Thin Solid Films 519 (2011) 6369–6373

Contents lists available at ScienceDirect

Thin Solid Films

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

Interpretation of the two-components observed in high resolution X-ray diffraction ω scan peaks for mosaic ZnO thin films grown on c-sapphire substrates using pulsed laser deposition

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ARTICLE INFO

Article history:
Received 30 August 2010
Received in revised form 3 January 2011
Accepted 10 April 2011
Available online 16 April 2011

Keywords:
Zinc oxide
Thin films
X-ray scattering
Transverse scans
Misfit dislocations
Heteroepitaxy

ABSTRACT

X-ray scattering methods were applied to the study of thin mosaic ZnO layers deposited on c-Al_2O_3 substrates using Pulsed Laser Deposition. High Resolution (HR) studies revealed two components in the ω scans (transverse scans) which were not resolved in conventional "open-detector" ω rocking curves: a narrow, resolution-limited, peak, characteristic of long-range correlation, and a broad peak, attributed to defect-related diffuse-scattering inducing a limited transverse structural correlation length. Thus, for such mosaic films, the conventional ω rocking curve Full Width at Half Maximum linewidth was found to be ill-adapted as an overall figure-of-merit for the structural quality, in that the different contributions were not meaningfully represented. A "Williamson-Hall like" integral breadth (IB) metric for the HR (00.l) transverse-scans was thus developed as a reliable, fast, accurate and robust alternative to the rocking curve linewidth for routine non-destructive testing of such mosaic thin films. For a typical ZnO/c-Al_2O_3 film, the IB method gave a limited structural correlation length of 110 nm ± 9 nm. The results are coherent with a thin film containing misfit dislocations at the film-substrate interface.

1. Introduction

Wurtzite zinc oxide (ZnO) is a remarkable multifunctional material with a wide range of established and emerging applications [1,2]. These include a variety of optoelectronic uses based on a distinctive combination of properties such as a direct wide bandgap (3.37 eV), relatively high exciton binding energy (60 meV), good transparency over the whole visible spectrum and a conductivity which can be readily tuned from semi-insulating to semi-metallic [3–8].

Since large area ZnO substrates are not yet available at a reasonable cost level, there is currently a need to grow ZnO on alternative substrates. The most widely adopted choice, for opto-electronic applications, is c-sapphire (c-Al_2O_3). Although, there are significant lattice and thermal mismatches [9], ZnO is a relatively compliant material [10], and it can be grown on c-Al_2O_3 in the form of epitaxial "blocks" with rotational misorientation (or "tilt") relative to one another. These monocrystalline or "mosaic" blocks scatter X-rays incoherently with respect to each other [11,12].

The most widely adopted metric for the comparison of the crystal quality for such films is the full-width at half maximum (FWHM) (or linewidth) of the (00.2) peak of the X-ray diffraction (XRD) "rocking-curve." However, this metric can be misleading in the characterisation of a thin film with such a mosaic structure. First of all, this is because this metric strongly depends on the experimental conditions, since, in the literature, the term "rocking-curve" is often used, confusingly, to refer not only to the conventional "open-detector" scan but also to the high resolution, HR, ω-scan experiments performed with "channel-cut" optics in the diffracted-beam path ("transverse scans"). In the case of epitaxial thin films, XRD ω-scan experiments should, ideally, be done with such a channel-cut in the diffracted beam path in order to differentiate contributions orthogonal and parallel to the sample surface. Indeed, the relatively low thickness of these ZnO layers in itself generates a widening of the diffraction peak, orthogonal to the sample surface. This is due to the presence of "crystal truncation rods", which resemble, but have nothing to do with, a defect-induced effect. Secondly, since the peak broadening has multiple origins, differentiation of these causes is desireable in order to compare samples. In this paper, we report on the development of a rapid, robust and reliable alternative to the conventional ω rocking curve figure-of-merit, which is better adapted for the characterisation of such mosaic thin films and which can be

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doi:10.1016/j.tsf.2011.04.036

readily extracted from the XRD transverse-scans. Moreover, the present method is applicable to other thin "mosaic-block" material systems, e.g. (00.*l*)-oriented wurtzite materials (such as GaN) and (00*l*)-oriented zinc-blende materials (such as GaP, InAs, etc.).

2. Experimental details

ZnO thin films were grown on c-Al_2O_3 substrates held at elevated substrate temperature in a home-made Pulsed Laser Deposition (PLD) system using a Coherent KrF excimer laser (248 nm) [13]. The laser spot was focused onto a 5 N sintered target to give a fluence of up to about 4 J/cm^2. During the growth, various parameters were adjusted in order to maintain a 2D growth. In particular pulse repetition rate was varied between 1 and 50 Hz and molecular oxygen (O_2) background pressure was varied between 1.3×10^{-4} and 1.3×10^{-1} Pa. HRXRD and Very HRXRD (VHRXRD) experiments were conducted in Panalytical MRD-Pro and Seifert PTS systems, respectively. For both, a $Cu_{K\alpha1}$ source ($\lambda=0.15406$ nm) with line focus was adopted. The HR and VHR experiments were carried out using four-bounce Ge (220) and (440) crystal monochromators in the incident-beam path, giving incident-beam divergences of 12 and 5 arcsecs and wavelength dispersions ($\frac{\Delta\lambda}{\lambda}$) as low as 1.4×10^{-4} and 5.5×10^{-5}, respectively. A multilayer mirror was employed to enhance the incident intensity. Two incremental encoders allowed an angle reading to an accuracy of $+0.0002°$ for both the ω and 2θ positions. The HR and VHR XRD were performed, respectively, with two-bounce Ge (220) and (440) channel-cut crystals in the diffracted-beam path, giving detector acceptance angles of 12 and 5 arcsecs, respectively (i.e. 0.0033° and 0.0014°). For X-ray Reflectometry (XRR), the measurements were performed using a detector slit of 0.1 mm with back Soller slits and a knife-edge located at 60 μm from the sample surface, so as to reduce the background signal to 0.05 counts per second. Thus, a dynamic intensity range of 10^7 could be achieved for the reflectivity curves.

