

Porosity-induced blueshift of photoluminescence in CdSe

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Porous CdSe layers have been fabricated by anodic etching of *n*-type single crystalline substrates with different values of conductivity. The morphology and porosity of the layers thus produced were found to be controlled by the conductivity of the material, anodization voltage, and conditions of *in situ* UV illumination. The porosity-induced changes in the photoluminescence spectra were studied. The decrease of the skeleton size down to 10–20 nm was found to result in a blueshift of the excitonic emission lines by 10 meV which was attributed to quantum-size effects in the nanocrystalline CdSe porous skeleton. An increase of the exciton–LO-phonon interaction by a factor of 1.5 in a weak-to-intermediate confinement regime was deduced from the analysis of temperature dependence of the free exciton luminescence line. © 2006 American Institute of Physics.

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INTRODUCTION

It is well known that material properties may be engineered by nanostructuring, i.e., by tailoring the architecture of macroscopic structures on the nanometer scale. Electrochemistry offers an accessible and cost-effective approach for tailoring the architecture of semiconductor materials on the submicrometer scale simply by “drilling” pores in bulk crystals and epilayers. The architecture of pores may be designed for the purpose of manufacturing integrated waveguides, Bragg-like mirrors, beam splitters, rotators of light polarization, etc.¹ Due to giant fluctuations of the electric field of electromagnetic radiation, nanoporous structures show fascinating nonlinear optical behavior, in particular, strongly enhanced second harmonic generation and terahertz emission.² Apart from these one-component nanostructures, porous semiconductors represent suitable templates for the fabrication of nanocomposites via filling the pores with other inorganic and organic materials including conducting polymers, which considerably extends the possibilities for developing light emitting devices and hybrid solar cells. When the characteristic dimensions of the porous skeleton entities correlate with or are much smaller than the wavelength of the electromagnetic radiation, a strong diffuse scattering of light takes place in the nanocomposite leading to the onset of light localization.³ Because of the nanoscale nature of light absorption and photocurrent generation in solar energy conversion, the advent of methods for controlling inorganic materials on the nanometer scale opens opportunities for the development of future generations of solar cells.⁴ Apart from

that, doping of nanoporous II–VI materials with transition metals⁵ opens prospects for the elaboration of midinfrared random lasers.

Even more spectacular changes in the material properties occur when the dimensions involved are comparable to or lower than the exciton Bohr radius. In this case, the quantum-size effects on free carriers give rise to a band gap increase of the semiconductor and sharp modification of optical and electrical properties.

Over the last decade, systematic study of porous Si and porous III–V compounds was undertaken. At the same time less attention has been paid to porous II–VI semiconductor compounds. Note that the effect of photoetching on photoluminescence (PL) of *n*-CdSe was studied many years ago,⁶ but the authors interpreted the results in terms of the formation of etch pits rather than pores. Formation of porous network in a *p*-type II–VI material, namely, in *p*-Cd_{1-x}Zn_xTe, was demonstrated by Erne *et al.*^{7,8} Recently we succeeded in introducing pores into *n*-type CdSe,⁹ and we observed gain of luminescence in porous regions characterized by strong light scattering.¹⁰ In this article, we show the possibility of introducing arrays of parallel pores with diameters as low as 10–20 nm into highly conductive *n*-CdSe single crystals. Porosity-induced blueshift of exciton bands in PL spectra of *n*-CdSe is also reported.

EXPERIMENTAL DETAILS

Wurtzite-phase *n*-CdSe single crystals were grown by chemical transport techniques. Two types of samples with the free electron concentrations of 3×10^{17} and 2×10^{18} cm⁻³ at 300 K were used in experiments. Electrochemical etching of samples with the dimensions of $5 \times 5 \times 2$ mm³ was carried out in 5% HCl aqueous solution at room temperature under

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