Blue shift in absorption edge of polycrystalline zinc oxide modified by nanoparticles before and after irradiation exposure

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ABSTRACT

The effect on band gap (E_g) and crystal structure of ZnO modified by Al_2O_3, ZrO_2, SiO_2, CeO_2, TiO_2 and Y_2O_3 nanoparticles at concentrations less than 30 wt% has been investigated. Established that change of E_g reach to 0.03 eV and determined by charge of cations and their radius, as well as the concentration of the nanoparticles. Lattice parameters changes at modifying by nanoparticles with a smaller and larger radius of cations than the ion Zn^{2+}. Influence of 100 keV protons irradiation result in blue shift in absorption edge of polycrystalline zinc oxide modified by Al_2O_3, ZrO_2, SiO_2, CeO_2, TiO_2 and Y_2O_3 nanoparticles.

1. Introduction

The band gap (E_g) is a semiconductor fundamental characteristic, its values correlated with optical, electrical and other properties. Therefore, the patterns of E_g changes can be informative for a study of these properties.

Zinc oxide powders have broad applications, where they are exposed to various types of radiation. First of all – it's space technology, in which the zinc oxide used as the main pigment of thermal control coating. Since the beginning of space exploration to the present time hasn't found another pigment, capable of competing in the photo- and radiation stability with zinc oxide, as well as on technological quality and initial optical properties [1,2]. Furthermore, it's has wide application for solar cell [3,4].

Modern requirements for space applications are primarily to increase the active lifetime of equipment at high operational reliability. Therefore the development of methods to improve the radiation stability of zinc oxide powder has a scientific and practical importance. One of the methods is modification by nanopowders, wherein changes not only the radiation stability but also initial optical properties [5,6].

Knowledge of the changes in spectral reflectance, the solar absorption and conductivity of powders at modification have practical importance, because these characteristics determine the area of the radiator panels, which affects to the weight and cost of the spacecraft [5,6].

The purpose of the paper is to perform analysis of influence of the oxide nanoparticles type and their concentration on the band gap and crystal lattice of zinc oxide powders with micron-sized grains at high temperature modification.

2. Experimental

The objects of research were commercial zinc oxide micropowder and ZrO_2, Al_2O_3, TiO_2, SiO_2, CeO_2, Y_2O_3 nanopowders with 99.8% purity, purchased from the company Aladdin Chemistry. The silicon oxide nanopowder has the amorphous state, other nanopowders have a crystalline structure. The average particle size of the micropowder was 500–800 nm, while the nanopowder was 40–50 nm as measured by a Horiba LA-920 particle size distribution analyzer. The specific surface area of powders Al_2O_3, ZrO_2, CeO_2 and Y_2O_3 differed slightly and amounted to 20–30 m^2/g. In powder TiO_2 it was less – 15 m^2/g, in powder SiO_2 it was much more – 285 m^2/g.

Types of nanopowders selected with pronounced dielectric (Al_2O_3, ZrO_2, SiO_2, Y_2O_3) and semiconductor (TiO_2, CeO_2) properties. Cations of these compounds have a different charge (Si^{4+}, Zr^{4+}, Ti^{4+}), (Al^{3+}, Y^{3+}) and ($Ce^{(4+ \rightarrow 3+)}$), with large (0.79 Å – Zr^{4+}, 0.89 Å – Y^{3+}, 0.92 Å – Ce^{4+}) and less (0.42 Å – Si^{4+}, 0.54 Å – Al^{3+}, 0.68 Å – Ti^{4+}) of ion radius Zn^{2+} (0.74 Å).

The concentration of nanopowders was selected under the preliminary tests, which had been performed in a wide range of

constituents (1, 3, 5, 7, 10, 15 and 30 wt%). The above nanopowders were dispersed in the distilled water with the imposition of ultrasonic fluctuations (2 min, 200 W), and followed by the addition of the ZnO powders into the solution. Then the mixture was treated by ultrasonic exposure and evaporation of water.