Two scan modes were employed: ω/2θ scans which provided information on crystal planes parallel to the sample surface, and ω rocking-curves (rotation of the sample around the ω axis, while keeping the detector at a fixed 2θ), which gave the dispersion in the orientation of the crystal planes for a given lattice spacing, plus information on the in-plane correlation lengths. In the following, we will refer to the HR version of the ω rocking-curves (performed with a channel-cut crystal in the diffracted beam path) as "transverse-scans".

The process of deconvoluting multicomponent peaks such as those observed for mosaic thin films is usually carried out using either the Fourier technique [14] or the variance method [15,16] plus direct modelling [17,18] of the diffraction-peak profiles. Fast analysis of the peak breadths [19], called the Integral-Breadth (IB) method, is adequate for practical purposes, however, when an estimation of the coherent domain size (termed "crystallite size") is required, even if this method tends to overestimate the domain size value when compared with alternative methods [20]. It should be noted that the IB, defined as the width of a rectangle having the same area and height as the observed line profile, has already been put forward as a more useful metric than the FWHM [21]. It is well-known, for instance, that the broadening of the (00.*l*) reflections in the ω/2θ mode can be used to estimate the correlation length of the diffraction domains (coherent domain size) in the growth direction, after separating both the strain and the correlation length components responsible for the IB widening, through the Halder and Wagner parabolic approach [22], a variant of the Williamson–Hall plots method. In particular, when considering the ZnO epitaxial thin films investigated in the present paper, the growth-direction coherent-domain-size has been found [23] to be comparable with the layer thickness (determined by XRR) bringing to the fore the high-crystalline-quality in the growth direction. Then, any overall measurement of the structural quality will include a contribution from in-plane defects. Thus, an appropriate "figure-of-merit" needs to be incorporate both the lateral correlation length and the mosaicity. We propose a method for this, in the following, based on a line-profile analysis of (00.*l*) XRD transverse-scans, through an IB approach. This can then be used as a reliable metric for comparing the structural quality of thin ZnO layers grown on c-Al_2O_3 substrates.

The interpretation of the results is facilitated by considering reciprocal space co-ordinates, which are related to the angular space co-ordinates by the following relationships:

$$S_x = \frac{2}{\lambda}\sin\theta\ \sin(\omega-\theta) \tag{1}$$

$$S_z = \frac{2\ \sin\theta}{\lambda} \tag{2}$$

where S_x and S_z are the diffraction vector along the sample surface and perpendicular to the sample surface, respectively (assuming that the diffraction planes are parallel to the sample surface, i.e. $\omega=\theta$). Therefore, the angular-space IBs $\beta(2\theta)$, from a ω/2θ scan, and $\beta(\omega)$, from a transverse scan, can be translated into reciprocal space coordinates of the variables S_x and S_z by the following relationships:

$$\beta_z(S) = \beta(2\theta)\frac{\cos\theta}{\lambda} \tag{3}$$

$$\beta_x(S) = \beta(\omega)\frac{2\ \sin\theta}{\lambda} \tag{4}$$

A process of deconvolution to allow for the instrumental profile was also carried out, as described elsewhere [23]. In the following, β refers to the instrument-corrected IB.

3. Results and discussion

Fig. 1 shows an XRR scan for a typical ZnO layer grown on a c-Al_2O_3 substrate. The Auto-Correlation Function (ACF) obtained through a Fourier transform of the XRR profile (corrected for refraction [24]) displays a peak centered at 178.1 nm ± 0.2 nm The thickness fringes could be followed up to an S_Z value as large as 0.55 nm^{-1}, indicating that both the film-air and film-substrate interfaces were relatively flat. In complement to the XRR, specular ω/2θ XRD analyses were performed around the (00.2) Bragg reflection, as shown in Fig. 2. The thickness fringes, in this case, extend up to 0.35 nm^{-1} around the Bragg peak indicating that the ZnO displays excellent crystalline quality over the thickness corresponding to the correlation length indicated by the fringes. The fringe spacing gives a correlation length of 177.5 nm ± 0.2 nm, which is very close to the thickness determined by XRR. Therefore, the entire film is scattering in phase, which shows that the crystalline quality is quasi-perfect along the growth direction.

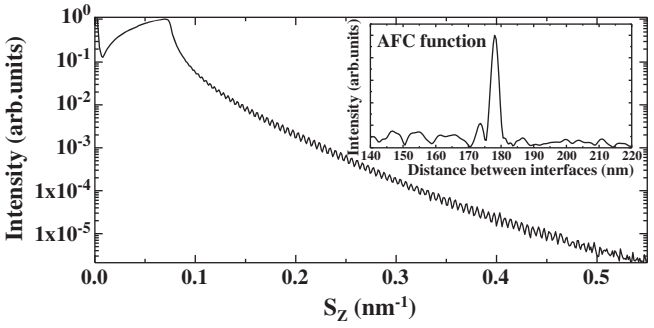

Fig. 1. An XRR scan for a ZnO thin film grown on c-Al_2O_3. Inset: ACF obtained from the XRR profile, corrected for refraction and normalised to the substrate Fresnel reflectivity, as described in ref 24. The ACF spectrum gives a thickness of 178.1 nm ± 0.2 nm.