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Visible Photoluminescence of Zinc Oxide Films Electrochemically Deposited on Silicon Substrates

E. B. Chubenko[a]*, V. P. Bondarenko[a], and M. Balucani[b]

[a] *Belarussian State University of Informatics and Radioelectronics, Minsk, 220013 Belarus*

[b] *University of Rome "La Sapienza," 00184 Rome, Italy*

**e-mail: eugene.chubenko@gmail.com*

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Abstract—Continuous crystalline films of zinc oxide (ZnO) with thicknesses of 6–10 μm were obtained by electrochemical deposition from aqueous zinc nitrate solutions on silicon substrates with a buffer nickel layer. X-ray diffraction measurements showed that the polycrystalline films possess a hexagonal crystal lattice with predominant (0002) orientation. The obtained ZnO films exhibit strong photoluminescence in the visible spectral range at room temperature.

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Zinc oxide (ZnO) is a direct-band semiconductor with a large bandgap (3.2–3.4 eV). This is a promising material for high-efficiency light-emitting devices, solar cells, and various sensors [1–3]. At present, singe crystal ZnO wafers are available from several manufacturers. However, these substrates are very expensive and have diameters not exceeding 2.5 cm [4]. This does not meet the requirements of modern microelectronic technologies, which are mostly adapted to processing wafers with large diameters, primarily those of single crystal silicon. Therefore, an important direction in the development of ZnO technology is related to the creation of methods for obtaining crystalline films of this compound on large substrates.

ZnO films can be obtained by various methods. However, electrochemical deposition techniques offer some advantages, in particular, as compared to molecular beam epitaxy or chemical vapor deposition [2]. The most important advantages are a lower cost of the process, low temperature, and the possibility of processing large-area substrates. In addition, the composition, morphology, and thickness of a deposited film can be easily controlled by varying the electric parameters. The electrochemical deposition of ZnO onto various substrates has been described in great detail [3, 5].

The formation of continuous ZnO films on silicon substrates is complicated by the difference of the crystal lattice types in the two materials. Another obstacle is the formation of a space charge region at the substrate/electrolyte interface during the electrochemical deposition. These problems can be solved using substrates with buffer metal layers.

In this investigation, the initial substrates were (100)-oriented n^+-type antimony-doped single crystal silicon wafers with a resistivity of 0.01 Ω cm. Initially, a 0.5-μm-thick nickel buffer layer was formed on the silicon surface by electrochemical methods using a standard sulfamic acid solution. This buffer ensured more uniform current distribution during the subsequent deposition of the semiconducting material (ZnO) from a 0.05 M aqueous solution of $Zn(NO_3)_2$ at pH 3.5. This process was carried out in a temperature-controlled three-electrode electrochemical glass cell equipped with a magnetic stirrer. The current and voltage sweep was provided by a PI-50-1.1 potentiostat, which was computer-controlled via an Advantech PCI-1710HG analog-to-digital converter. Prior to the deposition of ZnO, the surface of the nickel buffer layer was washed in distilled water. The open surface area was about 3 cm^2. The deposition was performed in a galvanostatic mode at a current density of 5 mA/cm^2 and a temperature of 70°C. The as-deposited films were homogeneous and had thicknesses within 6–10 μm. After the deposition, some samples were annealed in air at 500°C for 15 min.

The as-deposited ZnO films were studied by the electron-probe microanalysis on a Stereoscan 360 electron microscope (Cambridge Instruments) equipped with a Link Analytical AN 10000 energy-dispersive X-ray (EDX) microanalyzer. The results showed that ZnO films deposited on silicon substrates have a stoichiometric composition (50 at. % zinc and 50 at. % oxygen).

Figure 1 presents the X-ray diffraction (XRD) patterns of ZnO films measured before and after a 15-min annealing in air at 500°C. These diagrams show that the ZnO films have a hexagonal crystal lattice and possess a polycrystalline structure with the predominant

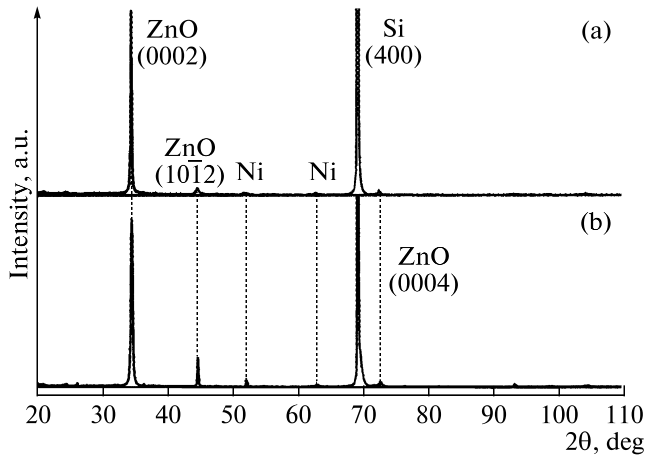

Fig. 1. XRD patterns of electrochemically deposited ZnO films (a) in the as-deposited state and (b) after a 15-min annealing in air at 500°C (CuK_α radiation).

