Thin Solid Films 518 (2010) 4529–4532

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

High quality ZnO films deposited by radio-frequency magnetron sputtering using layer by layer growth method

A.I. Ievtushenko [a,*], V.A. Karpyna [a], V.I. Lazorenko [a], G.V. Lashkarev [a], V.D. Khranovskyy [a], V.A. Baturin [b], O.Y. Karpenko [b], M.M. Lunika [b], K.A. Avramenko [c], V.V. Strelchuk [c], O.M. Kutsay [d]

[a] M. Frantsevich Institute for Problems of Materials Science, NASU, Krzhyzhanovskyy str. 3, 03680, Kyiv, Ukraine
[b] Institute of Applied Physics, NASU, Petropavlovskaya st. 58, 40030, Sumy, Ukraine
[c] V. Lashkarev Institute of Semiconductor Physic, NASU, Nauky pr. 45, 03028, Kyiv, Ukraine
[d] V. Bakul Institute for Superhard Materials, NASU, Avtozavodskaya str. 2, 04074, Kyiv, Ukraine

ARTICLE INFO

Available online 8 January 2010

Keywords:
ZnO
Magnetron sputtering
Structural quality

ABSTRACT

Three-layered ZnO films were deposited on Si substrates by radio-frequency magnetron sputtering using layer by layer growth method. The Raman scattering confocal analysis confirms that ZnO film quality is improving at increasing the number of ZnO layers at film deposition.
Applied method of deposition was used to realize homoepitaxial growth of ZnO films on *c*-Al_2O_3, Si, SiN_x/Si, glass and ITO/glass substrates. In order to improve the film quality we increased the number of deposition stages up to 5. X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmittance measurements were used to testify the quality of grown five-layered ZnO films. XRD results showed that all five-layered ZnO films have (002) texture. The second order diffraction peak (004) on XRD spectra additionally testifies to the high quality of all five-layered ZnO films. SEM results demonstrated that no defects such as cracks and dislocations caused by interruption of deposition ZnO films were observed. Transmittance measurement results showed that ZnO films deposited on transparent substrates have abrupt absorption edge and high optical transmission in the visible region of the spectrum.

1. Introduction

ZnO is a prospective wide-gap semiconductor for developing optoelectronic devices [1]. Therefore great attention is devoted to the growth of high quality ZnO films. But the lattice mismatch and different thermal expansion coefficients between ZnO and substrates prevent deposition of high quality free of stress ZnO films with low defect concentration. In order to obtain perfect ZnO films one can use the substrates with minimal lattice mismatch, e.g. ZnO (lattice misfit 0%), $ScAlMgO_4$ (0.09%), GaN (1.8%) and 6H-SiC (3.5%). However, these substrates are mainly expensive and some of them are technologically inconvenient. Besides that obtaining qualitative ZnO films on different substrates is important for designing various devices on their basis.

Radio-frequency magnetron sputtering (RF MS) is widely used in the industry for deposition of different semiconductor and metallic films. This technology of deposition is relatively low cost. In addition, among all methods for deposition of ZnO films, magnetron sputtering is characterized by several advantages: (i) process with low substrate temperature; (ii) good film adhesion; (iii) very good thickness uniformity and high density of the films; and (iv) deposition from metallic targets by sputtering in reactive gas mixtures [2]. Thus, RF MS is a very prospective technology for deposition of ZnO films and designing devices on their basis. However, the crystal quality of ZnO films deposited by RF MS is not good. Another way for the growth of high quality ZnO films is an application of buffer layers such as GaN [3], AlN [4], SiC [5], MgO [6] and ZnS [7]. However, in this case we need to use additional difficult and expensive technologies for the deposition of these layers. Application of low- or high-temperature ZnO buffer layers seems to be promising [8,9]. We presented earlier the multistage growth method for improving the crystal structure of the ZnO thin films deposited by RF MS on Si and sapphire substrates. This approach allows to grow ZnO thin films with higher crystal quality than the ones deposited by single-stage RF MS (for similar thickness) [10].

In this paper we study the structural and optical properties of ZnO films deposited on different substrates by RF MS method of layer by layer growth.

2. Experimental procedure

2.1. Sample preparation

Previously in the paper [10], it was demonstrated that application of multistage growth at magnetron sputtering allows us to grow ZnO

* Corresponding author. Tel.: +38 44 424 32 28; fax: +38 44 424 31 21.
E-mail address: a.ievtushenko@ipms.kiev.ua (A.I. Ievtushenko).

0040-6090/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2009.12.023

Table 1
Deposition parameters of five-layered ZnO films, deposited on different substrates and their thicknesses.

Sample	ZnO/ c-Al_2O_3	ZnO/Si (100)	ZnO/ SiN_x/Si	ZnO/ITO/ glass	ZnO/ glass
T_s, °C	400	250	300	250	300
P_{Oxygen}, Pa	0.5	0.3	0.7	0.5	0.7
Thickness, nm	1500	1000	1050	1750	1950

thin films with higher crystal quality compared to ones deposited by single-stage RF MS (for similar thickness). At that study the crystal quality of ZnO films was estimated by magnitude of in-plane film stress which was evaluated by XRD analysis. As the number of stages increased the magnitude of in-plane film stress decreased as we reported in [10]. Three-layered ZnO films were deposited on Si substrates by layer-by-layer RF MS at fixed parameters for each layer deposition using interruptions at growth film. Briefly, technological parameters were as follows: discharge power — 200 W, target–substrate distance — 7 cm, oxygen partial pressure — 0.2 Pa and argon partial pressure — 0.8 Pa. Pure metallic zinc (99.99 %) was used as a target.

