ISSN 1063-7850, Technical Physics Letters, 2018, Vol. 44, No. 6, pp. 528–531. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © A.M. Ismailov, L.L. Emiraslanova, M.Kh. Rabadanov, M.R. Rabadanov, I.Sh. Aliev, 2018, published in Pis'ma v Zhurnal Tekhnicheskoi Fiziki, 2018, Vol. 44, No. 12, pp. 52–61.

Synthesis of Highly Oriented Zinc-Oxide Films on Amorphous Substrates by the Method of Direct-Current Magnetron Sputtering

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Received March 24, 2017; in final form, February 6, 2018

Abstract—We describe the technology of obtaining highly oriented zinc-oxide (ZnO) films on amorphous substrates at high growth rates (up to 7 nm/s) by means of direct-current magnetron sputtering. It is suggested to optimize the substrate position with respect to magnetron and consider the floating potential to which the substrate is charged in magnetron discharge plasma as one of the main technological parameters. Electron-diffraction study of the structural characteristics of the obtained ZnO films showed that increase in the substrate temperature was accompanied by transformation of the crystallite shape from platelike to columnar.

DOI: 10.1134/S1063785018060202

At present, zinc oxide (ZnO) is considered to be a promising wide-bandgap semiconductor material drawing the attention of researchers due to a broad spectrum of possible applications. However, these possibilities are not yet fully implemented in practice because of technological problems encountered in the synthesis of ZnO with required and reproducible properties. The method of magnetron sputtering in various (direct current, reactive, high frequency, pulsed) modes proved to be advantageous for depositing thin ZnO films from the gas phase. As is known, ZnO possesses the maximum coefficient of electromechanical coupling (determining the efficiency of piezoelectric conversion) among piezoelectric semiconductors and is widely employed in piezo- and optoelectronics in the form of thin films on amorphous substrates [1]. The issues of structural refinement of these films (texture of deposit estimated by the misorientation angle θ of crystallites) have been among the main criteria in works devoted to technological features of the sputter deposition of piezoelectrically active ZnO films [2]. Numerous investigations of the magnetron sputtering of ZnO films have been reported, in which "optimum" technologies of obtaining highly oriented ZnO films are proposed [3–8].

Based on analysis of the available literature data, it is possible to conclude the following.

(i) The interval of substrate temperatures for the oriented growth of films on amorphous substrates reported by different researchers varies within broad limits (473–723 K). The minimum achieved misorientation angle of crystallites in ZnO film was 1.5° [3–6].

(ii) The structural perfection of ZnO films deteriorates with increasing deposition rate. The maximum film-growth rate in a magnetron system did not exceed 3 nm/s for textured films and 0.3 nm/s for epitaxial films [3–8].

(iii) The dependences of the structural perfection of ZnO films on deposition conditions reported by different researchers are rather contradictory.

The above conclusions are indicative of still insufficient understanding of processes involved in the formation of ZnO film structures in magnetron sputtering systems. The present work was devoted to obtaining highly oriented undoped ZnO films on amorphous substrates at high growth rates by means of dc magnetron sputtering.

ZnO films were deposited using a VATT AMK-MI automated multifunction complex (FerriVatt Co., Kazan) under dry vacuum conditions provided by a spiral forevacuum pump (Anest Iwata ISP-500C, Japan) and cryogenic high-vacuum pump (Cryogenics Cryo-Torr 8, United States). Prior to each sputter deposition cycle, the vacuum chamber was pumped to a residual pressure of ~9×10^{-5} Pa and the working gas (oxygen) was admitted to a pressure controlled by an RRG-10 valve (EltochPribor, Russia) valve and measured by a TELEVAC CC-10 wide-range vacuum gauge (United States). The experiments were performed using a classical dc planar magnetron system and ceramic ZnO disk target with a diameter of 50 mm and thickness of 5 mm mounted on a cooled magne-

tron base without clamps. Substrates with amorphous surface structure represented rectangular 15 × 15-mm plates of thermally oxidized (111)-oriented silicon.

