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PULSED LASER ASSISTED FABRICATION OF Co-DOPED ZnO NANOCRYSTALLINE LAYERS ON A GLASS SUBSTRATE

NATALIE TARASENKA[1], VLADISLAV KORNEV[1],
SVETLANA PASHAYAN[2] and NIKOLAI TARASENKO[1]

[1]*B.I. Stepanov Institute of Physics, National Academy of Sciences of Belarus, Minsk 220072, Belarus*

[2]*Institute for Physical Research, National Academy of Sciences of Armenia, 0203, Ashtarak-2, Republic of Armenia*

E-mail n.tarasenko@ifanbel.bas-net.by

Abstract. In this work, we present a new approach for fabrication of Co-doped ZnO nanocrystalline films based on the pulsed laser treatment of Co/ZnO layers on a glass substrate. The purpose is to achieve the incorporation of Co^{2+} ions on the Zn site inside ZnO nanoclusters through the fast laser induced heating, subsequent melting, and re-solidification processes at high cooling rates.

1. INTRODUCTION

Doped semiconductors nanostructures are of special interest in recent years due to the fact that their electronic, optical and magnetic properties can be tuned by varying their composition and size thus finding exceeding applications in electronics, engineering, plasmonics, biomedicine and catalysis (Yoo, Hocheon, et al. 2021, Wang, C. et al. 2012). The dependence of the doped NPs properties on size and composition explains the importance of control over their preparation procedure. Among the different techniques for NPs synthesis, plasma and laser assisted processes have received much attention last years due to the combination of such advantages, as high production rate, versatility and possibility of control over the NPs formation process (Tarasenka, N. et al. 2017, Kulinich, S. et al. 2013). However, although a number of successful applications of these processes for NPs production have been demonstrated, a task of the targeted fabrication of alloyed and doped NPs with controlled properties is still not completely solved.

This paper is focused on the pulsed laser assisted fabrication of Co-doped ZnO nanocrystalline layers on a glass substrate. Among the different doped ZnO structures, cobalt-doped ZnO films have attracted much attention because of their potential applications in magneto-electrical and magneto-optical devices, spintronics, and as laser passive Q-switchers. Zinc oxide is a wide band gap semiconductor which is promising for these applications because of its chemical stability, low toxity and low cost. The composition, morphology, and optical properties of the resulting nanoparticles and films have been studied.

2. EXPERIMENTAL

The developed method of doped ZnO nanoparticles preparation is based on laser irradiation of the bi-layer structure consisting of the ZnO and Co films. The scheme of the experimental procedure is presented in Figure 1. First, 100 nm ZnO layer was deposited onto a glass substrate by magnetron sputtering technique. For the Co layer, Co NPs colloid was prepared by laser ablation of Co target in acetone. For this, Nd:YAG laser, operating on the fundamental harmonic (1064 nm) with a pulse duration of 8 ns, energy 80 mJ/pulse, repetition rate 10 Hz was used. After that Co NPs deposition was carried out by spin-coating over the preliminarily formed ZnO layer. Finally, laser treatment of the Co/ZnO bilayer film was performed using the 4th harmonic of a ns Nd:YAG laser (wavelength 266 nm, pulse repetition 10 Hz, energy 0.5-5.5 mJ/pulse, laser beam diameter 2 mm). In order to establish the optimal conditions for the doping, the dependence of Co incorporation on the laser parameters was studied. After adjusting the laser fluence to provide several hundreds nanometer penetration depth for the incident laser radiation it was possible to deliver very rapid melt/solidification cycles.

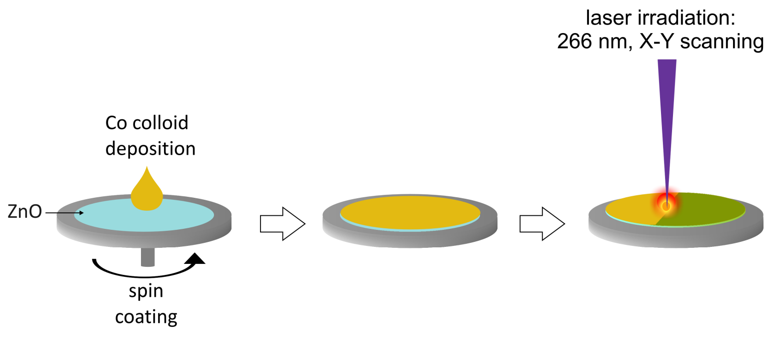

Figure 1: Scheme of the experiment on laser processing of the bilayer Co-ZnO structure

