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Multilayered ZnO Films of Improved Quality Deposited by Magnetron Sputtering

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Multilayered ZnO films were deposited by rf magnetron sputtering on silicon and sapphire substrates. The aim of this work is to improve structural quality of ZnO thin films grown on just listed substrates. Presented X-ray diffraction data testify to remarkable relaxation of compressive stress in two- and three-layered ZnO films in comparison with single-layer one.

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1. Introduction

In recent years a great attention has been paid to a wide gap semiconductor ZnO ($E_{\mathrm{g}} = 3.37$ eV at room temperatures). Like other wide-gap semiconductors, ZnO can be used to develop light emitting devices and detectors for blue and ultraviolet range of spectrum. Compared to well-known GaN, ZnO has a large exciton binding energy (60 meV) that allow to provide effective excitonic stimulated emission at room and higher temperatures. Thus, high quality ZnO films deposited by molecular beam epitaxy (MBE) demonstrate the so-called "lasing" at optical excitation with small lasing threshold [1].

Substrate material plays the key role in obtaining high quality ZnO layers. Usually ZnO films are deposited on glass, quartz, silicon and sapphire substrates. However, glass substrates are practically nasty for qualitative ZnO film growth.

Deposition on such substrates starts with a formation of ZnO amorphous layer. When it reaches some threshold thickness, formation of polycrystalline ZnO film layer takes place [2]. Thus, the quality of the film deposited on glass substrate is not high. The most suitable substrate for ZnO growth is $ScAlMgO_4$ (misfit of lattice periods 0.09%). As it is stated in [3] $ScAlMgO_4$ allows a growth of high structural quality ZnO films. It results in high carrier mobilities (60–100 $cm^2/(V\ s)$) and low carrier concentrations ($4\text{–}27\times10^{15}$ cm^{-3}). However, such substrates are expensive and technologically inconvenient. Some troubles arise at using Si and Al_2O_3 substrates for ZnO epitaxial growth. Lattice period of silicon and sapphire have large misfits with lattice period of hexagonal ZnO ($\approx 41\%$ and $\approx 18\%$, respectively) [4]. Moreover, Si undergoes oxidation in argon–oxygen ambient at ZnO growth and therefore formation of amorphous SiO_x layer occurs [5]. This layer causes deterioration of the crystal quality of growing ZnO layer. Also Si extracts oxygen from ZnO lattice at post-growth annealing which leads to formation of oxygen vacancies V_O. Therefore it results in a poor UV photoluminescence of ZnO/Si films [6].

One way to obtain high quality ZnO layers on Si and sapphire substrates is to use buffer layers such as GaN, AlN, ZnS. However, at high substrate temperatures 450–750°C, high quality ZnO films can be deposited without buffer layers by advanced technique such as MBE [7]. Crystal quality of ZnO films was estimated by film stress value σ.

In present paper we investigate structural quality of ZnO films deposited by magnetron sputtering on Si and sapphire substrates. Effect of substrate temperature on a quality of ZnO film was also studied. We suppose that the layer by layer growth method, at which ZnO homoepitaxy takes place, can significantly improve film quality as a whole.

2. Experimental procedure

Thin multilayered ZnO films with thicknesses about 300 nm were deposited by rf magnetron sputtering. The metallic Zn was used as a target. Substrate temperatures T_s, argon and oxygen partial gas pressure, rf discharge power, and target–substrate distance are the parameters that greatly influence on structural properties of growing ZnO film. But only the effect of substrate temperature was investigated. Other parameters were fixed: discharge power — 200 W, oxygen partial pressure — 0.2 Pa, argon partial pressure 0.8 Pa, target–substrate distance — 7 cm.