The floating potential of the substrate was measured by probes arranged at points *a*, *b*, and *c* (Fig. 1) at a distance of 5 mm from each other. The probes were made of 0.3-mm-diameter nichrome wire inserted into ceramic capillaries. The floating potential measurements were performed by a C503 electrostatic voltmeter (accuracy class 0.5) relative to a reference electrode (grounded anode of the magnetron system).

The thickness of deposited ZnO films was measured by a computer-controlled system based on a modified MII-4M interferometer (LOMO-Microsystems Co., Russia). The structural perfection of deposited films was characterized using electron-reflection-diffraction patterns (using an EG-75 electron diffractometer, Russia) by misorientation angle θ of crystallites estimated from the angular width of reflection arcs (fringes) on the diffraction pattern.

At the first stage, we have experimentally determined the optimum position of substrates in the magnetron sputtering system, which ensured the best structural perfection of deposited ZnO films at other technological parameters fixed: substrate temperature, T_s = 333 K; working gas (oxygen) pressure, P = 1 Pa; discharge current density, j = 12 mA/cm^2. The structural perfection of deposited films was assessed after every deposition cycle by electron-diffraction scanning over sample length between points *a* and *c* (Fig. 1).

Experiments showed that the structural perfection of sputter-deposited ZnO films strongly depends on the position of a substrate in the magnetron system as set by geometric parameters α, *r*, and φ (Fig. 1). Values of these parameters corresponding to the most structurally perfect of ZnO films were determined. This optimum arrangement of substrates must be ensured to within $\Delta r = \pm 3$ mm, $\Delta\alpha = \pm 5°$, and $\Delta\varphi = \pm 3°$. Analysis of the electron-diffraction patterns of ZnO films showed that the [0001] axis of texture coincided with the direction of the normal to the substrate surface, while ZnO crystallites were misoriented within $\theta = 5°$. A structurally perfect region of the film with uniform thickness was observed at the substrate center (in the vicinity of point *b*, Fig. 1) and had dimensions about 5 × 5 mm.

As is known, the structure and properties of deposited films strongly depend on the substrate temperature. Without preliminary heating, the substrate temperature increased to 333 K under the action of discharge for 15 min and then remained constant until termination of the deposition process. Then, the temperature dependence of structural perfection of obtained ZnO films was studied at fixed values of other technological parameters (optimum substrate position, P = 1 Pa, and j = 12 mA/cm^2).

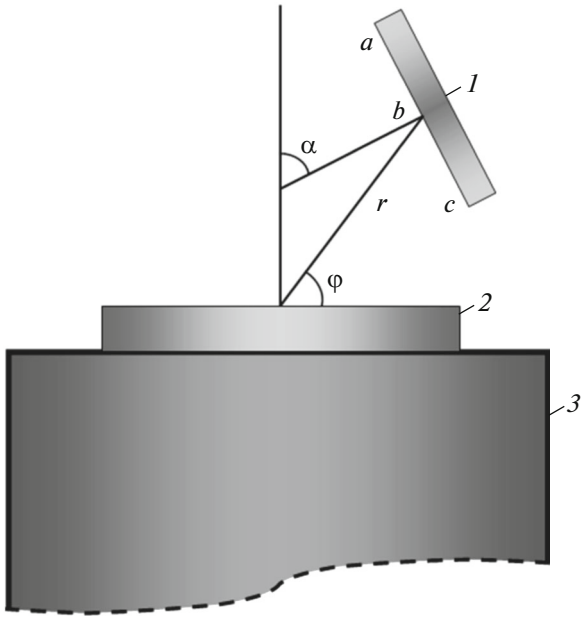

Fig. 1. Substrate positioning in a dc magnetron sputtering system set by parameters *r*, φ, α (*r* and φ are polar coordinates of the substrate center relative to the target center; α is the angle between normal to the target and substrate surfaces): (*1*) substrate, (*2*) target, and (*3*) magnetron; (*a*, *c*) substrate edges, (*b*) substrate center.

