Photoluminescence Quenching in Zinc Oxide Modified by Al₂O₃ and Al₂O₃ ⋅ CeO₂ Nanopowders under Proton Irradiation

M. M. Mikhailov, V. V. Neshchimenko, Chundong Li, and Bang-Jiao Ye

Abstract—The photoluminescence spectra of initial ZnO powder and that modified by Al₂O₃, Al₂O₃ ⋅ CeO₂ nanopowders are investigated in the range 360–660 nm before and after 100-keV proton irradiation. It is found that the introduction of nanoparticle powders causes a decrease in the UV-band intensity and a change in the luminescence bands in the visual spectrum due to V⁺ O₂, oxygen vacancies, O⁺ int, interstitial oxygen, and V⁺ Zn, zinc vacancies. Luminescence quenching in the UV and visible spectra occurs under the effect of protons. The decomposition of the spectra into elementary defects and analysis of changes in their integrated intensity during modification and irradiation of the powders are carried out.

INTRODUCTION

Zinc oxide powders are widely used in many technological fields, including in the space industry as pigments in thermal-control coatings. Therefore improvement in their optical properties is of scientific and practical interest. In particular, an increase in the resistance to photon and charged-particle irradiation is important and can be achieved by the modification of zinc oxide by white oxide nanopowders in which recombination of electron–hole pairs occurs with high probability [1, 2].

The effect of photons with an energy above 3.3 eV on zinc oxide results in the appearance of luminescence in the UV spectrum, which is due to free exciton recombination [3–5]. Photon emission in the visible spectrum is caused by intrinsic defects in zinc oxide [6–11]. Therefore analysis of the luminescence spectra provides the determination of changes in the concentration of excitons and intrinsic defects caused by external effects (irradiation or the introduction of modifiers). The prolonged exposure of initial and modified zinc oxide powders to ionizing radiation leads to the accumulation of radiation defects in them. By studying the regularities of their accumulation, which is reflected in the dependence of variation in the photoluminescence-band area caused by some types of defects, we can determine the relative radiation resistance of pigment powders.

The aim of this work is to study the effect of proton irradiation on the photoluminescence spectra of zinc oxide powder modified by Al₂O₃ and Al₂O₃ ⋅ CeO₂ nanopowders.

EXPERIMENTAL

The object of the study was zinc oxide powder (chemically pure, TOR 10262–73) with an average particle size of 700–800 nm. Nanopowders of Al₂O₃ and Al₂O₃ with an addition of 10 wt % CeO₂ were obtained by the plasma chemical process [12]; the characteristic size of the nanopowders was 10–30 nm. The conditions, sample preparation procedure, and photoluminescence-spectra measurements were the same as in [13]. Irradiation of the samples with 100-keV protons was performed in a vacuum chamber with a residual pressure of 2.5 × 10⁻⁴ Pa at a flux density of 5 × 10¹¹ cm⁻² s⁻¹ with a fluence (Φ) of (0.5, 1, 2, 5, and 10) × 10¹⁵ cm⁻² (Φ is the number of particles incident per unit area perpendicular to the sample during the time of the experiment).

RESULTS AND DISCUSSION

Two bands are recorded in the photoluminescence spectra (Fig. 1) of the initial zinc oxide and that modified by the nanopowders: in the UV region near 3.1–3.2 eV and in the visible region with a peak near 2.3–2.5 eV. The UV band of the unmodified powder has the highest intensity. Introduction of the nanopowders causes a shift of this band from 3.16 to 3.19 eV. The band intensity in the visible region also changes depending on the modification conditions.

The results of decomposition of the photoluminescence spectra into Gaussian components show that the UV band consists of two bands at 3.17 and 3.07 eV whose occurrence is due to free exciton recombin-
tion: A excitons with the absorption of one (A + LO) and two (A+2LO) longitudinal-optical phonons [3–5]. The band in the visible spectral region consists of three bands at 2.55, 2.34, and 2.12 eV, which according to [6–11, 13, 14] can be caused by $V_O^-$ oxygen vacancies, $O_{int}$ interstitial oxygen, and $V_{Zn}$ zinc vacancies, respectively.

Under the effect of protons, the band intensity in the UV and visible regions decreases (Fig. 2). The decrease can be due to concentration quenching consisting in the scattering of emitted quanta at radiation defects, a part of which are at the same time absorption and emission centers. Luminescence quenching also seems to be related to scattering at complex defects involving hydrogen ions, e.g., $V_{Zn}H$ [15], which may lead to the formation of low-lying traps at 0.2–0.3 eV and determine quenching of the UV luminescence band. Before and after the effect of accelerated protons, the visible spectral bands of the powders modified by nano-$Al_2O_3$ have a higher intensity as compared to those of the powders modified by nano-$Al_2O_3$.

Analysis of the photoluminescence spectra was performed based on the integrated band intensity, which is a more accurate characteristic than the band intensity (table). Among the unirradiated samples, the A + LO band of initial zinc oxide has the highest integrated intensity ($S = 230$ eV rel. unit). Then in decreasing order of integrated intensity ($S = 98.7$ eV rel. unit), zinc oxide modified by nano-$Al_2O_3$ follows. The introduction of $Al_2O_3$ + CeO$_2$ nanopowder results in a decrease in the integrated intensity of this band by 89%. The integrated intensity of the A + 2LO band is much lower for all modified samples than that for the initial powder (the decrease is 80–90%).

Irradiation causes a shift of the UV photoluminescence band to the high-energy spectral region. Thus, at a proton fluence of $5 \times 10^{14}$ cm$^{-2}$ it shifts to 3.17 eV in comparison with 3.16 eV of unirradiated zinc oxide. The short-wavelength shift of the UV band with a simultaneous decrease in its intensity during modification or proton irradiation of the zinc oxide powder.