DETERMINATION OF RESIDUAL STRESS IN THIN FILM BY GIXRD

Patrik Novák[1], Edmund Dobročka[2], Dalibor Búc[3], Jaroslav Kováč[3]

[1] Institute of Nuclear and Physical Engineering, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology,
[2] Institute of Electrical Engineering, Slovak Academy of Science,
[3] Institute of Electronics and Photonics, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology,

E-mail: patrik.novak@stuba.sk

Received 06 May 2014; accepted 23 May 2014

1. Introduction

Significant research effort is underway on ZnO nanostructures due to their unique properties for application in transparent electronics, photovoltaics, ultraviolet light emitters, piezoelectric devices, chemical sensors and spin electronics. Our investigations may allow finding the optimal technology for deposition of very thin ZnO films of the different morphology to cover cylindrical GaP nanowire surface using MOCVD technology. This paper is focusedon investigationof residual stress which is a characteristic parameter of the material properties. Residual stress is the stress that exists within a material without application of an external load. Nowadays, residual stress evaluation by X-ray diffraction is a well-known technique, and is frequently used for material characterisation. For characterization of residual stress we used Grazing Incidence X-rayDiffraction (GIXRD). This technique has been well established as an efficient tool for studies surface and subsurface structures [1, 2, 3] and there are a possibilitiesfor study of residual stress in thin film by GIXRD.For determination of stress state it is useful to restrict the effective penetration depth to a defined small value when the stress state at close to the surface of body has to be determined by GIXRD. We used ZnO thin films on GaP substrate and GaP nanowires by RF magnetron sputtering.

2. Theoretical background

To determine the residual stress in the sample by symmetric x-ray diffraction, the specimen must be rotated about two axes. The first rotation is characterized by the tilt angle ψ between the normal to the specimens surface and the normal to the diffracting planes of spacing d_{hkl}, which is parallel to the diffraction vector. The second rotation is characterized by the azimuth angle φ and is executed about an axis parallel to the specimen normal [4]. The strain $\varepsilon_{\varphi\psi}(hkl)$ can be determined from a change in the interplanar spacing $d_{\varphi\psi}$ of the diffracting planes (hkl),

$$\varepsilon_{\varphi\psi}(hkl) = \frac{d_{\varphi\psi} - d_0}{d_0} \qquad (1)$$

where d_0 is the interplanar spacing of the unstrained material.The strain results can then be converted into stress using a suitable value of the stiffness (elasticity) [5].The strains are generally represented in so-called $\sin^2\psi$ plots (plots of the strain versus $\sin^2\psi$).

The geometry based on Grazing Incidence X-ray Diffraction (asymmetric diffraction) can be applied to measure of residual stress in surface layers. Themethod is based on the use of a small constant incidence angle α and collecting diffraction intensity for different orientations of the scattering vector. In this geometry the diffraction plane is always perpendicular to the surface. Analogically to the standard methodthe stress can be determined from the interplanar spacings measured in direction of the scattering vector. In this case different ψ is calculated,

$$\psi_{hkl} = \theta_{hkl} - \alpha \tag{2}$$

where $\theta_{hkl}$is the Bragg angle.In contrast to conventional X-ray diffraction, where the angles ψ and θ can be chosen independently, with GIXRD the dependence between the angles ψ and θ, for given α places a constraint on the possible measuring combinations.

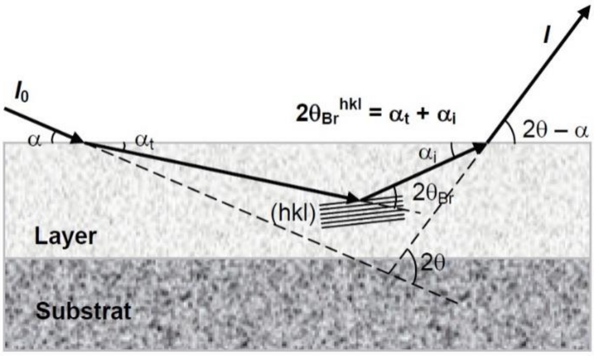

Fig.1: *Measuring geometry in GIXRD experiment: α – the angle of incidence, α_t – the refraction angle, α_i – the angle of the diffracted beam within the layer.*[6]

