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Swift Xe^{26+} Ion Irradiation Effect on Luminescent Properties of Undoped and Cd-Doped ZnO Films

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Here we report the effect of the irradiation by 167 MeV Xe^{26+} ions (in the fluence range up to 3×10^{12} ions/cm^2) on the undoped and Cd-doped (0.4, 0.5 at.%) ZnO films deposited by radiofrequency magnetron sputtering. As-grown and irradiated samples were investigated by cathodoluminescence spectroscopy. It was found that the radiation causes a decrease in intensity of luminescent peaks and a redistribution of the radiative recombination channels. We revealed that the cadmium incorporation into ZnO lattice enhances the radiation resistance of ZnO film.

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1. Introduction

Trends in the electronic engineering lead to the conditions for technological breakthrough in the field of power electronics and optoelectronics. The basis of this breakthrough is the new class of semiconductor materials — wide-gap semiconductors (GaN, ZnO, SiC) and various heterostructures based on them. They can be used at high temperatures (400–500 °C) and high voltages (3 MV/cm). Another important property is their stability in extreme conditions under high radiation. According to above mentioned factors the most promising candidate for these applications and suitable for using in high background radiation, for example, in outer space is ZnO [1, 2]. The benefits of zinc oxide are low cost and large reserves of raw deposits. It is due to large degree of ionicity of the chemical bonds [3]. The fraction of swift heavy ions (SHI) in spectrum of the galactic cosmic rays is about 1% only, but they have the most damaging ability due to high level of specific ionization energy losses. Due to the inelastic interaction with matter, swift heavy ions leave a trail of changed material along its path through the medium. There are two main mechanisms responsible for this process [4]: the passing ion transfers its energy to electrons by inelastic collisions, causing their ejection from the atoms. During the electron explosion, the core ions gain kinetic energy due to a repulsive Coulomb interaction which forces them to move away from the core — Coulomb explosion — introducing defects and vacancies in the material; the energy from a projectile ion deposits firstly in the electron subsystem and subsequently relaxed to the lattice subsystem through electron–phonon coupling, leading to a large local temperature increase. The last can provide the phase transition in the cylindrical region. As the process is very rapid, the column of transformed material will be quenched, resulting in the "freezing" of defects.

In this study we report the use of cathodoluminescence (CL) as a tool for an investigation of optical properties for undoped and doped with small amount of isoelectronic cadmium content ZnO films under swift heavy ions irradiation. This method is used to obtain detailed luminescence information about the origin of specific emissions and distribution of radiative defects in ZnO. The incident electron beam produces free electron–hole pair which recombinate across the band gap or between deep levels and the band edges. The characteristic feature of CL is a possibility of excitement of internal part of material whose depth is determined by accelerating voltage.

The doping by isoelectronic impurities can significantly increase the chances of applications [5, 6]. In particular, it was found that the small concentration of the cadmium (0.4 at.%) significantly enhances the ultraviolet emission associated with excitonic transitions. The enhancement effect mainly results from an appearance of the cadmium isoelectronic traps, which may bind an exciton, thereby increasing the probability of radiation recombination [5]. It was found that irradiated Cd-doped ZnO films demonstrate an improvement of crystal structure in comparison with undoped ones. It can be explained by the (i) an increase in size of crystalline blocks, (ii) a relaxation of strain between grains in the films and (iii) a reduction of defects in ZnO crystal lattice [6]. We suppose that cadmium can act as getter in zinc oxide, absorbing defects, which were generated during heavy ions irradiation. The aim of this work is to study the influence of swift heavy Xe ions irradiation on luminescent properties of undoped and Cd-doped ZnO films.

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2. Experimental details

The ZnO films were deposited on *c*-orientation sapphire substrates at 400 °C using the radio frequency magnetron sputtering technique. The Zn metal targets with cadmium tablets inserts were installed at 40 mm from substrate. The mixture of high purity argon and oxygen at 2:1 ratio was used as working and reaction gases, respectively. The power of magnetron system was 200 W. The time of deposition was 1 h for all films. The other details of the films deposition process can be found elsewhere [5].

The films were irradiated by Xe^{26+} ions with energy of 167 MeV to a fluence 3×10^{12} ions/cm^2. Irradiation was performed using IC-100 cyclotron at Flerov Laboratory of Nuclear Reactions JINR, Dubna. Accordingly to SRIM code [7], the electronic stopping power of 167 MeV Xe ions in ZnO is 25.9 keV/nm while nuclear stopping power is 0.124 keV/nm that is much less as compared to the electronic one. The projected range of Xe ions was calculated to be 11.54 μm so that the ions penetrated the substrate far beyond the film thickness ($\leq$ 1μm). Therefore, any structural modification in the film was expected to be due to the damage produced by swift xenon ions only.