When the substrate temperature was increased from 333 to 673 K, grain-misorientation angle θ remained almost unchanged, but the contrast of the electron-diffraction pattern was enhanced, which showed an increase in the size of crystallites. Further increase in the substrate temperature from 673 to 773 K was accompanied by gradual decrease in θ and the appearance of strands (Fig. 2a). Diffraction reflections (reciprocal lattice sites) are always extended in the direction parallel to the shortest size of the crystal cell. According to the reflection geometry of diffraction, this direction is perpendicular to the substrate, which indicates that crystallites have platelike shapes and are oriented parallel to the substrate, while a significant amorphous background is indicative of the presence of wide intercrystalline boundaries. ZnO films with this structure usually possess a resistivity of ~10^6 Ω cm and are photosensitive in a visible wavelength range with maximum at 385 nm.

As the substrate temperature was increased from 773 to 923 K, the length of vertical strands in the electron=diffraction pattern decreased. The diffraction pattern of ZnO film deposited at 923 K consists of point reflections (Fig. 2b), which is characteristic of extended objects with a rather perfect structure. A decrease in the length of reflection strands in this temperature interval is explained by the increasing size of crystallites in the direction of film thickness. The point character of the diffraction pattern is retained up to T_s = 973 K. Thus, it can be ascertained that ZnO

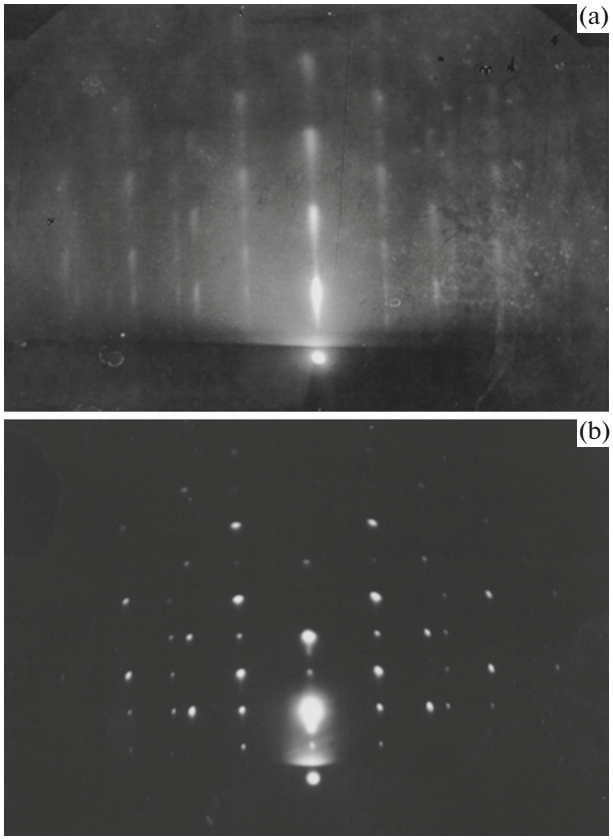

Fig. 2. Reflection-electron-diffraction patterns of ZnO films deposited at substrate temperatures (a) 773 and (b) 923 K.

films grown in the interval of substrate temperatures from 923 to 973 K possess a columnar structure.

When the sample is rotated about an axis perpendicular to the film surface, the electron-diffraction pattern (such as in Fig. 2b) remains unchanged, which corresponds to the total azimuthal misorientation of crystallites. Therefore, the structural perfection of these ZnO films (Fig. 2b) should be considered as the limiting case of a uniaxial texture with zero angle of axial misorientation of crystallites (to within the instrumental line width of the diffractometer). In other words, the polar [0001] direction of all crystallites in the ZnO film is perpendicular to the substrate surface, while their azimuthal orientations on the substrate plane are fully disordered.

