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c-texture versus *a*-texture low pressure metalorganic chemical vapor deposition ZnO films: Lower resistivity despite smaller grain size

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ABSTRACT

Recently, it has been shown that it is possible to tune the morphology of zinc oxide films deposited by low-pressure metalorganic chemical vapor deposition (LP-MOCVD) while preserving good electrical conductivity. Here a closer look is taken at films deposited under two different deposition conditions; one leading to LP-MOCVD *a*-texture (i.e., with the *a*-axis perpendicular to the substrate), the other resulting in *c*-texture (i.e., with the c-axis perpendicular to the substrate), with the aim of correlating their structural and electrical characteristics. We introduce the concept of a "selection layer" to indicate the initial region of growth that precedes the establishment of a clear preferential crystallographic film orientation. With a strong preferential *c*-texture of initial nucleation the selection layer for *c*-texture films is minimal (<50 nm), while for *a*-texture it extends for about 0.25 μm of film thickness. The non-intentionally doped *c*-textured material has an electrical resistivity lower by an order of magnitude than the *a*-textured one, due to a higher carrier concentration and higher carrier mobility. Electrical transport measurements indicate that grain boundaries are the main limitation to conductivity for both film textures; in which case it is unexpected that the *c*-textured films show higher carrier mobility despite having smaller grains (i.e., greater grain boundary density). This inconsistency is explained by referring to their thinner selection layer, and lower activation energy for inter-grain transport as determined by temperature-dependent Hall measurements.

1. Introduction

Due to its wide and direct band gap (3.4 eV), large exciton binding energy (60 meV) and inherent n-type conductivity, zinc oxide (ZnO) is exploited in several photonic and electronic applications, such as gas sensors [1,2], light emitting diodes [3] and as transparent conductive electrodes in thin film solar cells [4,5]. Furthermore, the ability to tune the surface morphology of the ZnO films is of great interest for the functionalization of the material, broadening its applications. The surface morphology of ZnO is related to the preferential crystallographic orientation of the films, which in turn can be tuned by adjusting the deposition parameters. For example, by decreasing the flow of oxygen gas during sputtering, it is possible to switch the film texture from *a*-axis oriented to *c*-axis oriented [6,7]. Similarly, with low-pressure metalorganic chemical vapor deposition (LP-MOCVD), it is possible to switch the film texture from *a*-axis oriented to *c*-axis oriented by decreasing the water to diethylzinc ratio (H_2O/DEZ) of the precursor gases [8,9]. It is assumed that these deposition parameters control the mobility of the atoms adsorbed on the surface (ad-atom mobility) that governs the material growth kinetics and the resulting crystallographic orientation [10,11]. In our case, the modification of the ZnO film morphology is correlated to the change between *c*- to *a*-axis growth orientation which correspond to the (0001) and ($11\bar{2}0$) planes, respectively, the lowest and the second lowest surface energies [6,12].

It is well established that the microstructure of ZnO thin films can have a strong influence on their electrical properties [13,14]. Particularly important for polycrystalline films is that, during the deposition immediately after nucleation, numerous crystallites grow thus creating a very fine grain structure; larger, well-defined grains only form later [15]. This first layer is highly resistive due to its high grain boundary concentration, and we introduce the concept of a "selection layer" in order to relate this disordered microstructure with the electrical properties of the film.

In this study, a detailed investigation of the structural, optical and electrical properties of *c*-textured and *a*-textured LP-MOCVD ZnO films is presented; x-ray diffraction (XRD) and transmission electron microscopy (TEM) have been used to reveal structural differences between the two films. Furthermore temperature-dependent Hall effect measurements have been performed to shed light on the mechanisms regulating the carrier transport through the film.

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2. Experimental details

ZnO samples were deposited by LP-MOCVD on 0.5-mm-thick AF32 Schott glass substrates. Diethylzinc $(C_2H_5)_2Zn$ and water vapor were used as precursors for zinc and oxygen respectively. Notice that DEZ and H_2O are brought in the chamber by simple precursor evaporation without carrier gas. The *a*-textured films were obtained with a H_2O/DEZ flow ratio ≈ 1.2 and a substrate temperature around 160 °C. For the *c*-textured films, the H_2O/DEZ flow ratio ≈ 0.6 [9], and the substrate temperature was around 150 °C [11]. During deposition, the total pressure of the chamber was kept at 35 Pa. The thickness of the films was varied between 0.05 and 2 μm. Note that in this study, all films (except the ones analyzed for carrier transport) were non-intentionally doped (nid), i.e., grown without extrinsic dopants. For the carrier transport analysis, films were doped extrinsically with diborane (B_2H_6, diluted at 1% in argon), with the B_2H_6/DEZ flow ratio varied between 0 and 1.5.