The CL spectra were taken in a JEOL 35C scanning electron microscope equipped with an Oxford Instruments MonoCL2 CL system and Hamamatsu R943-02 Peltier cooled photomultiplier. The incident electron accelerating voltage is 15 kV. All CL spectra discussed here were taken at room temperature. The incident electron accelerating voltage of 15 kV used in this study corresponds to primary electron penetration range $R_e = 0.77$ μm, with intensity maximum at $\approx$ $2/3R_e$ [8].

3. Results and discussion

The analysis of CL spectra of as-grown samples was discussed in our previous work [5]. Figure 1 illustrates the CL spectra of as-grown and irradiated undoped and Cd-doped ZnO films. For better understanding the spectra were plotted as a function of energy. This conversion needs the transposition of the Y-axis by a factor λ^2/hc [9]. The intensity is expressed in arbitrary units of photon counts.

The high energy emission peak observed in as-grown undoped ZnO film was composed of intense near band edge (NBE) emission with a maximum at $\approx$ 3.21 eV and violet peak at $\approx$ 3.06 eV (Fig. 2). The first one is due to radiative recombination of free excitons. It is noteworthy that the energy position of the NBE peak for ZnO films is shifted towards low energy side by 50 meV in comparison with similar peak for bulk ZnO (3.26 eV at room temperature [10]). It can be caused by elastic tensile strain is a result of the misfit between substrate and film. The 3.06 eV peak in the violet region is due to band transition from the zinc interstitial (Zn_I) level to the valence band [11]. The peak position and full width at half maximum (FWHM) of irradiated film are not changed.

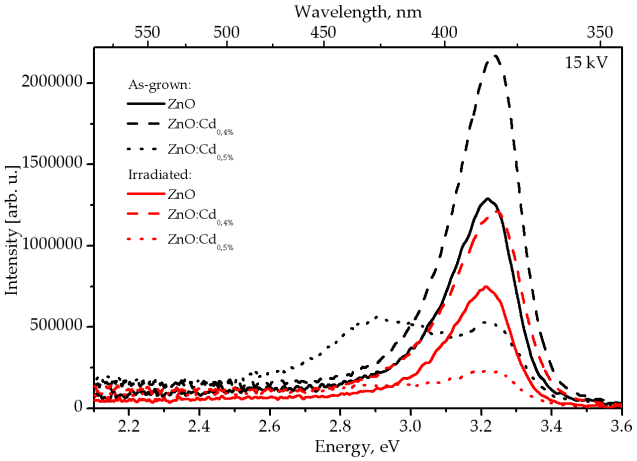

Fig. 1. CL spectra of as-grown and SHI irradiated undoped and Cd-doped ZnO films.

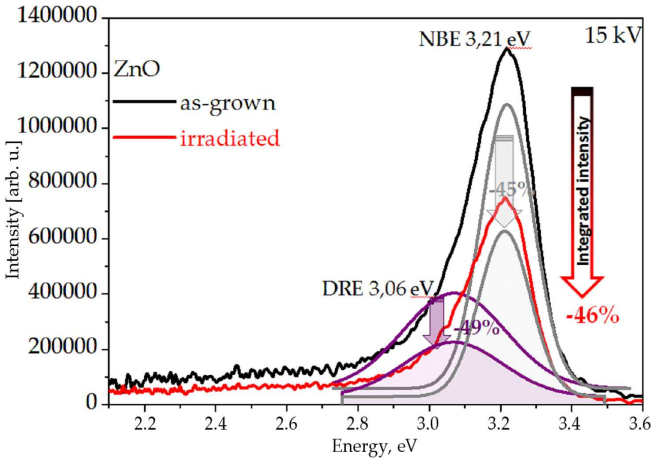

Fig. 2. Deconvolution of CL spectra of as-grown and irradiated undoped ZnO film.

Comparison of the spectra of the as-grown and irradiated samples shows that SHI promotes reducing the intensity of near-band edge (NBE) emission peak, which can be associated with an increase in density of the defects playing roles of nonradiative recombination centers. To clarify the nature of the optical transitions we have performed a deconvolution of all spectra using Gaussian fitting procedure. At the next stage, we calculated the percentage ratio between integral intensity of NBE peak (I^V_{NBE}) of virgin samples and similar one for irradiated counterparts (I^{irr}_{NBE}). The same procedure was applied for the comparison of the defect related emission (DRE) peaks (I^V_{DRE} vs. I^{irr}_{DRE}) for our samples. Let us explain obtained results. It was found that I^{irr}_{NBE} is 45% smaller than I^V_{NBE}, while the I^{irr}_{DRE} is 49% weaker than I^V_{DRE} (Fig. 2). Obviously, such behavior of the CL peaks is because of damage introduced by SHI irradiation.