ZnO films with this type of structural perfection possess a resistivity of ~10 Ω cm, which can be increased by doping films with the corresponding impurities. In the case of high resistivity ($\rho > 10^4$ Ω cm), ZnO films with this structural perfection on amorphous substrates represent ideal materials for effective device structures of piezo- and optoelectronics [1, 2]. In particular, a rapidly developing field is related to a new class of devices operating on surface acoustic

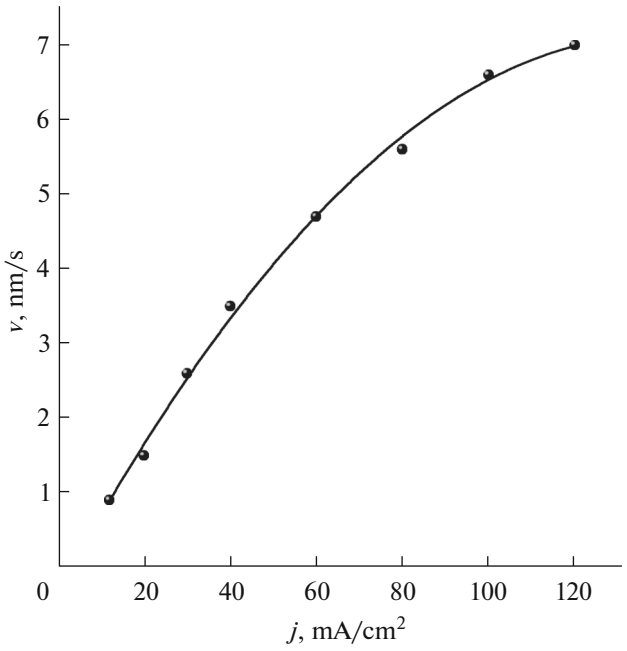

Fig. 3. Plot of the growth rate of highly oriented ZnO films vs. magnetron discharge current density.

waves. Structures of the $ZnO/SiO_2/Si$ type provide a basis for these devices [9, 10].

Films deposited in the interval of substrate temperatures from 973 to 1073 K are characterized by increasing angle of misorientation of crystallites. In the entire range of substrate temperatures studied (333–1073 K), the films exhibit reflections of (0001) oriented texture and exhibit a constant growth rate of 0.9 nm/s corresponding to a discharge-current density of $j = 12$ mA/cm^2.

In the literature, there is a commonly accepted belief that structural perfection of a growing ZnO film depends on the deposition rate and perfect films cannot be obtained at rates above 3 nm/s [3–8]. In order to check for this statement, we have frown ZnO films at various densities of discharge current and fixed values of other technological parameters (optimum substrate position, $T_s = 923$ K, $P = 1$ Pa). Results showed that the ZnO target could operate for a long time at current loads up to $j = 120$ mA/cm^2, which corresponded to a deposition rate of 7 nm/s (Fig. 3). These conditions provide for the formation of films with the same structural perfection as that for $j = 12$ mA/cm^2 (Fig. 2b). Finally, it was established that, for the optimum position of substrate in the magnetron deposition system, the above-described temperature dependence of ZnO film structure is independent of the discharge-current density (i.e., of the film growth rate).

It should also be noted that the aforementioned deposition rate of 7 nm/s is not a limiting value above which the structural perfection of ZnO films begins to deteriorate. The structure quality is limited by maxi-

mum power dissipated by the target during stable operation of the magnetron discharge. Increase in the discharge current density to $j > 120$ mA/cm^2 leads to growth in temperature of the sputtered target surface. The rear surface of the target is in thermal contact with a water-cooled magnetron base. The temperature gradient related to low thermal conductivity of ZnO ceramics may cause fracture of the target.

Increase in the working gas (oxygen) pressure above 3 Pa leads to growing misorientation of crystallites in the deposited ZnO film. In addition, the probability of sputtered atoms to return back to the target due to collisions with working gas molecules also grows, which leads to a drop in the deposition rate. Variation of the working gas pressure within 1–3 Pa does not significantly influence the film structure and this interval is considered as operating (at $P < 1$ Pa, the magnetron discharge switches off).