Fig. 1 shows the GIXRD geometry used in these experiments. The X-rays are penetratingthe sample at a small angle α, it turns out that below a critical angle α_c the effect of total external reflection will occur. The refracted X-rays travel in the sample with an angle α_t, diffract through the Bragg scattering angle $2\theta_{Br}$, and are then refracted again as they exit the sample. The measured scattering angle is 2θ, which is different from $2\theta_{Br}$. From Fig. 1, $2\theta_{Br}$ is equal to[6]:

$$2\theta_{Br} = \alpha_t + \alpha_i \tag{3}$$

where α_t and $\alpha_i$are given as:

$$\tan\alpha_t = \frac{\frac{1}{\sqrt{2}}\left\{\sqrt{(\sin^2\alpha - 2\delta)^2 + 4\beta^2} + (\sin^2\alpha - 2\delta)\right\}^{1/2}}{\cos\alpha} \tag{4}$$

$$\tan\alpha_i = \frac{\frac{1}{\sqrt{2}}\left\{\sqrt{(\sin^2(2\theta-\alpha) - 2\delta)^2 + 4\beta^2} + (\sin^2(2\theta-\alpha) - 2\delta)\right\}^{1/2}}{\cos(2\theta-\alpha)} \tag{5}$$

3. Experiment and results

The GaP nanowires were prepared in an AIX 200 MOCVD low-pressure reactor by a vapour-liquid-solid method from 30 nm BBI colloidal gold particles. The Au particles were randomly distributed over the substrate at a density of ~ 2 × 10^8 cm^{-2}. Nanowires deposition was performed in palladium purified H_2 carrier gas from phosphine (PH_3) and trimethylgallium (TMGa) used as the phosphorus and gallium sources and provides the continued growth of nanowires with an extremely high length to diameter ratio (60 - 80). ZnO n-type conductivity thin films were next deposited on GaP substrate and GaP substrate with NWs by using RF reactive magnetron sputtering at room temperature. A sintered disk of ZnO:Al (of 99.99 % purity for both ZnO and Al_2O_3) with 2 at. % Al_2O_3 was used as a target. The diameter and the thickness of the target were 76 mm and 5 mm, respectively. Sputtering was carried out in on-axis target-substrate geometry. The distance of substrate and target center was fixed at 60 mm, while central axes of the sample and target was tilted under angle φ. Substrates with GaP-NWs were placed on the rotating substrate holder with tilting arrangement. Within our deposition we used tilting angles φ of 82°, 65°, 45°, and 0°. The vacuum chamber was evacuated to a base pressure of 2.10^{-3} Pa before sputtering. Then high-purity Ar and O_2 (99.999 % purity for both gases) were introduced as sputtering gas and reactive species, respectively. The total pressure was fixed at 0.15 Pa. The Ar/O_2 partial pressure ratio was set up to be equal to 15:1. Prior to film deposition, the target was pre-sputtered for about 10 minutes to remove the surface contaminants. The films were deposited on substrates at 13.56 MHz at a power of 125 W. ZnO films were sputtered at room temperature with a sputtering rate of ~10 nm/min and their thickness on GaP substrates was determined by Dektak 150 instrument. This new concept allowed studying the influence of different tilting angle on the film morphology and structure.

Bruker D8 DISCOVER diffractometer was used with X-ray tube with rotating Cu anode operating at 12 kW. All measurements were performed in parallel beam geometry with parabolic Goebel mirror in the primary beam. The X-ray diffraction patterns for stress evaluation were measured in grazing incidence set-up (Fig. 2). In order to determine the changes of the strain and the stress with depth, three values for the angle of incidence α were chosen, 3°, 1.5° and 0.3° for sample with tilting angles of deposition φ = 82°.

The critical angle α_c for total external reflection of X-rays for crystalline ZnO is 0.332°. For α = 3° and 0.3° the penetration depths $z_{1/e}$ for ZnO are 196 and 4.5 nm, respectively, i. e. at 3° the X-ray beam penetrates the whole volume of the 140 nm thick layer, while at 0.3° the gain of the information is restricted to the topmost layer with the thickness less than ~ 5 nm. The stress was evaluated by multi-reflection method [7] with correction for the refraction of X-rays. The layers of polycrystalline ZnO deposited on (111) oriented GaP substrates exhibit strong (001) texture without any pronounced azimuthal dependence as it is shown in Fig. 2. Due to this texture only three reflections (002, 103, 203) with sufficient intensities could be used for stress evaluation. The in-plane strain components $\varepsilon^{||}$of the 140 nm thick layer were determined as -0.020 and -0.015 for α = 3° and 0.3°, respectively. The reference lattice parameters of the bulk ZnO were taken from PDF No. 36-1451. These values clearly show that the strain at the surface of the layer strongly decreases and reaches about 75% of the value averaged across the whole layer thickness. The corresponding values of compressive stress are 1.7 and 1.3 GPa, resp., when the isotropic stress factor E/(1+ν) = 86.1 GPa [8] is used. Distribution function of crystallite orientation is defined by the reference spherical area and pole figure is a projection of this area to the plane. Middle of the pole figure corresponds to the surface normal of the sample and consequently planes (002) are parallel to the sample surface. [9]

