On the question of structure of ZnO thin films formed by IBAD and subsequently implanted with silver ions

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Abstract. Nanocrystalline ZnO thin films with a thickness of ~235 nm were synthesized by ion beam-assisted deposition (IBAD) technique using a metal target of zinc and oxygen (O₂) as a reactive gas. The near-surface region of the synthesized films was subsequently implanted with 30 keV Ag⁺ ions in the fluence range of (0.25–1)×10¹⁷ ion/cm² at high ion current density of 12 μA/cm². The structure parameters and morphology of as-deposited and subsequently implanted with silver ions ZnO films were investigated by X-ray diffraction and scanning electron microscopy techniques. It was found that the as-deposited ZnO films have inhomogeneous structure, which consists of nanocrystallites and disordered amorphous phase. The nanocrystallites of the obtained ZnO thin films have values of lattice parameters higher than for a bulk ZnO. Subsequent implantation with silver ions leads to a significant radiation heating and microstress relaxation of the film as well as to an increase in the size of nanocrystallites due to the amorphous phase.

1. Introduction
Zinc oxide is a n-type semiconductor with direct bandgap of ~3.4 eV and high exciton binding energy of 60 meV at room temperature [1]. These properties make ZnO an advanced material for optoelectronic devices creation based on it. In addition, zinc oxide has a high optical transparency (T ~ 90%), low resistivity and high radiation resistance [2]. Currently, ZnO is widely used in solar cells as planar transparent electrodes [3,4]. From a practical point of view, such a successful combination of physical-chemical properties of ZnO makes it promising to create UV, blue, white and green light-emitting diodes, optical and gas sensors, HUD-displays etc [5,6]. Additional doping with various impurities is carried out in order to expand the range of ZnO thin films application. In particular, doping of N or Ag is used to change the type of charge carriers from n-type to p-type, for instance [7–9]. Ion implantation is one of the most precise and widely used methods for introduction of impurities into semiconductor materials among other technics of doping. It is well known, that ion implantation leads to structural irradiation-induced defects and even to amorphization of irradiated layer [10]. Since ZnO is a radiation-resistant material [1,2] and does not amorphize even
at high fluence and irradiation energies, so study of the effect of ion implantation on the structural properties of ZnO is an actual topic. In addition, methods and conditions of film synthesis significantly affect the structure [11]. Energy of condensing atoms on a substrate is three orders of magnitude higher for ion beam synthesis of thin films in comparison with other methods, which can lead to the implantation of target atoms into the film during the growth process. Thus, IBAD is a promising technique for thin films synthesis with attractive physical-chemical properties associated with features of the structure during film formation [12,13]. The main aim of this work was to study the structural properties of ZnO thin films obtained by the IBAD technique, as well as to investigate the effect of subsequent silver ion implantation.

2. Experimental details
ZnO thin films were deposited by the IBAD technique onto plane-parallel plates of quartz glass with a diameter of 20 mm and a thickness of 2 mm. Chemically pure Xe (99.99% purity) was used as a working gas. The sputtered target was a metal disk of Zn (99.99% purity) with a diameter of 100 mm and a thickness of 4 mm. The oxygen (99.99% purity) was used as a reactive gas. The pressure during deposition was 2×10^{-2} Pa. The deposition time was 45 min. Subsequent implantation of 30 keV silver ions into the synthesized films was carried out by using ILU-3 ion accelerator in the fluence range of (0.25-1)×10^{17} ion/cm^{2} at ion current density of 12 μA/cm^{2}. The morphology and thickness of the films were determined using a scanning electron microscopy (SEM, Zeiss EVO 50 XVP) technique. The elemental composition of films was investigated by energy-dispersive X-ray spectrometer (EDX, Inca Energy-350) built-in into the vacuum chamber of SEM and X-ray photoelectron spectroscopy setup (XPS, by SPECS). The crystal structure and the phase composition of the films were studied using X-ray diffractometer (XRD, Dron 7) with an X-ray source of Cu-Kα (0.15406 nm).

3. As-deposited ZnO films
Figure 1a shows SEM cross-section of the as-deposited ZnO film. The thickness of the film was obtained from SEM image and was about ~235 nm. The calculated deposition rate was 6 nm/min. The surface morphology of the as-deposited ZnO films is smooth without noticeable features even at high magnification (Fig. 1b).

Elemental analysis of the as-deposited ZnO films was performed using 5 keV electron energy probing beam. Low energy of the beam gave an option to exclude the signal from the substrate (Si). It was found that composition of the obtained films was 49 at.% and 51 at.% for Zn and O, respectively. Elemental composition of the as-deposited ZnO thin films was obtained by EDX and is in a good agreement with XPS data.