The obtained powders were ground in a mortar and heat-treated for 3 h in ambient. According to previous research the temperature of heat treatment with various powders was 800 °C [7]. Hence the heating rate was set at 50 °C/min while a cooling speed at 9 °C/min was used.

X-ray diffraction (XRD) analysis was performed using the X-ray diffractometer Philips X'Pert PRO MRD (V = 40 kV, I = 40 mA, CuKa = 1.5405) using the Debye–Scherrer method. The phase composition and unit cell parameters were calculated using the MDI Jade software package.

Samples were prepared by pressing under 10 MPa of pressure for 2 min to form discs on an aluminum substrate, each with a diameter of 17 mm and a height of 4 mm. The reflective spectra of the samples were measured using a Perkin Elmer Lambda 950 spectrophotometer with a scanning rate of 5 nm/s and wavelengths between 250 to 500 nm. The ρ_λ is defined as an average of two experimental spectra.

The samples were irradiated with protons and electrons under identical conditions: the particle energy was 100 keV, the fluence was 5×10^{15} cm^{-2}, the flux density was 1×10^{12} cm^{-2} s^{-1}, and a vacuum was maintained at 2.5×10^{-4} Pa for protons exposure, 1×10^{-5} Pa for electrons.

3. Results

The obtained SEM micrographs show (Fig. 1) that the modification results in the deposition of nanoparticles on the grain surface with the formation of a single or double layer shell.

The modification of ZnO powder modified by Al_2O_3, ZrO_2, SiO_2, Y_2O_3, TiO_2, CeO_2 nanoparticles lead to formation of additional phases Al_2ZnO_4, $ZnZrO_3$, Zn_3Zr_3O, Zn_2SiO_4, Zn_2TiO_4 and unidentified phase $Ce_xZn_{1-x}O_y$, $Y_xZn_{1-x}O_y$ at high concentrations (Fig. 2). Thus nanoparticles deposited on the surface of the zinc oxide grain form chemical bond, so the nanoparticles are fixed on the pigment surface.

The calculations of cell lattice parameters of the modified zinc oxide performed based on six peaks (102, 110, 103, 200, 112, and 201) show that introduction of nanoparticles lead to change in lattice parameters. Parameter a and c decreases at modification by TiO_2, CeO_2, Y_2O_3 nanoparticles (Fig. 3), for Al_2O_3 nanoparticles a parameter decreases but c parameter increase, for ZrO_2 nanoparticles it is conversely, for SiO_2 nanoparticles both parameter increase. Changes of the zinc oxide lattice parameters can be caused by the introduction of the nanoparticles cations in the lattice zinc oxide.

UV–vis diffuse reflectance spectroscopy is one of the most employed methods for measuring forbidden energy gap of powders as well as a qualitative analysis of the color centers concentration. Electron and proton exposure on zinc oxide powders leads to the formation of different concentrations of a radiation defects, which are manifested as bands of induced absorption (Fig. 4). The spectra of induced absorption obtained by subtracting spectra after irradiation from spectra before irradiation.

The reflectance spectra following irradiation by protons show a high intensity of the absorption bands in the UV and visible region. In the near-IR region, the intensity of the bands is insignificant. However, the spectra after irradiation by electrons have a negative intensity of the bands in the entire spectral range. This effect can be due to radiation bleaching of powders – desorption of gas molecules and a decrease in the concentration of native defects. The integral absorption band can be due to various types of defects absorbing photon in UV and visible region.

