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Dominant ultraviolet-blue photoluminescence of ZnO embedded into synthetic opal

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Abstract

The temperature-dependent photoluminescence (PL) characteristics of zinc oxide (ZnO) embedded into the voids of synthetic opal were studied. ZnO was infiltrated into opal from aqueous solution with zinc nitrate precursor followed by thermal annealing. The PL spectra of the ZnO powder exhibit very high and broad emission peaks in the green region due to crystal defects, such as oxygen vacancies and zinc ion interstitials. In contrast to the PL spectra of ZnO powder, nanocrystals of ZnO embedded into the voids of FCC packed opal matrix exhibit dominant ultraviolet (UV)-blue and rapidly decreasing green PL emissions with decreasing temperature. The temperature-dependent PL characteristics show that the green band suppression in the ZnO nanocrystals is due to the influence of photonic crystal. The infiltration of nanoparticles into synthetic opal may be used for the fabrication of polycrystalline ZnO with dominant UV-blue PL. These results indicate that the luminescent materials embedded into photonic crystal may be promising for the fabrication of the RGB pixels in full-color displays.

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1. Introduction

Zinc oxide (ZnO), a wide band gap semiconductor, has recently attracted attention due to its remarkable optical properties, and is considered a promising material for potential applications in

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optoelectronic devices operating in ultraviolet (UV) and visible spectra [1,2]. On the other hand, photonic crystals (PhC), proposed by Yablonovitch [3], can be applied to improve the optical properties of semiconductors. Apart from many possible applications of PhCs, their ability to suppress a radiative emission [4] may also be useful for optical device fabrication. For instance, the feasibility of a strong modification in PL due to the inhibition of spontaneous emission was demonstrated for CdS embedded into an opal matrix [5]. Particularly, this ability of PhCs can be used to suppress the undesirable green photoluminescence (PL) band in ZnO.

Different methods such as pulsed laser deposition, magnetron sputtering, chemical vapor deposition (CVD) and molecular beam epitaxy (MBE) are used for ZnO depositions [6–9]. However, these methods need the highly expensive equipment and the complicated fabrication growth technology of ZnO. Among all the available methods, spray pyrolysis is technologically simple, inexpensive and, at the same time, very efficient deposition technique, which has many advantages over others. The recent publications show that spray pyrolysis is successfully used for fabrication of the high-quality phosphors like blue-emitting thin films of cerium-doped barium chloride hydrate [10], green-, blue-, and yellow-emitting $Ba_2B_5O_9Cl$ thin films doped with Tb^{3+}, Tm^{3+} and Mn^{2+} [11], and blue-emitting alkaline earth chloroborate thin films doped with Eu [12]. Another significant advantage is that the spray pyrolysis can be very useful technique to fill the voids inside the volume of the porous material.

Many recent studies have been devoted to luminescent materials infiltrated into matrix opal [5] and inverted matrix opal [13,14]. The first successful attempt to combine ZnO with PhC has been recently reported by Gruzintsev et al. [15,16]. These publications show the PL spectra of the ZnO thin (90 nm) film deposited on the surface of opal matrix by electron-beam sputtering. In this structure, ZnO quantum dots represent a 2D periodic array exhibiting a narrow excitonic emission due to the quantum confinement.

However, this approach can also be extended for 3D periodic structure by growth of ZnO inside PhC in the solution containing a zinc nitrate or zinc acetate precursor. In particular, the complete filling of the synthetic opal volume with ZnO nanocrystals by using spray pyrolysis as a useful technique to modify the PL spectra of ZnO has been proposed [17,18]. The green porous opal has been chosen since its photonic band gap overlaps the electronic band gap of ZnO to suppress undesirable spontaneous emission in the spectral region associated with native defects.

Preliminary studies concerning optical properties of ZnO nanocrystals inside the synthetic opal obtained by using the spray pyrolysis method have been reported [17–23]. Despite the high density of crystal defects, a strongly dominant UV-blue emission in the PL spectra of polycrystalline ZnO was observed. However, the low-temperature PL spectroscopy of ZnO nanocrystals embedded into opal has not been investigated yet and the assumption that the dominant UV-blue PL emission is due to the influence of PhC must be verified more conclusively.

This paper reports the temperature-dependent PL showing the green band suppression in ZnO embedded opal. Presumably, the green PL band in the ZnO nanocrystals might be suppressed since a photonic band gap of synthetic opal overlaps a spectral region of radiative recombination originating through deep levels (DL). As a result of the inhibition of spontaneous emission, the recombination rate through DL is decreased and this effect can be clearly observed in the temperature-dependent PL spectra.

The PL spectroscopy shows that a peak intensity ratio for ZnO embedded opal is significantly higher compared to that for reference sample and exhibits a rapid increase with decreasing temperature. These two factors support an assumption that the green band suppression is due to the influence of PhC.

2. Experimental

The silicon dioxide (SiO_2) spheres were synthesized in Stober–Fink–Bohn process through the hydrolysis of tetraethyl orthosilicate (TEOS) in ethanol solution containing ammonium hydroxide