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Epitaxial growth of non-polar ZnO films on MgO substrate

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ABSTRACT

The pulsed laser deposition of pure and doped (Nd or Fe) ZnO films on (001) oriented MgO substrates was investigated. Polar (alternate Zn and O planes along the main axis growth), or non-polar ZnO films were obtained according to the growth conditions, and epitaxial relationships were observed in both cases. For the non-polar films, different in-plane orientations were observed, and the domain matching epitaxy was used in order to describe the in-plane relationships of the film with respect to the MgO substrate. These relationships correspond to different angles between the in-plane $[001]_{ZnO}$ and $[100]_{MgO}$ directions and are different from those previously proposed for the epitaxy of non-polar ZnO on MgO. In addition to the lattice mismatch between film and substrate, an important parameter governing the in-plane orientation is the minimum size of the epitaxial domain which mainly determines the in-plane alignment. Indeed, for doped-ZnO films, the coherence length, *i.e.* the spatial extension of the crystallites is limited by the presence of the dopants. This leads to different epitaxial relationships with respect to undoped films, and which are related to the epitaxial domain size.

1. Introduction

The piezoelectric properties of ZnO and its potential high electrical conductivity and high optical transparency have led to the use of this material in a large number of applications: optical waveguides, piezoelectric transducers, transparent conducting electrodes, light emitting diodes (LED) [1–4]. Most of them are based on ZnO films grown along the polar *c*-axis direction, which is the preferential texture of ZnO films onto the majority of the substrates [5,6], *i.e.* the growth occurs by the stacking of alternate Zn and O planes leading to polar (001) oriented ZnO films. However, such *c*-axis polar films exhibit electrostatic fields that spatially separate electrons and holes in active layers, and this induces deleterious effects in the case of LEDs [7]. Non-polar ZnO films have been envisaged in order to overcome this drawback, and in addition, such non-polar ZnO films are also of interest for some applications in surface acoustic waves devices in liquids [8]. The growth of non-polar ZnO films, *i.e.* (110) or (100) ZnO films, has thus been investigated [8–14]. The epitaxial growth of such films has been reported for various single crystal substrates like R-cut sapphire, GaN, and others, and using various deposition methods [8–19].

In the case of (001) oriented MgO substrates, the epitaxial growth of (100) ZnO films has been reported [15–19], *i.e.* this corresponds to the formation of the so-called *m*-axis ZnO film. However, the in-plane epitaxial relationships between film and substrate together with the parameters governing them are still open questions. Actually, two in-plane orientations have been proposed to describe the growth of (100) ZnO film on (001) MgO substrate: (i) the alignment of the $[101]_{ZnO}$ with the in-plane $[110]_{MgO}$ direction with a $\pm$ 1.5° precision [17–19]; and (ii) the alignment of the $[001]_{ZnO}$ with the in-plane $[110]_{MgO}$ with a 30° twist [15,16], leading in this case to a 15° angle between the $[001]_{ZnO}$ and the $[100]_{MgO}$ directions. Our aim in this work was to bring some new insights on the epitaxial growth of non-polar *m*-axis ZnO films on MgO substrates.

In this work, pure and doped (Nd or Fe) ZnO films were grown by pulsed-laser deposition (PLD) on (001) oriented MgO substrates, in order to precisely study the epitaxial relationships between film and substrate. Doping of oxide films by some elements does not only modify their properties [20–24], but may induce in addition structural defects in the oxide matrix, and modify the epitaxial growth. The growth of non-polar pure or doped ZnO films, has been specifically considered in this work, and the in-plane orientations between such non-polar films and MgO substrate were investigated by asymmetric X-ray diffraction

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(pole figure measurements). The domain matching epitaxy approach [25–27] was used to interpret the epitaxial relationships between film and substrate, while the correlation between the doping and epitaxial relationships was evidenced.

2. Experimental

The pure and doped ZnO films were grown by PLD onto (001) oriented MgO single crystal substrates. A frequency quadrupled Nd:YAG laser was used in the experimental set-up presented elsewhere [28]. Pulses around 10^8 W/cm^2 were fired onto ceramic targets (ZnO, Nd (2%):ZnO and Fe (5%):ZnO). The film growths were carried out under different oxygen pressures in the 1 to 10^{-5} Pa (residual vacuum) range, with different substrate temperatures between 300 and 700 °C.

