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Surface and defect modifications in mixture of ZnO and carbon nanocrystals at mechanical processing

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ABSTRACT

The Raman scattering and photoluminescence (PL) spectra, PL temperature dependences and scanning electronic microscopy (SEM) images have been studied in the mixture of ZnO + 1.0%C nanocrystals (NCs) before and after intensive mechanical processing (MP). The study reflects the diversity of physical processes occurring at MP: the amorphization of the ZnO NC surface, transforming an amorphous graphite into graphene monolayers covered of ZnO NCs, changing the ZnO NC shape owing to the plastic deformation and crushing the individual ZnO NCs, the partial oxidation of graphene layers with the formation of graphene oxide passivating ZnO NCs, the formation of graphite oxide when temperature increasing at MP, as well as the ZnO defect modification near the surface of ZnO NCs, etc. Additionally the new 'blue" PL band peaked at 2.82–2.92 eV has been revealed in PL spectra after MP, which is assigned to emission of graphite (graphene) oxides. All mentioned processed have been studied and discussed in details.

1. Introduction

ZnO nanocrystals (NCs) with native defects or different type dopants are the most popular new systems owing to the exceptional physical properties [1]. ZnO NCs with a wide direct band gap (3.37 eV) and a high exciton binding energy (60 meV) at 300 K promise numerous applications in optical and electronic devices [1,2], such as: solar cells [3], field emission cathodes [4,5], light-emitting diodes [6] and ultraviolet nano-lasers [7], as well as luminescent [8] and catalytic materials [9] etc. ZnO is characterized by flexibility of forming the different shape nanostructures that is of great interest and due to this ZnO is promising material for piezoelectric transducers [10], electrodes for solar cells [11], catalyst for electronics [12], field-effect transistors [13], thin-film printing [14] and transparent conductors [15]. Additionally ZnO is characterized by the easily tuned electronic properties, high thermal stability and oxidation resistance compared with most other semiconductor materials [4].

Important electronic properties have been revealed recently in the nanocrystalline composite ZnO + xC, which permits improving the field emission characteristics of cathodes [5], engineering the room-temperature ferromagnetism [16], modifying luminescence properties [17], and creating the selective solar light absorbing coating [18]. It was suggested as well that the Graphene-semiconductor nanostructures, like Gr-ZnO, will show improved optical switching and catalytic properties [19].

A number of technological methods has been used to synthesize ZnO NCs: the hydrothermal synthesis [20], conventional ball-milling [21], microwave-assisted synthesis [22], spray pyrolysis [23], hydrolysis/condensation [24] and sol-gel [25]. From all of them the ball-milling is interesting owing to the facile and costless fabrication procedure. Milling can be applied effectively for reducing the crystallite size down to the nanometer scale. In addition, this technique permits controlling the microstructure and morphology of ZnO NCs, which influent on the electronic and optical properties.

At mechanical and thermal treatments during ball milling a large set of defects can be produced in ZnO NCs that permits to exhibit the certain characteristics, which cannot be obtained in the bulk crystals. The creation of optoelectronic devices requires the study of emission mechanisms and the process of defect generation in ZnO NCs. In present paper the transformations of Raman scattering spectra, SEM images, photoluminescence (PL) and PL temperature dependences have been investigated for the mixture of ZnO + 1.0% C NCs with the goal to study the nature of radiative defects, PL quenching mechanisms, carbon impact and the defect generation at mechanical processing.

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2. Experimental details

ZnO NCs (99.5% purity, Reasol Co, with the size 100–400 nm) and carbon nanoparticles (EPRUI Nanoparticles & Microspheres Co, with the size smaller 50 nm) were mixed. Mechanical processing (MP) of the ZnO + 1% C mixture was carried out in a Planetary Ball-Mill (PM 400/2, Retsch Inc.). The 50 ml grinding chamber with tungsten carbide balls: 3 units of 20 mm and 10 units of 10 mm, was used. The weight ratio of balls to the mixture powder was 28:1. MP is realized at the rotation speed 400 rpm for MP times (t_{MP}): 1, 3, 9, 30, 90 and 390 min.

PL spectra were measured in the temperature range of 20–300 K at an excitation by a He-Cd laser with a wavelength of 325 nm and a beam power of 46 mW using a PL setup on a base of spectrometer SPEX500 and a closed cycle He cryostat described in [26–28]. The morphology study and images of the ZnO + 1% C NC mixture for different MP times have been obtained using the scanning electron microscopy (SEM), model Quanta 3D FEG-FEI. Raman scattering spectra were measured in the backscattering geometry using a Jobin-Yvon LabRAM HR 800UV micro-Raman system at the excitation by a solid state LED with a light wavelength of 785 nm [29–31].