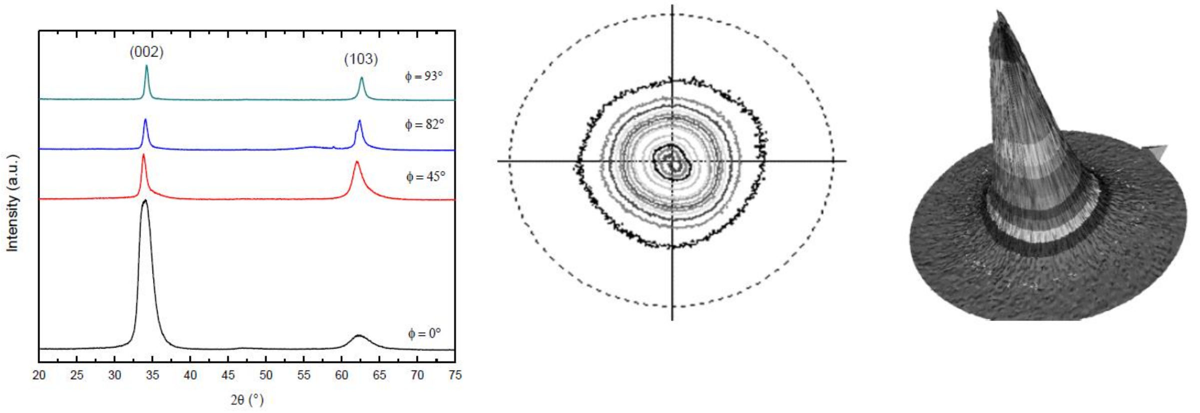

Fig 2: *GIXRD patterns of the ZnO layers (left) deposited at different tilting angles. The X-ray incidence angle was α=1.5°. Pole figure* 002 *(middle) and the corresponding 3D view (right) of the textured ZnO layer deposited at the tilting angle 82°.*

4. Conclusion and discussion

In this paper, we have evaluated theresidual stress of ZnO polycrystalline films deposited by RF magnetron sputtering on GaP substrates and core-shell GaP/ZnO nanowires and method for correct $2\theta_{Br}$ calculation was shown.GIXRD measurements confirmed the internal compressive residual stress which bends the GaP/ZnO core/shell NWs along the downstream direction of bombarding particles.

Acknowledgement

The work was supported by the Slovak Research and Development Agency under the contracts APVV-0246-12, grant of Science and Technology Assistance Agency "GRONA" no. APVV-0301-10 and VEGA projects 1/1106/12, 1/0228/14, 1/0439/13, 1/0534/12, 2/0147/11.

References:

[1] R. Feidenhans´l: *Surface Science*,**186**, 499 (1987)
[2] H. Dosch: Tracts in Modern Physics, Springer, Berlin Germany (1992)
[3] H. Rhan: *Journal Applied Physics*, **74**, 146 (1993)
[4] M. J. Marques: *Materials Science and Engineering,* **A287**, 78 (2000)
[5] M. Birkholz: Thin film analysis by X-ray scattering, Wiley-vch, Weinheim Germany (2006).
[6] Bruker: Diffracplus Leptos 6 – User Manual, Bruker AXS GmbH, Karlsruhe Germany (2008)
[7] A. Baczmanski: *Surface and Coating Technology*, **182**, 43 (2004)
[8] H. Morkoç: Zinc Oxide: Fundamentals, Materials and Device Technology, Wiley-vch, Weinheim Germany (2009)
[9] D. Buc, J. Kovac, V. Kutis, J. Murin, M. Caplovicova, J. Skriniarova, P. Novak, J. Novak, S. Hasenohrl, E. Dobrocka: in preparation