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Defect states and morphological evolution in mechanically processed ZnO + *x*C nanosystems as studied by EPR and photoluminescence spectroscopy

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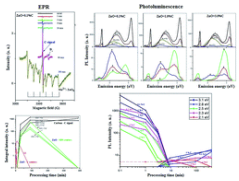
Abstract

An evolution of electron paramagnetic resonance (EPR) and photoluminescence (PL) spectra of various active states (hydrogen donor D_H EPR centers, Zn vacancy-related EPR centers $\left(V_{Zn}^{-}:Zn_i^0, V_{Zn}^{-}, \left(V_{Zn}^{-}\right)_2\right)$, EPR D_S centers from shallow donors (g = 1.9640) in ZnO_W, Mn^{2+} ions in ZnO_{ZB}, C EPR centers in carbon nanoparticles, forming the near-band-edge (NBE) PL emission, PL emission typical for Zn-, O- and N-enriched ZnO_W particles, as well as oxidized carbon nanodots (OCN)) was observed in the mixtures of ZnO + *x*C nanoparticles during prolonged high-energy mechanical processing (MP) in a hermetically sealed grinding chamber. The results of EPR and PL spectroscopy, X-ray diffraction analysis, as well as morphological analysis by means of atomic force microscopy (AFM) and laser particle sizer (LPS) measurements show a wide variety of interrelated series–parallel processes in the samples with increasing MP processing time (t_{MP}). These processes include: (a) dramatic reduction in intensity of the D_H EPR signal and PL bands at 3.14 (1.57), 2.53 and 2.3 eV during the first minutes of MP, which correlate with sample disaggregation; (b) grinding of ZnO particles and formation of Zn vacancy-related EPR centers in the area of destruction (**AD**); (c) an increase in sample temperature; (d) annealing of the Zn vacancy-related EPR centers formed; (e) initiation of carbon nanoparticle interaction with oxygen in the grinding chamber; (f) formation and growth of the EPR signal due to carbon nanoparticles; (g) formation of a reducing environment in the grinding chamber; (h) stabilization of donor D_S-centers in **AD** of ZnO nanoparticles; (i) an increase in CO concentration in the grinding chamber; (j) inhibition of D_S paramagnetic centers in ZnO; (k) initiation of the EPR signals due to Mn^{2+} ions in ZnO_{ZB} sphalerite phase in the sample with the lowest carbon content; (l) inhibition of nitrogen PL centers in ZnO; (m) the formation of oxidized carbon nanodots (OCN) showing a PL band at 2.8 eV. A detailed analysis for the localization of EPR and PL centers in the MP samples is presented.



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