The morphology, structure and optical characteristics of the fabricated films depending on the experimental conditions were analyzed. To quantify the Co content in the sample after laser treatment, LIBS analysis of the samples composition was performed. The results showed the formation of the films with a rather homogenous distribution of cobalt ions inside the ZnO matrix with a dopant concentration of about 5%. The incorporation of Co ions into the ZnO structure could be also elucidated from the Raman spectra and XRD analysis.

3. RESULTS AND DISCUSSION

Incorporation of dopants has substantial effect on the optical properties of ZnO that were studied by measuring UV-Vis absorption spectra of the prepared films. The analysis of the absorption spectra was used to determine the changes in the energy band structure of ZnO in result of Co doping. The absorption spectrum of the ZnO film has a typical form for the zinc oxide structures, and, as can be seen in Figure 2, it consists of a wide band in the ultraviolet region of the spectrum with a rapid increase in the absorption near the band gap (at a wavelength of ~ 370 nm). The absorption spectrum of ZnO-Co sample after laser irradiation shows the absorption (Figure 2a) around 370–395 nm, and the absorption edge is slightly shifted upon cobalt doping in ZnO, which confirms the presence of Co in the crystal lattice of ZnO. In addition, in the irradiated sample several additional absorption bands at around 565 nm, 603 nm and 644 nm were observed that are typical to the Co-doped ZnO samples and correspond to the d–d transition of Co^{2+} ions in the tetrahedral field of ZnO (Ji, H. et al. 2018).

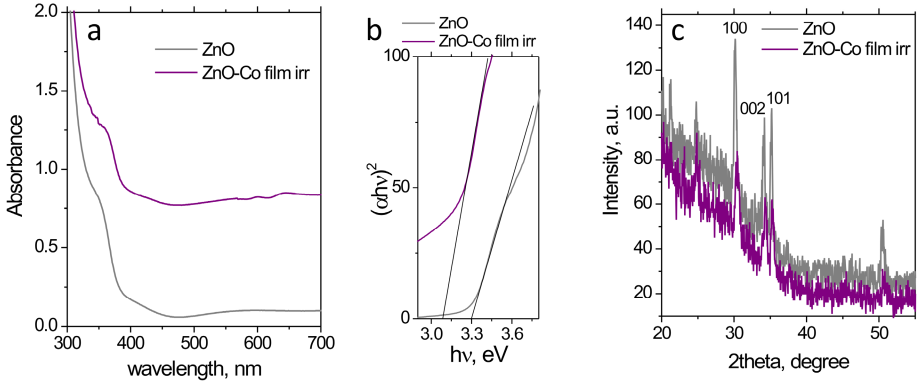

Figure 2: Properties of the ZnO and Co/ZnO films on the glass substrate after laser treatment (5.5 mJ/pulse): a – optical absorption spectra; b – Tauc plots: c – XRD patterns

The band gaps of the prepared ZnO samples were estimated using the Tauc`s model, being 3.13 eV and 3.3 eV for the Co-doped ZnO and pure ZnO films, respectively (Figure 2b). As can be seen the band gap values for both films were slightly lower than the tabulated value for the bulk material (Eg = 3.37 eV). This can be caused by the formation of defective energy levels near the bottom of the conduction band, for example, due to the partial non-stoichiometry of the film composition.

XRD of the fabricated thin films presented in Figure 2c, revealed the wurtzite-type structure of the formed samples. Cobalt ions introduced as dopants shifted the diffraction peaks to higher angles, suggesting the unit cell contracting. Variation of the ZnO XRD peaks relative intensity additionally supports the conclusion on Co^{2+} substitution of Zn^{2+} in the ZnO lattice with the Co-doped ZnO formation.

Thus, the performed studies have shown the possibility of Co-doped zinc oxide thin films formation in the process of laser treatment of zinc and cobalt films. The results obtained are of interest for further development of laser ablation methods for solving practical problems of the doped nanostructures synthesis with controlled size and composition.

Acknowledgments

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