X-ray diffraction analysis has shown that ZnO thin films have a polycrystalline wurtzite type structure (Fig. 2). Positions and intensity of reflexes for the powder diffraction pattern of ZnO are
shown with blue lines on Fig. 2 [14]. Intensity of the reflection from the (002) plane is much larger than intensities of other reflections. This indicates an orientated growth of crystallites. We calculated the lattice parameters using the analytic expression in quadratic form for the hexagonal crystal system:

\[ Q = \frac{1}{d^2} = \frac{1}{a^2} \left[ \frac{4}{3} (h^2 + k^2 + hk) + \frac{t^2}{(\frac{c}{a})^2} \right] = \frac{1}{a^2} \left[ \frac{4}{3} s + \frac{t^2}{(\frac{c}{a})^2} \right], \]  

(1)

where \( s = h^2 + k^2 + hk = k^2 + i^2 + ki = i^2 + h^2 + ih, i = -(h + k), h, k \) and \( l \) are Miller indices.

Table 1. Structural parameters of as-deposited ZnO thin films by IBAD technique on quartz glass

| (hkl) | \( \theta \) | \( d_{\text{exp}} \) (Å) | \( d_{\text{lit}} \) (Å) | \( \Delta d \) (%) | \( a=b \) (Å) | \( c \) (Å) |
|------|--------|----------------|----------------|----------------|-------------|----------|
| (100) | 31,00° | 2,882 | 2,814 | 2,4 | 3,327 | - |
| (002) | 33,40° | 2,681 | 2,613 | 2,6 | - | 5,361 |
| (110) | 55,56° | 1,652 | 1,625 | 1,7 | 3,305 | - |
| (103) | 61,45° | 1,507 | 1,481 | 1,7 | 3,285 | 5,428 |

Crystal lattice parameters of the as-deposited ZnO films obtained from the diffractogram (Fig. 2) are represented in Table 1. The lattice parameters \( a \) and \( c \) have values of 3.327 Å and 5.361 Å, respectively, which are much larger than for bulk ZnO (3.250 Å and 5.250 Å). Such increase in values of unit cell parameters may be due to the tensile microstresses that arise from implantation of zinc atoms into the interstitial positions during the growth of the ZnO film.

Let us consider the possibility of this process. In radiation physics, the maximum energy transferred by the incident ion to the target atom in the case of an elastic collision is determined by the following expression:

\[ T_{\text{max}}(E) = \frac{4 M_1 M_2}{(M_1 + M_2)^2} \cdot E, \]  

(2)

where \( M_1 \) and \( M_2 \) are the masses of the incident ion and the target atom, respectively, and \( E \) is the energy of the incident atom. \( T_{\text{max}} \) determines the maximum possible energy of sputtered zinc atoms, which come to the surface of the deposited film and lead to the structural deformation of ZnO.
nanocrystallites. Standard atomic weights of Xe and Zn are 131.29 and 65.38, respectively. The energy of the primary beam (primary ions) is 1 keV. Thus, according to expression (2), \( T_{\text{max}} \) in our case is equal to 0.887 keV.

In the case of ion sputtering, the energy distribution of sputtered zinc atoms \( E_{\text{Zn}} \) is given by:

\[
\frac{dN}{dE} \sim \frac{E_{\text{Zn}}}{(E_{\text{Zn}}+E_b)^3}
\]

This distribution has a maximum at the energy of sputtered zinc atoms \( E_{\text{Zn}} \approx E_b/2 \), where \( E_b \) is the binding energy of surface atoms estimated as \(-4E_s\) (\( E_s \) is the energy of sublimation). Sublimation energy for zinc has a value of 1.356 eV/atom [15]. Therefore, \( E_b \) will have a value of \(-4E_s = 5.424 \) eV. According to the obtained data, we have plotted energy distribution of condensing zinc atoms (Fig. 3). As it can be seen from the Figure 3 there is a high-energy tail in the energy distribution of the condensing zinc atoms. High-energy zinc atoms from this distribution region can be implanted into a near-surface thin region of the film during deposition and produce microstresses in it. Magnitude and sign of microstresses depend on the structure of the film. We have determined the average projection range \( R_p \) and the standard deviation \( \Delta R_p \) of Zn ions implanted into the ZnO matrix using the “SRIM” algorithm [16].

Further, we have plotted zinc distribution profile according to the formula taken from Ref. [17] (see Fig. 4). The energy of the Zn ions was taken \( T_{\text{max}} = 0.8 \) keV and the radiation fluence was equals \( 1 \times 10^{15} \) ion/cm\(^2\). The obtained profile has the Gaussian-shape distribution form with \( R_p \approx 1.6 \) nm and \( \Delta R_p \approx 0.73 \) nm. Consequently, the maximum depth distribution of zinc ions is equal to \( R_p + 2\Delta R_p = 3.06 \) nm for \( T_{\text{max}} = 0.8 \) keV. Thus, we can conclude that a small part of the high-energy sputtered zinc atoms were implanted into the surface layer during the deposition of ZnO films. Possibly, zinc atoms implantation leads to the structure deformation of ZnO nanocrystallites. We assume that this process can explain the observed shift of the (002) reflection from ZnO nanocrystallites to the small-angle region of the diffractogram (Fig. 5a). At the same time, the wide arm relating to the amorphous component of ZnO remains at the standard position (002). We note that a shift in the position of reflexes is usually observed from both the nanocrystalline and amorphous components in the case of metal films [18]. The observed changes in the structural parameters of the lattice of ZnO nanocrystallites are about 2-2.5% (see Table 1), which are significantly exceed the limit of elastic deformation of solids.
4. As-implanted with silver ions
Figure 5a shows a decomposition of reflex (002) for the as-deposited ZnO film by two components. The first narrower component (blue line) can be attributed to the nanocrystallites of ZnO. The second component (pink line) is assigned to the intercrystalline amorphous region with crystal lattice parameters corresponding to the literature data for ZnO.