3. Experimental results and disscusion

3.1. SEM images

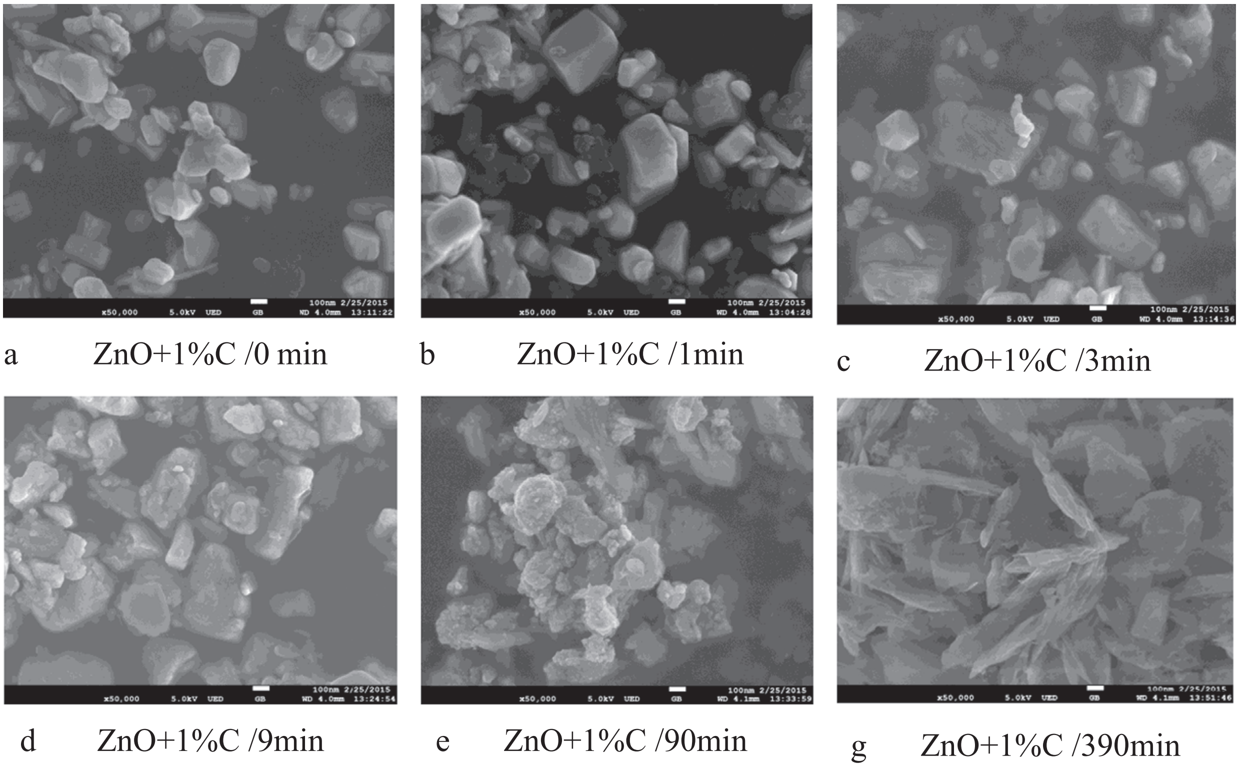
SEM images of the ZnO + 1% C mixtures for different MP times are presented in Fig. 1. ZnO NCs with the individual NC size from the range of 100–400 nm have been seen clearly in Fig. 1a–c. Carbon nanoparticles owing to the small C concentration (1%) in a mixture and the small sizes ($\leq$ 50 nm) do not visible in Fig. 1. The shape of majority ZnO NCs does not change very much after the first 3 min of MP (Fig. 1a–c). Then the amorfization of the ZnO NC surface and NC agglomeration have been seen for 9–90 min of MP (Fig. 1d and e). The NC size decreases at MP for 9–90 min owing to the plastic deformation and crushing the individual ZnO NCs (Fig. 1d and e). Finally after the long MP (390 min) the ZnO NCs transform their shape into the ZnO nanosheets (NSs) with the sheet sizes nearly 50–100 nm × 500–600 nm (Fig. 1g). At the same time the agglomeration dominates in ZnO nanosheet ensembles (Fig. 1g).

3.2. Raman scattering spectra

Raman scattering spectra of the ZnO + 1%C mixtures for different MP times are presented in Fig. 2a. Raman peaks at 196, 323 and 430 cm^{-1} related to scattering in ZnO NCs have been seen clearly in the range of Raman shifts of 80–500 cm^{-1} (Fig. 2a, Table 1). Note that the positions of Raman peaks related to ZnO NCs do not change at MP (Table 1).

Group theory predicts that in the perfect wurzite ZnO structure the Raman active phonons in the Brillouin zone center are involved in first-order Raman scattering, such as (i) A1 symmetry polar phonons with transverse (TO) at 379 cm^{-1} and longitudinal (LO) at 574 cm^{-1} optical phonons, (ii) E1 symmetry polar phonons with transverse (TO) at 410 cm^{-1} and longitudinal (LO) at 591 cm^{-1} optical phonons, and (iii) E2 symmetry non-polar phonons with different frequencies E2 (low) at 102 cm^{-1} and E2 (high) at 439 cm^{-1}. The E2 (low) mode was assigned to the vibration of the heavy Zn sublattice and the E2 (high) mode was connected with the oxygen sublattice vibration [33–36]. The Raman peak at 430 cm^{-1}, apparently, corresponds to the E2 (high) vibration mode, which is the characteristic of the wurtzite ZnO phase [33,34]. The Raman peak at 523 cm^{-1}, which appears after 390 min of MP, can be assigned to the surface phonons (SP) in ZnO NCs [31].

The comparison of obtained and published results permits to assign the Raman peak at 196 cm^{-1} to the acoustic phonon overtones and the peak at 323 cm^{-1} to the second order Raman peaks arising from the zone boundary phonons $3E_{2H}$-E_{2L}[30].



a ZnO+1%C /0 min
b ZnO+1%C /1min
c ZnO+1%C /3min
d ZnO+1%C /9min
e ZnO+1%C /90min
g ZnO+1%C /390min

Fig. 1. SEM images of the mixture of ZnO + 1%C NCs obtained after MP during: 0 min (a), 1 min (b), 3 min (c), 9 min (d), 90 min (e) and 390 min (g).