The absorption band energy of the formed defects depends on their type and correlates with their level in band gap. The energy levels of donor defects in ZnO, in the Kroger-Vink notation, belong to interstitial zinc ions Zn_i^X – 0.05, 0.061 or 1.03 eV [8–12], Zn_i^t – 0.031, 0.1 or 0.46 eV [9,12–14], $Zn_i^\cdot$ – 0.2, 0.25, 0.5 or 0.99 eV [10,11,15], $Zn_i^{\cdot\cdot}$ – 0.08 or 0.15 eV [11,16] and oxygen vacancy V_O^X – 0.05, 1.62, 2.3, 2.56, 3.0 eV [8–14], $V_O^\cdot$ – 0.84, 2.0, 2.36, 3.1 eV [10,11,15], $V_O^{\cdot\cdot}$ – 0.25, 0.61, 1.2 eV [8,9,11,16]. The energy levels of acceptor defects include the following: interstitial oxygen O_i^X – 2.28 or 2.96 eV [11,13,14], O_i' – 1.83 or 3.02 eV [11], O_i'' – 2.41 or 2.61 eV [11], and zinc vacancy V_{Zn}^X – 1.72, 1.93, 2.2, 3.06 eV [13,14,15], V_{Zn}' – 2.11, 2.6, 2.66, 2.95, 3.14 eV [10,11,15], V_{Zn}'' – 0.56, 3.05 eV [8,10,11,15], antisite oxygen O_{Zn} – 2.38 eV [13,14], complex of oxygen vacancy and zinc interstitial V_O-Zn_i – 2.16 eV [14]. Thus, the defects of the interstitial zinc and anionic vacancies in a different charge state probably can determine the absorption of photons in the short-wave region of the spectrum, but the transitions between donor and acceptor defects levels as well as a complex defects can determine the absorption in the long-wavelength region. The presence of radiation-induced defects may eventually lead to changes in the electronic subsystem zinc oxide and affect on the band gap.

The optical excitation of the electrons from the valence band to the conduction band is evidenced by an increase in the absorbance at a given photon energy (band gap energy). Fig. 5 shows the reflectance spectra in the region near fundamental absorption edge. The reflectance of the all powders increases linearly with decreasing photon energy. Proton exposure (Fig. 5C and F) lead to decrease of spectral reflectance in the region beyond the fundamental absorption edge, after electron exposure significant changes are not observed. The modification leads to blue shift in absorption edge.

To evaluate band gap of powders from diffuse reflectance spectra measured on integrated spheres developed several methods: extrapolating the linear line of the reflectance curve with the photon energy
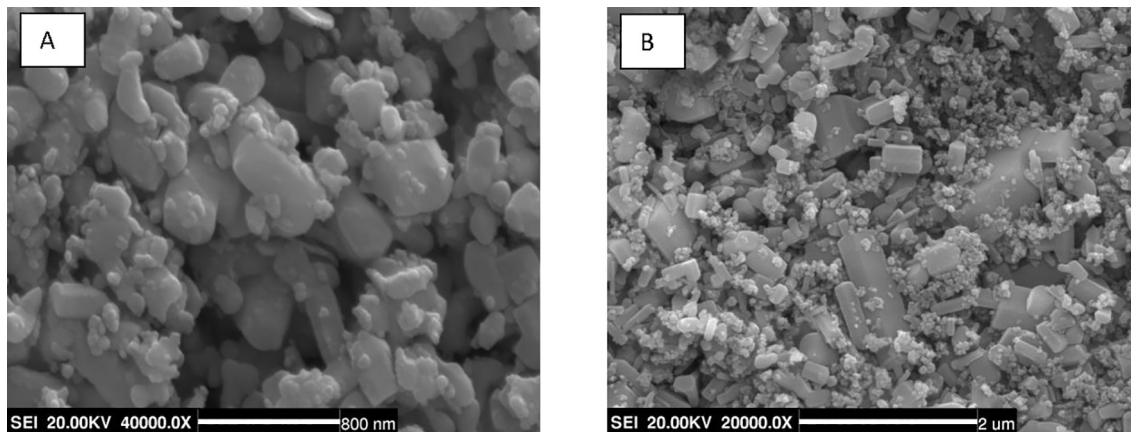

Fig. 1. The photograph of the modified powder of the zinc oxide modified by the nanoparticles ZrO_2 (A) and SiO_2 (B).