Optical Properties of Nanoscale BiFeO$_3$/BaTiO$_3$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ Composite Films Obtained by the Pulsed-Laser Deposition Method

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Abstract—Nanoscale (30–100 nm) films of BiFeO$_3$/BaTiO$_3$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ complex composition have been obtained by the pulsed-laser deposition method. Optical properties of the films were studied in the wavelength range of 250–1000 nm. It is shown that the optical properties of amorphous films deposited at room temperature are explained by the Tauc model for amorphous semiconductors. An increase in the optical gap from 1.7 to 1.95 eV was observed with decreasing film thickness. Allowed direct-band transitions ($E_g = 3.1$ eV) were observed after annealing of films independent of their thickness.

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1. INTRODUCTION

Materials possessing simultaneously ferromagnetic and ferroelectric properties attract at present considerable attention. These materials (multiferroics (MF)) having a remarkable magnetoelectric effect find wide application to information technologies, sensors, and devices of rapidly developing spintronics [1, 2]. However, at present stage, only several single-phase MF are the most studied, such as BiFeO$_3$ and RMnO$_3$ (with R being rare-earth metal). Optical properties of films of these materials are recently studied in detail [3–5].

In connection with intensive development of spintronics as a competing direction in raising the effective frequency of operation of processors, as well as because of commercial prohibition of using lead in materials (lead-free) of functional electronics, the demand for films of new, multiphase (MP) materials is essentially increased in spite that obtaining high-quality MP MF films is hitherto a very complicated problem.

In the present work we obtain for the first time nanoscaled composite BiFeO$_3$/BaTiO$_3$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ (BFO/BTO/NZF) films with use of pulsed-laser deposition technique and study their optical properties.

2. TECHNIQUES OF EXPERIMENT

By the method of vacuum ($4\times10^{-5}$ mm Hg) pulsed-laser (wavelength 1.064 μm, pulse duration 30 ns, energy 0.7 J, intensity in the region of target irradiation $\sim 10^7$ W/cm$^2$, and the repetition rate of evaporating pulses 1 Hz) deposition from the target ($1-x-y$) BiFeO$_{3-x}$BaTiO$_3-y$Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ ($x = y = 0.3$) onto the sapphire (c-Al$_2$O$_3$) substrate nanosize (30–100 nm) films were obtained of complex composition. Substrates of c-Al$_2$O$_3$ were degreased in pure acetone, washed in bidistilled water and dried with the compressed air jet. Short-term (20–30 min) annealing of substrates was performed prior to film deposition at temperature 100°C in $4\times10^{-5}$ mm Hg vacuum. Films were deposited at room temperature (RT) and at the temperature of substrate 400°C.

Crystalline structure of films was studied by the method of diffraction of high-energy electrons in the reflection regime (accelerating voltage 75 kV) with electron diffractometer EMP-100M. The thickness of films was measured with profilometer AMBIOS XP-2. The thickness per a single evaporating pulse was...
determined by division of the measured thickness of a relatively thick layer by the number of evaporating laser pulses. Measurements have shown that the thickness of a layer deposited during a single evaporating pulse amounts to 0.7–1 nm.

We performed independent measurements of coefficients of transmission \( T \) and reflection \( R \) with a spectrometer StellarNet BLK-CXR-SR (wavelength range 250–1000 nm). The frequency dependence of the absorption coefficient \( \alpha \) of films was determined on the basis of these data. We also studied the crystalline structure and optical properties of films two hours annealed in air at the temperature 750°C.

3. RESULTS AND THEIR DISCUSSION

It was established from electron-diffraction investigations that films obtained at RT and 400°C have amorphous structure independent of their thickness. But annealed films had polycrystalline structure. It should be noted that after annealing of films deposited at RT, some increase in their thickness is observed.

Optical properties of deposited films (thickness 30–100 nm) were studied in the wavelength range 250–1000 nm (at smaller thicknesses the experimental error increases for annealed films because of weak absorption). We conducted independent measurements of \( T \) and \( R \) for normal incidence of light. Figure 1 shows the transmission spectra of films with different thicknesses deposited at RT. For comparison Fig. 1 shows also the transmission spectrum of a 80 nm-thick film deposited at RT after annealing.

Comparison of transmission spectra of the obtained films has shown that the difference in transmission of films obtained at RT and 400°C is small. Noticeable increase in transmission in visible and near IR wavelength ranges is observed after annealing of films deposited at RT (Fig. 1).

![Fig. 1. Transmission spectra of BFO/BTO/NZF films of different thicknesses deposited at RT: (1) 35nm, (2) 45 nm, (3) 56 nm, (4) 80 nm, and (5) 80 nm film after annealing.](image)

Frequency dependence of \( \alpha \) of obtained films is determined by means of the well-known formula

\[
T = (1 - R)^2 e^{-\alpha d} \left(1 - R^2 e^{-2\alpha d}\right)
\]

where \( d \) is the film thickness. For further processing of data of performed measurements it was taken into account that optical properties of both amorphous and crystalline materials may completely be derived from the general single-electron expression for the imaginary part of the dielectric constant \( \varepsilon_2(\omega) \) [7]. Behavior of \( \varepsilon_2 \) in a crystal is determined by the requirement of momentum conservation in optical transitions. A peculiarity typical for amorphous semiconductors, which is caused by violation of momentum conservation rule, is quadratic dependence of the absorption edge on the photon energy. For materials with magnetic properties it is necessary to allow, in general case, for also the magnetic permeability \( \mu \) and its dispersion depending on the inner structure of material. For bulk materials the \( \mu \)-dependence of optical constants, even in ferromagnetic materials, may be neglected in visible and UV spectral ranges, since at these frequencies of electromagnetic field \( \mu \) slightly differs from unity. This statement is for films not always valid, however, for subsequent description of optical properties of amorphous films obtained by us at RT we take \( \mu = 1 \). In this case the problem of determination of \( \varepsilon_2 \) is simplified. Using the concepts of coefficients of refraction \( n \) and extinction \( k \) introduced at interaction of electromagnetic wave with isotropic medium and the relations connecting different optical functions, \( \alpha = 4\pi k/\lambda \), \( R = \left( (n-1)^2 + k^2 \right)/\left( (n+1)^2 + k^2 \right) \), \( \varepsilon_2 = 2nk \), and