Silver ion implantation leads to a sequential change in the structure of films, which is reflected in the change of the reflex (002) shape (Fig. 5b and Fig. 5c). In particular, quantitative content of 1 and 2 components of as-implanted ZnO film decreases from 40 and 60% to 17 and 38%, respectively (see Table 2) for the minimal radiation fluence ($0.25 \times 10^{17}$ ion/cm$^2$) in our experiments.

![Figure 5. Decomposition of the reflex (002) by components for as-deposited and subsequently implanted with silver ions ZnO films. The blue, pink and green lines correspond to the 1, 2 and 3 components on the diffractogram.](image)

The formation of the third component (green line), corresponds to ZnO crystallites with a standard lattice parameters. The content of the third component increases to 48% at the maximum implantation fluence of $1 \times 10^{17}$ ion/cm$^2$. This indicates a partial recovery of the crystal structure. The content of "deformed" nanocrystallites and amorphous component decrease to 8% and 24%, respectively. Obviously, the observed changes in the structure of the films are due to their thermal annealing during implantation process. Thus, at the high ion current density, the irradiated film is heated because of the low thermal conductivity of the quartz glass substrate.
Table 2. Decomposition parameters of the reflex (002) for as-deposited and subsequently implanted with silver ions ZnO film.

| Components (%) | FWHM (2θ) | d (Å) | Δd (%) | c (Å)   | Center (2θ) | ΔL (2θ) |
|----------------|-----------|-------|--------|---------|-------------|---------|
| 1 (40 %)       | 0.894     | 2.683 | 2.7 %  | 5.367   | 33.36       | 0.97    |
| 2 (60 %)       | 2.44      | 2.610 | 0.1 %  | 5.220   | 34.33       |         |

ZnO:Ag (Fluence – 0.25×10\(^{17}\) ion/cm\(^2\))

| Components (%) | FWHM (2θ) | d (Å) | Δd (%) | c (Å)   | Center (2θ) | ΔL (2θ) |
|----------------|-----------|-------|--------|---------|-------------|---------|
| 1 (17 %)       | 0.894     | 2.679 | 2.5 %  | 5.359   | 33.41       | 1.02    |
| 2 (38 %)       | 2.44      | 2.602 | 0.4 %  | 5.205   | 34.43       |         |
| 3 (45 %)       | 0.724     | 2.611 | 0.07 % | 5.222   | 34.32       |         |

ZnO:Ag (Fluence – 1×10\(^{17}\) ion/cm\(^2\))

| Components (%) | FWHM (2θ) | d (Å) | Δd (%) | c (Å)   | Center (2θ) | ΔL (2θ) |
|----------------|-----------|-------|--------|---------|-------------|---------|
| 1 (8 %)        | 0.894     | 2.681 | 2.6 %  | 5.361   | 33.40       | 0.99    |
| 2 (24 %)       | 2.44      | 2.605 | 0.3 %  | 5.211   | 34.39       |         |
| 3 (68 %)       | 0.731     | 2.605 | 0.3 %  | 5.211   | 34.39       |         |

Finally, dependence of the intensity and position of component 1 on the fluence of implantation was investigated. One could expect a gradual shift of this component towards the standard value of the diffraction angle 2θ (see parameter ΔL (2θ) in Table 2) at a constant intensity, which corresponds to the gradual stress decrease during annealing. Conversely, we observe another situation, which we associate with the nanometer size of the crystallites and the surface closeness. The value of 2θ for "deformed" nanocrystallites does not change (Table 2), but the intensity of the reflex decreases while the intensity of component 3 increases. The interstitial atoms, which produce stresses, can quickly diffuse to the surface due to the small size of the crystallites. Therefore, stresses in the nanocrystallite decrease to zero and intensity of the component 3 increases as a result of a such rapid process.

5. Conclusions
In summary, we have investigated the structural properties of the ZnO thin films formed by IBAD technique and the effect of subsequent implantation with silver ions. The structure of the as-deposited ZnO film consists of nanocrystallites with lattice parameters of 2-2.5% higher than standard values and amorphous regions. The mechanism that can lead to increase of the lattice parameter of nanocrystallites is suggested. Also it is associated with the implantation of the most high-energy sputtered zinc atoms into the near-surface region of a growing film. It was shown that such process is possible due to the presence of the high-energy tail in the energy distribution of the deposited zinc atoms. Silver ions implantation at high current density is responsible for radiation heating and the recovery of the crystalline structure of the irradiated ZnO film. The quantitative content of the "deformed" nanocrystalline and amorphous components of the thin film decreases as a result of heating. The later lead to formation of nanocrystallites with the standard crystal lattice parameters. Thus the content of nanocrystallites prevails at the maximum fluence of silver ion implantation.

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