In a magnetron sputtering system, plasma is localized near the target surface and has a nearly toroidal shape. The degree of ionization is maximum in a central region above the zone of sputtering and decays with increasing distance from this region. Evidently, the floating potential U_f of spatially inhomogeneous plasma at various points (including sites *a*–*c* of substrate, Fig. 1) takes different values and is a function of parameters r and φ, so that $U_f = F(r, \varphi)$ [11]. Therefore, the floating potential to which the substrate is charged in magnetron sputtering system is among important technological parameters significantly influencing the structural perfection of obtained films. The U_f value measured in the region of point *b* (Fig. 1) corresponding to the maximum structural perfection of ZnO film (Fig. 2) was within 9–12 V. On approaching the edges of substrate (points *a* and *c*), where the floating potential is 4–6 V and 16–18 V, respectively, the angle of misorientation of crystallites in the film smoothly increases. Note that, in the case of scaling of the sputtering process (using extended targets of greater dimensions), the spatial inhomogeneity of the floating potential distribution would decrease, thus making it possible to obtain structurally perfect highly oriented ZnO films of uniform thickness on greater substrates (up to several dozen square centimeters in size). This possibility is important for large-scale fabrication of related devices.

In concluding, highly oriented ZnO films on amorphous substrates have been obtained at high growth rates (up to 7 nm/s) by means of dc magnetron sputtering. It is shown for the first time that the floating potential to which the substrate is charged in magnetron discharge plasma strongly influences the structural perfection of deposited ZnO films. Therefore, this parameter should be considered one of the main technological parameters. The structural perfection of ZnO films deposited at a substrate temperature of 773 K corresponds to a platelike shape of crystallites, while the deposition at 923 K yields a film with crystallites of a columnar shape and *c*-axis oriented perpendicular to the substrate plane. A possible mechanism of the floating potential influence on the process of ZnO-film-structure formation during sputter deposition in dc magnetron discharge will be considered in subsequent publications.

Acknowledgments. This work was supported in part by the Russian Foundation for Basic Research, project no. 16-02-00227.

REFERENCES

1. J. Zelenka, *Piezoelectric Resonators and Their Applications* (Academia, Praha, 1983; Mir, Moscow, 1990) [in Czech].
2. T. D. Shermergor and N. N. Strel'tsova, *Film Piezoelectrics* (Radio Svyaz', Moscow, 1986) [in Russian].
3. T. K. Subramanyam, N. B. Srinivasulu, and S. Uthanna, Opt. Mater. **13**, 239 (1999).
4. J. Daugela, S. Joneliunas, A. Jotautis, R. Naujokaitis, and E. Klovaite, Elektron. Elektrotech. **63** (7), 70 (2005).
5. R. Subba Reddy, A. Sreedhar, A. Sivasankar Reddy, and S. Uthannal, Adv. Mater. Lett. **3**, 239 (2012).
6. S. Singh, T. Ganguli, R. Kumar, R. S. Srinivasa, and S. S. Major, Thin Solid Films **517**, 661 (2008).
7. T. Hata, T. Minamikava, O. Marimoto, and T. Hada, J. Cryst. Growth **47**, 171 (1979).
8. J. Nomoto, T. Hirano, T. Miyata, and T. Minami, Thin Solid Films **520**, 1400 (2011).
9. Y. Q. Fu, J. K. Luo, X. Y. Du, A. J. Flewitt, Y. Li, G. H. Markx, A. J. Walton, and W. L. Milne, Sens. Actuators, B **143**, 606 (2010).
10. J. Singh, S. Ranwa, J. Akhtar, and M. Kumar, AIP Adv. **5**, 067140 (2015).
11. M. Panjan and A. Anders, J. Appl. Phys. **121**, 063302 (2017).

Translated by P. Pozdeev