeleton is stoichiometric.

Figure 3 illustrates the PL spectra of as-grown CdSe measured under excitation power densities of 300 and 3 W/cm^2 (curves 1 and 2, respectively) as well as the spectrum of photoelectrochemically etched sample (curve 3).

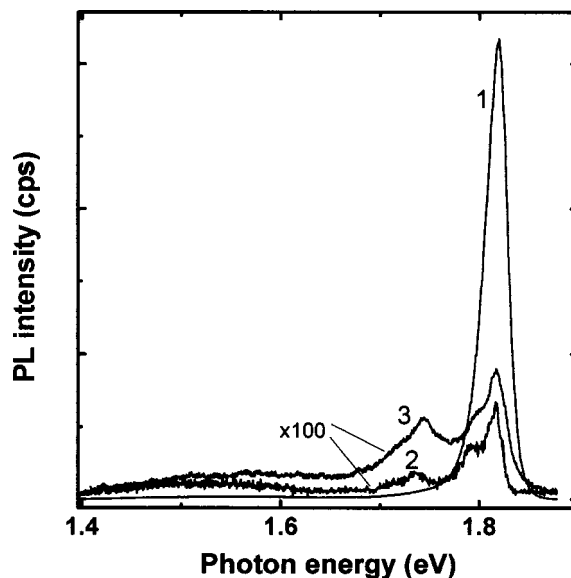One can see that at high excitation power density, the spectrum of the as-grown sample is dominated by a single PL band with the maximum at 1.819 eV. With the decrease of the excitation power density, two less intense PL bands at 1.797 and 1.74 eV along with a broad band at 1.4–1.7 eV emerge in the PL spectrum. According to previous studies, the PL band at 1.74 eV corresponds to nonequilibrium carrier recombination via donor-acceptor pairs (DAPs).[9] We propose that the other two PL bands at 1.819 and 1.797 eV labeled as BX1 and BX2 in Fig. 4 are related to the recombination of bound excitons.[10]

Photoelectrochemically introduced porosity leads to a decrease in the PL intensity by more than two orders of magnitude, and the spectrum of the nanostructured sample is similar to that of the bulk material measured under excitation power density as low as 3 W/cm^2 (compare curves 2 and 3
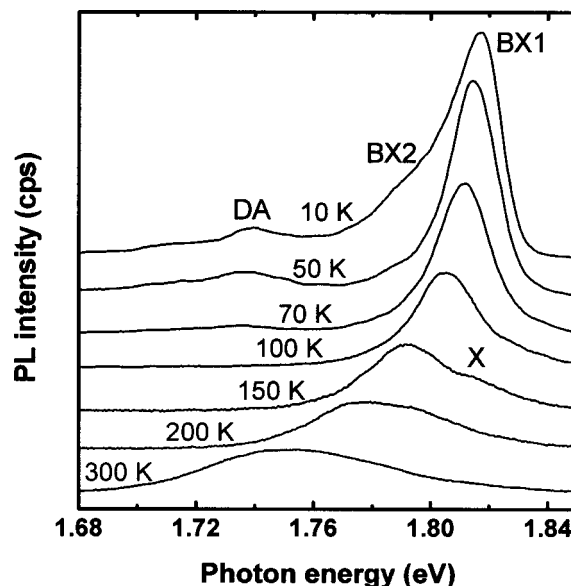

FIG. 4. Temperature dependence of the near-band-gap PL spectrum in porous CdSe.
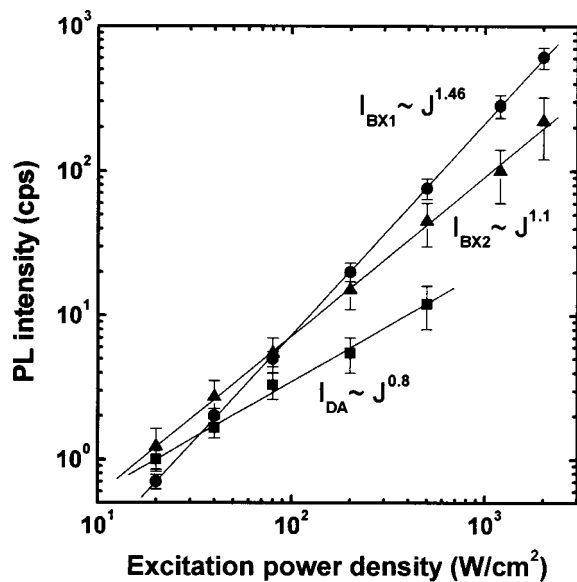
FIG. 5. Dependence of the intensity of PL bands upon the excitation power density in porous CdSe.

in Fig. 3). These results show that porosity effectively inhibits luminescence, this effect being probably caused by the enhanced surface recombination in the porous matrix characterized by high surface-to-volume ratio. Note that a similar phenomenon was observed recently in porous InP.[11]

With increasing temperature, the intensity of PL bands inherent to both bulk and porous CdSe decrease and a new PL band, marked X, is observed on the high-frequency wing of the BX1 band (see Fig. 4). This PL band is related either to the recombination of free excitons or to free-to-free transitions. The analysis of the dependence of the PL intensity upon the excitation power density **J** (Fig. 5) shows a sublinear dependence for the DA band with a slope of 0.8, similar to that reported earlier for DAP recombination in CdSe.[12] The dependence of the BX2 PL band is nearly linear, while that of the BX1 band is highly superlinear with a slope of 1.46. Note that a slope of 1.5 was recently deduced for biexciton luminescence in ZnO epitaxial films.[13] However, we consider that the biexciton origin of the PL band in our samples is unlikely since it is observed at excitation power densities as low as 20 W/cm^2. Additional experiments are required to throw light upon the nature of the PL band involved.

These results show that porosity is a promising tool for manufacturing CdSe nanotemplates. Nowadays, nanotemplates based on porous alumina are commercially available. However, the high-resistivity nanomatrix of porous alumina plays only a passive role in nanofabrication. The properties of the semiconducting CdSe can be easily changed by exter-

nal illumination, applied electric fields, etc. It means that CdSe nanotemplates may play an active role in nanofabrication. In particular, the semiconductor component can be responsible for the high conductivity of polymer-semiconductor nanocomposites fabricated by filling in the pores with polymers.[14] According to our preliminary study of pore growth in CdSe substrates with different electrical characteristics, development of CdSe nanotemplates with pore diameters as low as 20 nm is feasible.

In conclusion, anodic etching of *n*-CdSe substrates in the dark leads to the nonuniform attack of the material. The local dissolution starts at surface imperfections, with subsequent formation of porous domains underneath the initial surface of the sample. *In situ* UV illumination results in a uniform pore nucleation leading to the growth of parallel pores stretching perpendicular to the initial surface of the specimen. Porous CdSe layers show less luminescence than the bulk material. This phenomenon is explained by the enhanced surface recombination in the porous network. These results show that porosity is a promising cost-effective tool for the fabrication of CdSe-based semiconductor nanotemplates with the pore diameters of 200 nm and smaller.

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