Photoluminescence and resonant Raman scattering from ZnO-opal structures

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We study photoluminescence (PL) of ZnO-opal structures excited by a 351.1 nm laser line. The structures were fabricated by infiltration of ZnO from an aqueous solution of zinc nitrate into opal matrices. The emission spectrum of thick ZnO layers grown on the surface of bulk opals exhibits narrow PL bands associated with the recombination of bound and free-excitons. The free-exciton lines are discussed taking into account the polariton phenomena. The width of the excitonic lines (2–3 meV) along with their energy position is indicative of high quality and strain-free state of the layer. The emission from ZnO crystallites embedded into bulk opal is dominated by near band gap luminescence, a weak quantum confinement effect being observed for crystallites with sizes around 50 nm. Thin ZnO films grown on single-layer opals exhibit enhanced resonant Raman scattering, phonon confinement effects, and surface-related modes. Strong exciton-LO phonon and exciton-Fröhlich mode coupling in ZnO nanostructures is deduced from the analysis of multiphonon excitonic resonant Raman scattering.
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1. INTRODUCTION

The increasing interest in low-dimensional quantum systems such as arrays of quantum dots and wires realized in one-, two-, and three-dimensional (1D, 2D, and 3D) periodic structures is stimulated by their growing applications in nanoelectronics, optoelectronics, and photonics. Crystalline arrays of colloidal spheres represent one of the most promising templates for nanofabrication. 3D opal structures are ideal matrices for the purpose of filling with semiconductors, metals, magnetic materials, etc., in order to fabricate photonic crystals, arrays of quantum dots and other low-dimensional systems. The possibility to fabricate multilayer and single-layer ordered SiO_2 spheres on glass substrates has been recently demonstrated.[1,2] Growth of ordered metal and semiconductor structures inside the opal voids was reported[3–5] Note that single-layer opal structures can be used as nanomasks for the purpose of depositing different materials on substrates. This approach referred as ''nanosphere lithography'' enabled one recently to fabricate metal and semiconductor 2D arrays using polystyrene beads and molecular materials as nanomasks.[6] In many cases, the nanomasks must be resistant to thermal treatment, plasma etching, etc. Taking this into account, inorganic nanomasks and especially opal spheres are the most promising materials for nanolithography. The occurrence of physical properties in low-dimensional semiconductor materials-opal structures with potential exploitation in microelectronic and optoelectronic devices constitutes the motivation of the growing interest in these systems. For specific applications, the semiconductor component of these structures should also be resistant to hard environmental conditions. Zinc oxide (ZnO), a direct wide band gap (3.37 eV at 300 K) semiconductor with large exciton binding energy (~ 60 meV), is a promising material in this regard. The goal of this work was to fabricate different ZnO-opal structures and to study their radiative properties.

2. EXPERIMENTAL DETAILS

Silica opal spheres were synthesized through the hydrolysis of tetraethyl orthosilicate in water-ethanol solution in the presence of ammonium hydroxide following Stöber's method[7] with some modification of the component ratio.[2] 2D opal structures were prepared using the procedure of natural sedimentation combined with capillary contraction.[2] Multilayer and single-layer opal structures were fabricated by deposition on nearly vertical substrates during evaporation of the solvent. 3D opal matrices (bulk opals) were manufactured by natural sedimentation of the silica particles in a water suspension. After drying procedure at 150 °C, the samples were annealed at 1020 °C for 5 h. These technological steps resulted in opal structures exhibiting face-centered cubic lattice with the diameter of silica spheres $D_{SiO_2} \approx 220$ nm. This lattice possesses octahedral and tetrahedral voids with dimensions of $0.41\times D_{SiO_2}$ and $0.22\times D_{SiO_2}$, respectively. ZnO layers with the thickness ranging from 100

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