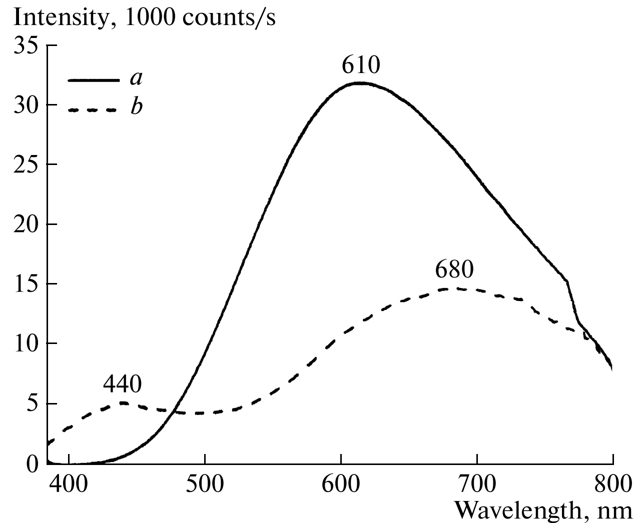

Fig. 2. PL spectra of ZnO films measured at 20°C for samples (*a*) in the as-deposited state and (*b*) after a 15-min annealing in air at 500°C. The samples were excited by radiation with a wavelength of 360 nm.

crystallographic orientation (0002). An increase in the ZnO ($10\bar{1}2$) phase after the annealing can be related to a partial crystallization of amorphous ZnO, which is also present in the film.

Figure 2 shows the spectra of photoluminescence (PL) of ZnO films also measured before and after the annealing. The samples were excited by a xenon lamp. The PL measurements were performed at 20°C. The emission was detected by a photoelectron multiplier operating in the photon count mode. As can be seen from Fig. 2, the spectrum of the unannealed sample displays a single broad PL band with a maximum in the orange spectral range (at about 610 nm). After thermal annealing in air at 500°C, this peak shifts toward longer wavelengths (to ~680 nm). Since the material was undoped and the EDX analysis revealed no foreign impurities, this PL band may be related to some intrinsic defects of the material. According to the published data [6], this band can represent a superposition of two independent bands related to the recombination via levels in the bandgap of the semiconductor, which are created by the ionized oxygen vacancies and interstitial oxygen atoms in the crystal lattice of ZnO. The PL component due to oxygen vacancies is peaked at shorter wavelength (550 nm), while the component due to interstitial oxygen atoms is peaked at a greater wavelength (650 nm). The positions of these maxima can vary depending on the excitation wavelength [6] and the material structure [6, 7]. During the annealing of samples in air, free oxygen adsorbs at the film surface and incorporates into the crystalline lattice of ZnO. As a result, the major fraction of oxygen vacancies is compensated, while the concentration of interstitial oxygen atoms in the film volume remains unchanged (or even increases in the near-surface layers). These processes account for a decrease in the intensity of the PL band (550 nm) related to the ionized oxygen vacancies. The intensity of the PL band related to the interstitial oxygen atoms remains unchanged or slightly increases [6]. The proposed mechanism explains a shift of the PL band in the red-orange spectral range and a decrease in its intensity, which were observed after the annealing of electrochemically deposited ZnO films.

Figure 3 presents the spectra of PL excitation in the ZnO films under consideration. The maximum excitation of the PL band in the orange spectral range both before and after the annealing was observed at 370–375 nm, which corresponds to a quantum energy of 3.35–3.3 eV. This value coincides with the bandgap width of bulk ZnO. Therefore the excitation of this PL band is related to the direct electron transitions from the valence band to conduction band of the semiconductor under the action of exciting radiation. After the annealing of ZnO films in air, the excitation spectrum for this PL band exhibited no significant changes except a small shift toward longer wavelengths. This change is related to the fact that the PL was detected at a greater wavelength (680 nm instead of 610 nm) [6].

The PL band in the region of 440 nm, which appeared after annealing of the samples, can be also related according to [8, 9] to some defects in the volume of ZnO films (e.g., to the presence of interstitial oxygen atoms). However, the true reason for the PL in this spectral range is yet not unambiguously established so far. The maximum of the excitation spectrum for this band is situated in the region of 370 nm. This band is also excited due to the direct electron transitions from the valence band to conduction band of the semiconductor. The efficiency of PL excitation in this band by high-energy quanta is lower than that for the PL band in the orange spectral range.

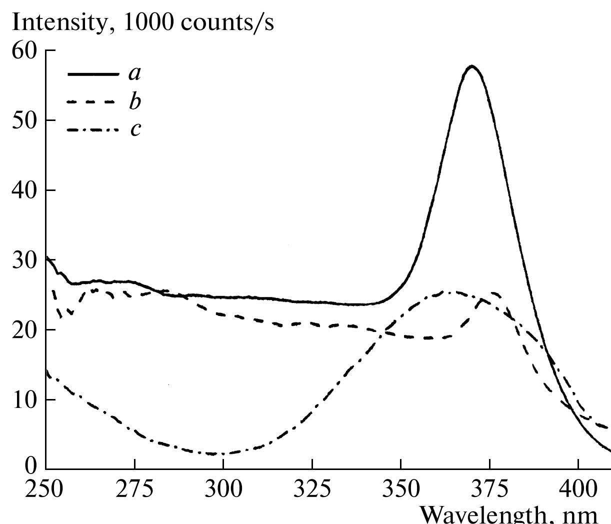

Fig. 3. Excitation spectra for various PL bands in ZnO films measured at 20°C: (*a*) PL at 610 nm in the as-deposited state; (*b*, *c*) PL at 680 and 440 nm, respectively, after a 15-min annealing in air at 500°C.

In conclusion, the results obtained in this study are indicative of the possibility of obtaining continuous, highly textured crystalline ZnO films on silicon substrates with a thin nickel buffer layer using a relatively simple and economically profitable electrochemical method. The obtained films exhibit a high (for the given method of synthesis) PL intensity in the visible spectral range. It is established that the thermal annealing in air significantly influences the PL spectra of samples, leading to a decrease in the intensity of a PL band in the orange spectral range (related to the intrinsic defects) and to an increase in the intensity of high-energy PL bands. ZnO films obtained using the proposed technique can be used for manufacturing the active regions of light-emitting and photovoltaic devices, in particular, those integrated with electronic devices on silicon substrates.

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