Figure 3 shows the deconvoluted CL spectra of as-grown and irradiated ZnO films doped by

0.4 at.% cadmium. One can see decrease of NBE emission intensity. In addition, we can also observe the redistribution of peak intensities similar to the undoped ZnO. However, integrated intensity of the whole spectrum and the intensity of the free excitonic emission at 3.22 eV of the irradiated samples are 38% and 37% lower than those of virgin counterparts, respectively (Fig. 3). At the same time $I^{\mathrm{irr}}_{\mathrm{DRE}}$ is 44% weaker than $I^{\mathrm{V}}_{\mathrm{DRE}}$ (Fig. 3).

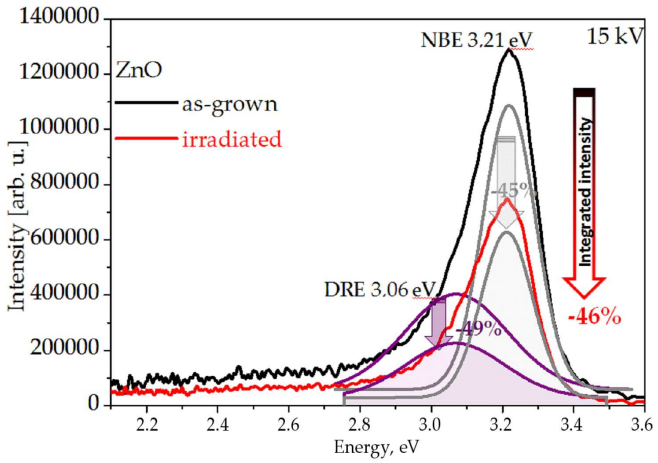

Fig. 3. Deconvolution of CL spectra of as-grown and irradiated ZnO:$Cd_{0.4\ at.\%}$ film.

A pronounced quenching of the defect luminescence is observed in the case of irradiated doped ZnO:$Cd_{0.5}$ at.% sample (Fig. 4). The peak, which corresponds to Zn_I intrinsic defect, is reduced by 80% compared to initial one (Fig. 4). Simultaneously the intensity of the NBE decreases only to 37% relatively to conformable intensity of as-grown sample. In addition it was revealed the appearance of the small peak of structureless green luminescence at 2.4 eV, which is associated with the donor level of oxygen vacancy (V_O) [12].

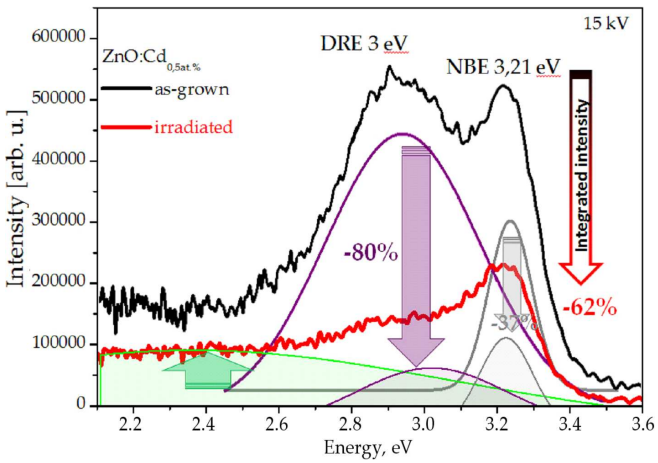

Fig. 4. Deconvolution of CL spectra of as-grown and irradiated ZnO:$Cd_{0.5\ at.\%}$ film.

A significant decrease in the intensity of violet emission after irradiation may be due to SHI influence on Zn_I. The latter are considered to be the most mobile defects in ZnO [13], which can create nonradiative recombination centers.

Ratheesh Kumar et al. [14] reported that blue-green emission in ZnO film (which is due to the antisite oxygen) decrease as the ion fluence increases. This process was explained by depletion of the defect level related to the antisite oxygen. Burlacu et al. [15] also observed the redistributions of electronic transitions in ZnO nanostructures and films introduced by high dense ion irradiation in the same conditions. It was shown the change of excitonic luminescence to the luminescence related to the tailing of the density of states. On the one hand, authors found that ZnO nanorods and nanodots grown by MOCVD exhibit enhanced radiation hardness as compared to films, and on the other hand the introduction of isoelectonic doping is an effective tool for reducing damage effect of SHI irradiation, too.

4. Conclusions

We have studied the influence of swift Xe^{26+} ion irradiation on luminescent properties of undoped and Cd-doped ZnO thin films. Irradiated samples exhibit lower emission intensity since they suffer from higher defect densities created by swift heavy ions, compared to as-grown ones. The analysis of composition for cathodoluminescence spectra of ZnO with small Cd content demonstrates that Cd ions incorporating into ZnO lattice enhance the radiation resistance of ZnO and improve the relation between the near band emission and defect related emission of cathodoluminescence.

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