Multilayered ZnO films were deposited in layer by layer mode i.e. process of growth of ZnO film was carried out in several stages. At the next stage of film deposition we keep all mentioned parameters fixed and change only substrate temperature. After deposition of every single ZnO layer deposition process was interrupted and X-ray diffraction (XRD) measurements were carried out. Thus, the process of layer by layer growth represents a deposition of next ZnO film on ZnO film already grown on substrate. Therefore the substrate significantly impacts only on nucleation and growth of the first ZnO layer. Next ZnO layers grow in homoepitaxy conditions. Using this deposition procedure we obtain one-, two- and three-layered ZnO films. Multilayered ZnO films were deposited on Si (100) and c-sapphire (0001) substrates. For comparison we deposited one layer ZnO films on glass substrate as well as on a- and r-cuts of sapphire substrates.

Crystal quality of multilayered ZnO films was investigated by XRD diffractometer DRON-4 (Cu K_α radiation with wavelength $\lambda = 0.1541$ nm). The peak positions were compared with reference data from powder diffraction file for ZnO [8]. Scherrer's formula was used to determine grain size

$$D = \frac{0.9\lambda}{W\cos\theta}\,,$$

where D — average grain size, W — full width at half maximum (FWHM) in radians, θ — Bragg's angle.

ZnO film stresses were evaluated accordingly [9] by the following formula:

$$\sigma = -233\frac{c - c_0}{c}\,,$$

where σ is the film stress (GPa); c is the lattice period determined from interplanar spacing d of (002) reflex ($c = 2d$); $c_0 = 0.5206$ nm — lattice period for ZnO powder [8].

3. Results and discussion

Figure 1 shows XRD spectra for ZnO films deposited at the same technological conditions on various kinds of substrates. Silicon and glass substrates as well as a- and c-sapphire substrates provide ZnO growth in $\langle 001\rangle$ direction i.e. c-axis of ZnO is perpendicular to substrate plane. Growth along c-axis is inherent to ZnO having hexagonal crystal lattice with lowest free energy for (0001) plane [4]. However, depending on deposition conditions (especially T_s) crystallites of polycrystalline ZnO film can have other orientations. Thus, either textured or untextured films can be obtained. In the case of $T_\mathrm{s} = 300°$C that allowed us to grow polycrystalline textured ZnO films on oriented (Si, Al_2O_3) as well as on amorphous (glass) substrates. As can be seen from Fig. 1 oriented substrates provide good high textured film growth (intensive peaks with low FWHM). Most intensive peak (002) was observed for ZnO films grown on c-sapphire as a result of similar crystal structure for ZnO and Al_2O_3. ZnO grown on a-cut of Al_2O_3 also have orientation $\langle 0001\rangle$ accordingly to epitaxial relationship $(0001)_{\mathrm{ZnO}}//(11\bar{2}0)_{\mathrm{Al_2O_3}}$ [4]. But ZnO film grown on r-Al_2O_3 has another texture (110) accordingly to relationship $(11\bar{2}0)_{\mathrm{ZnO}}//(01\bar{1}2)_{\mathrm{Al_2O_3}}$. Table summarizes XRD data of ZnO films shown in Fig. 1. Notably, ZnO films deposited by magnetron sputtering have fine grain structure with grain size in the range 16–26 nm. The strongest deformation of ZnO lattice was observed in ZnO/Si films as a result of large lattice misfit ($\approx 41\%$) [4].

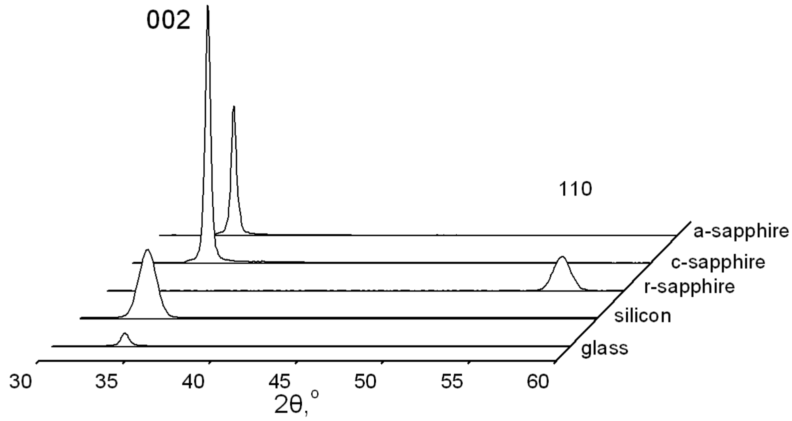

Fig. 1. XRD spectra of ZnO films deposited on various substrates at $T_s = 300°C$.