The sheet resistance of the films was evaluated by a four-point probe measurement. By means of an Ecopia Hall effect measurement system, Hall mobility (μ_H), charge carrier density (N_H) and resistivity (ρ) were determined using the Van der Pauw configuration; Hall effect measurements at variable temperatures (80–350 K) were performed using a cryostat fueled with liquid nitrogen. The film absorptance (A) was calculated by measuring the total light transmittance (TT) and reflectance (TR) through the sample, A = 1 – TT– TR. By measuring the diffuse transmittance (DT), we calculated the haze factor as the ratio DT/TT for λ = 600 nm. These optical measurements were performed in the spectral range of 320–2000 nm using a spectrophotometer equipped with an integrating sphere. XRD measurements were performed using Cu-Kα radiation (λ = 1.542 Å) in the 2θ range of 30–70° (0.05°-step, 1 s/step). The surface morphology of the films was analyzed by scanning electron microscopy (SEM, $V_{ac} \approx 5$ kV). With TEM, bright-field imaging, selected area diffraction pattern acquisition and scanning TEM (STEM) were performed to investigate the microstructure of the films, using 120 kV LaB_6 and 200 kV FEG instruments. The surface roughness (R_{rms}) was obtained from atomic force microscopy performed on a 2 μm × 2 μm area.

3. Results

3.1. Film surface morphology and crystalline microstructure

The stable crystal structure of ZnO is the hexagonal wurtzite phase, and in this study, we refer to two of its main directions: the *a*-axis (lying in the basal plane and joining two opposite corners of the hexagonal prism, Fig. 1a) and the *c*-axis (perpendicular to the hexagonal basal plane, Fig. 1b). The *a*-textured films have a surface roughness of about 70 nm for a film thickness of 2 μm, while the *c*-textured films have a surface roughness of about 15 nm for the same thickness [9]. The *a*-textured films are characterized by a surface with large 3-sided surface pyramids, while the *c*-textured surface presents small-rounded features as shown in Fig. 1.

Fig. 2a compares the XRD patterns for the two film types, showing the strong preferential orientations (0001) for the *c*-texture and $(11\bar{2}0)$ for the *a*-texture, respectively. While for both 1-μm-thick films the preferential orientation is strongly developed, the rate at which it is established is markedly different. To assess this rate in a quantitative way, texture coefficients TC(abcd) for a generic plane (abcd) are calculated for the different prevalent planes [16,17], defined as follows:

$$TC(abcd) = \frac{I(abcd)/I_{ICSD}(abcd)}{\frac{1}{N}\sum_{(hkil)=1}^{N} I(hkil)/I_{ICSD}(hkil)} \quad (1)$$

where *I(abcd)* is the measured intensity of the (abcd)-peak, I_{ICSD} is the standard intensity for ZnO powders indicated in the Inorganic Crystal Structure Database (ICSD) [18] and *N* is the number of XRD peaks considered, in our case $(10\bar{1}0)$, (0001), $(10\bar{1}1)$, $(11\bar{2}0)$ and $(10\bar{1}3)$, and therefore, $N = 5$. Eq. (1) shows that for randomly distributed powders the TC values for all peaks is 1; in the case of textured film, the TC of the preferential orientation increases reaching a maximum value of *N* only when no other peaks are present in the XRD pattern. Fig. 2b shows the evolution of the crystallographic orientation for the *a*- and *c*-textured films in the thickness range of 0.05–1.5 μm. It is clear that the *c*-texture film

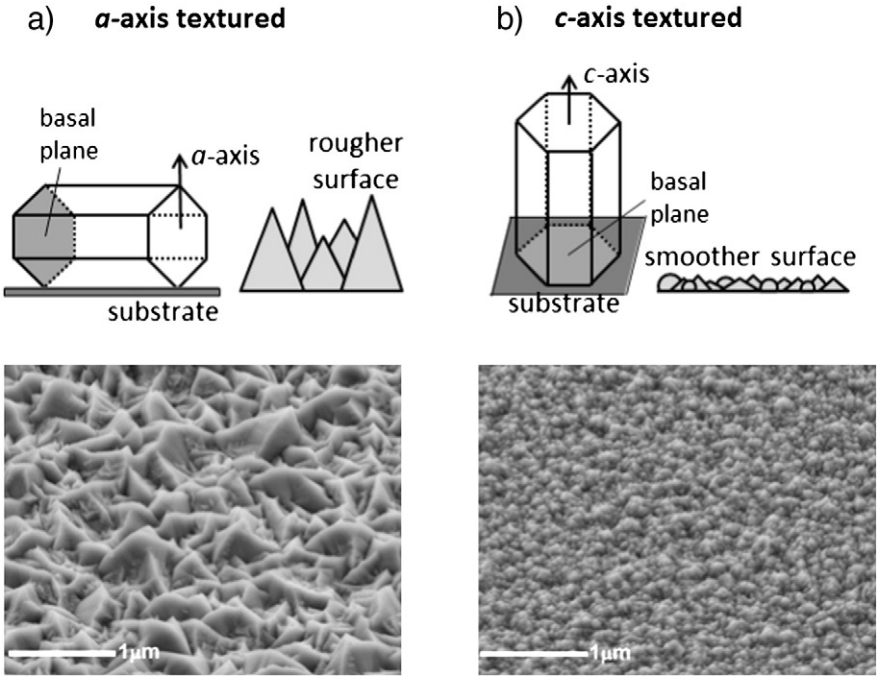

Fig. 1. Orientation of the hexagonal structure with respect to the substrate and 50°-tilted-view SEM micrographs for (a) *a*-textured and (b) *c*-textured films. Film thickness ≈ 2 μm.