To improve the quality of ZnO films on *c*-Al_2O_3, Si, SiN_x/Si, glass and ITO/glass substrates we introduced five stages of deposition. It is known that the texture of ZnO films depends on oxygen partial pressure and substrate temperature at ZnO film deposition on different substrates [11,12]. So, for deposition of the first-layer of ZnO with (002) texture on the above mentioned substrates, the substrate temperatures and oxygen partial pressures were set up individually for each substrate (see Table 1). Discharge power and target–substrate distance were the same as mentioned above. Argon partial pressure was fixed at 1 Pa. Total time of deposition was 75 min. The thicknesses of the deposited five-layered ZnO films are presented in Table 1.

2.2. ZnO films characterization

The structural properties were investigated by X-ray diffraction (XRD) using DRON-4 diffractometer, utilizing Cu-Kα radiation (λ = 0.1542 nm). The thickness of the films was measured with interferometer MII-4. The micro-Raman measurements were carried out in backscattering geometry at room temperature using Horiba Jobin Yvon T64000 system, equipped with an Olympus confocal optical microscope. Scanning electron microscopy (SEM) was used to reveal the uniformity of films (Leo 1550 Gemini SEM). Transmittance of ZnO samples deposited on transparent substrates was investigated by spectrophotometer Specord M 400 (Germany).

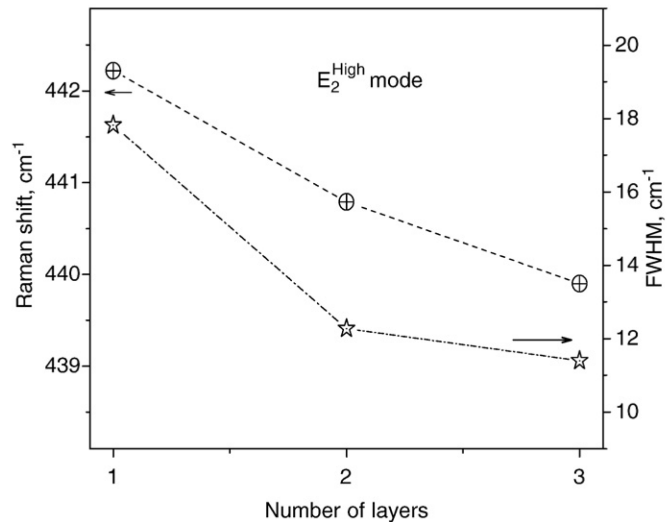

Fig. 2. Raman shift and FWHM of E_2(*high*) mode dependence *versus* number of ZnO layers.

3. Results and discussion

XRD analysis was carried out previously in our paper [10] for three-layered ZnO films deposited on Si substrates. All ZnO layers were textured with *c*-axis oriented perpendicular to film plane (002). It was shown that compressive stresses in films decrease with increasing number of ZnO layers, i.e. the improvement ZnO film quality. However it is important to determine the quality of multilayer ZnO films using another method of investigation. Raman scattering is a very useful and sensitive method for evaluating crystal perfection including structural defects. Micro-Raman measurements were carried out in $z(x, x)\bar{z}$ backscattering geometry with z direction oriented parallel to the *c*-axis. In this configuration, only E_2(*low*), E_2 (*high*) and A_1(*LO*) modes around 101, 437 and 574 cm^{-1} are allowed according to the Raman selection rules. The E_2(*low*) and E_2(*high*) modes are the intrinsic characteristics of the Raman-active mode of wurtzite hexagonal ZnO and associated with Zn sublattice and with

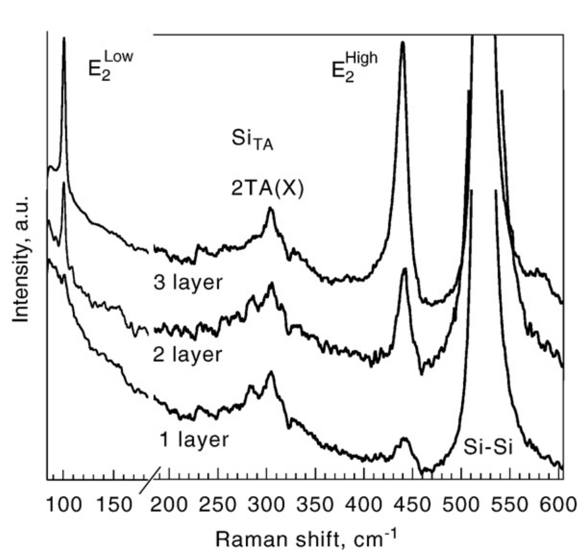

Fig. 1. Raman spectra of three-layered ZnO films deposited on Si substrate.

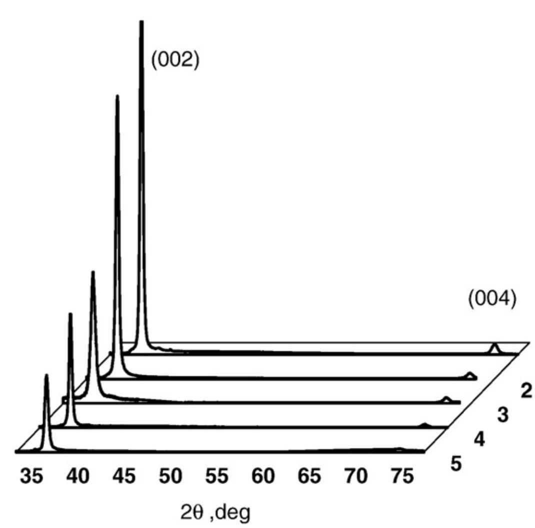

Fig. 3. XRD spectra of as-grown ZnO films deposited on 1) c-Al_2O_3, 2) glass, 3) ITO/glass, 4) SiN_x/Si and 5) Si (100) substrates.