TABLE

XRD parameters of ZnO films shown in Fig. 1.

Substrate	Peak position 2θ (texture) [degree]	c [nm]	W [degree]	σ [GPa]	D [nm]
a-Al_2O_3	34.313 (002)	0.522	0.34	−0.63	24
c-Al_2O_3	34.359 (002)	0.521	0.32	−0.33	26
r-Al_2O_3	56.375 (110)	–	0.62	–	23
Si	33.96 (002)	0.528	0.47	−2.9	16
glass	34.213 (002)	0.524	0.48	−1.29	17

We investigated the possibility of obtaining more perfect ZnO films by formation of two and three ZnO layers during consecutive stages of deposition. We have deposited the first ZnO layer with thickness about 200 nm on Si substrates, having a large lattice misfit. The second and the third ZnO layers had thicknesses about 50 nm each. Figure 2 shows XRD data for multilayered ZnO/Si films. As can be seen, layer by layer technique for ZnO film deposition leads to improving of film quality. Thus, reflex from (002) planes of ZnO lattices tends to $2\theta = 34.42°$ that is the reference value for (002) plane of ZnO powder [8]. At that, relaxation of compressive stress in films was observed (Fig. 2b).

Figure 3 shows the dependences for σ and lattice period c of two-layered ZnO film on substrate temperature at deposition of the second layer. Variation of substrate temperature in the range 200–350°C at deposition of the second ZnO layer slightly influences on ZnO/Si film quality. ZnO films deposited at $T_s = 250°C$ have the least lattice deformation and the smallest value of σ. At deposition the third ZnO layer at $T_s < 300°C$ other insignificant peaks corresponding to (100) and (101) crystalline orientation in XRD spectra appeared. Thus high quality

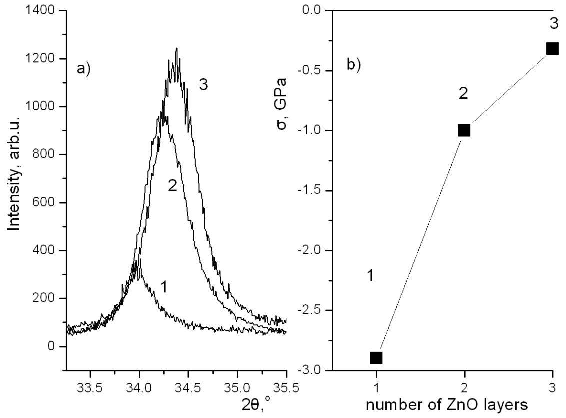

Fig. 2. XRD spectra for multilayered ZnO/Si films (a) and stress in the films (b) (ZnO films of: 1 — one-layer, 2 — two-layer and 3 — three-layer).

multilayered ZnO films on silicon substrates can be grown at substrate temperature 300°C by the process of layer by layer growth.

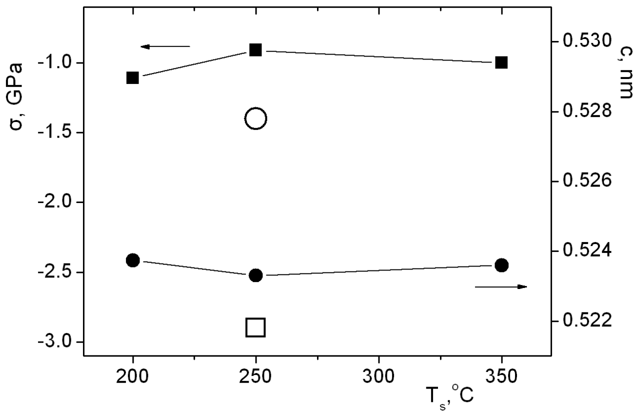

Fig. 3. Dependences of film stress σ and lattice period c for two-layered ZnO/Si films on substrate temperature T_s after growing the second ZnO layer (● — period c, ■ — film stress σ). Open symbols ○ and □ denotes c and σ for initial (one-layer) ZnO/Si film deposited at $T_s = 250$°C.

Multilayered ZnO films of total thicknesses about 300 nm were also deposited on c-sapphire substrates. Figure 4a shows XRD spectra of $ZnO/Al_2O_3(0001)$ films. Film stress dependence on substrate temperature at deposition each single layer of ZnO is represented in Fig. 4b.As can be seen from Fig. 4b three-layered ZnO films display total relaxation of compressive stress. Parameter σ becomes positive that testify to the formation of low tensile stress. It should be noted that intermediate ZnO layer, deposited at $T_s = 200$°C have a stress. Besides that one can see that

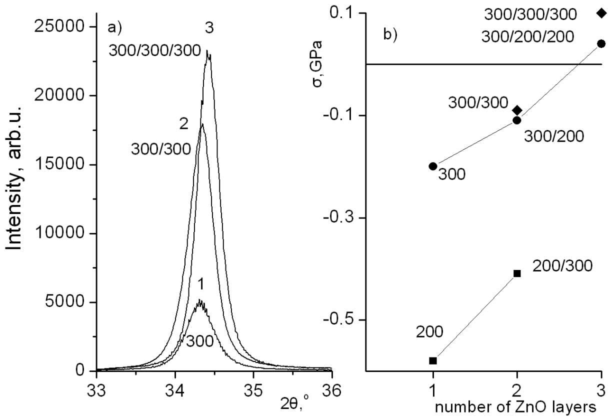

Fig. 4. XRD spectra for multilayered $ZnO/Al_2O_3(0001)$ films (a) and stress in the films (b). 1, 2, 3 — number of ZnO layers. Substrate temperature is pointed at growing of each layer (T_s of first layer/T_s of second layer/T_s of third layer).

one-layer ZnO films deposited at $T_s = 300°C$ have less stress compared to the film deposited at $T_s < 300°C$ (including multilayered), and therefore, a higher crystal quality.

To elucidate the effect of film thicknesses on film stress relaxation we investigated the film stress in two ZnO films deposited at $T_s = 300°C$ during 0.5 h and 1 h, respectively. ZnO films have compressive stress –0.33 GPa and –0.2 GPa, respectively. Though film stress decreases at growing film (i.e. at increase in thickness), we could not obtain non-stressed ZnO film during one stage of deposition even at high growth temperature (300°C). Thus, applying process of layer by layer growth, textured non-stressed ZnO films on $Al_2O_3(0001)$ substrate by magnetron sputtering system were obtained.

Homoepitaxy of ZnO was studied in [10] at deposition ZnO film on thin ZnO buffer layer. As a result the structural quality of these films has been improved. We assume that improving of film perfectness is due to smaller misfit between ZnO layers. It results in homoepitaxy and relaxation of strain in multilayered films with increasing number of ZnO layers even when thickness of next ZnO layer is not large (50 nm). Indeed, top layer of multilayered ZnO films is of very high structural quality compared to underlying ZnO layers. As a result, in XRD spectra we observed very intensive peak (002) obliged mainly top ZnO layers.

4. Summary

Multilayered ZnO films were deposited by magnetron sputtering on Si and sapphire substrate. One-layer ZnO films are characterized by a presence of residual stress. Applying layer by layer growth method, one obtains ZnO films of an improved quality which results in significant increasing intensity of diffraction peaks, lowering FWHM and lowering or disappearance of stresses in ZnO films.

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