The thickness (in the 50 to 150 nm range) and composition of the films were measured by Rutherford backscattering spectrometry using the 2.5 MeV Van de Graaff accelerator of the SAFIR IBA laboratory, University Pierre et Marie Curie. X-ray diffraction analyses using a Philips X-pert diffractometer (CuK_α radiation), allowed the study of the film structure. The analyses were carried out in the θ–2θ Bragg conditions, and in asymmetric geometry for the pole figure measurements [27]. For higher resolution phi-scans we used a Brucker D8 Discover with CuK_α radiation. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) measurements were used to obtain information on the surface morphology of the films.

3. Results

The substrate temperature and oxygen pressure play a major role on the ZnO film texture on MgO. Fig. 1 displays the XRD patterns for pure ZnO films grown at 300 and 500 °C under 1 Pa oxygen pressure. At 300 °C, the diagram only shows the 002 ZnO peak indicating a *c*-axis texture, while at higher T, pure *m*-axis oriented films are obtained, as shown by the sole presence of the 100 ZnO peak, in agreement with results previously reported for growth on sapphire substrates [18,29]. Differently, in the 10^{-2} - 10^{-5} Pa range, all the undoped ZnO films show mainly the *m*-axis non-polar (100) texture, whatever the substrate temperature. For the Nd and Fe-doped ZnO films, non-polar *m*-axis (100) films were solely obtained under 1 Pa at temperatures ≤ 500 °C. A clear difference between the pure and doped ZnO non-polar films appears in the full width at half maximum (FWHM) of their respective 100 rocking curves (*i.e.* ω-scans). Indeed the width of these rocking curves is largely higher for the doped films (between 2.5 and 3°), while it is around 1.5° for the pure ZnO films. The dopants thus induce structural defects in the ZnO network. In fact, it must be noticed that

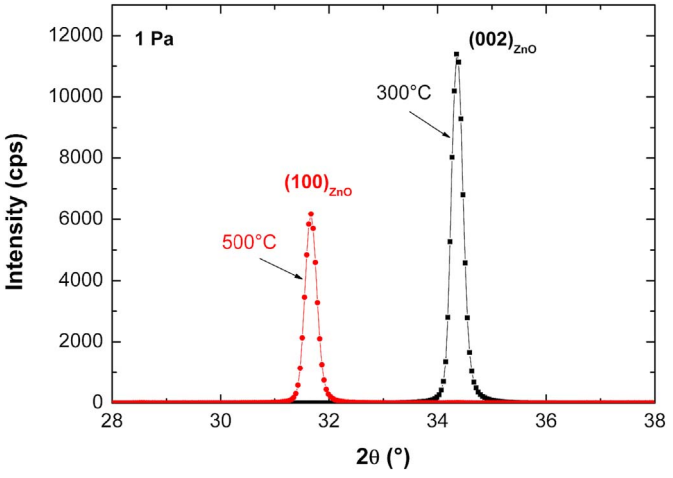

Fig. 1. XRD diagrams for (100) and (001) ZnO on (001) MgO grown under 1 Pa O_2 pressure at 500 and 300 °C.

the behavior of Nd and Fe in the ZnO network is different. Actually, the rare earth ions (Er, Nd,…) are difficult to incorporate in the ZnO network, since during the growth rare earth segregation occurs [20,30,31]. These ions in ZnO act as grain growth inhibitors and tend to aggregate at the grain boundary [30], limiting thus the size of the crystallites, as it has been previously observed [30,31]. In the case of Fe, the situation is different since Fe can be easily incorporated in the ZnO network [32]. However, this incorporation leads to a severe deformation of the network (increase of the lattice parameter), associated with a small crystallite size and an amorphization [32]. In the two cases, a decrease of the ZnO crystallite size is observed, however for different reasons.

Fig. 2 shows typical SEM and AFM images corresponding to *m*-axis non-polar ZnO (Fig. 2a and b) and *c*-axis polar ZnO (Fig. 2c) films. Elongated stripes are observed in Fig. 2a and b, indicating anisotropic growth rates of the ZnO crystallites. These elongated stripes are aligned along the *c*-axis of the ZnO cristallites, as indicated in Fig. 2a, by the respective $[001]_{ZnO}$ direction for the two domains which are present in the SEM image. The presence of such nanostripe arrays is characteristics of the growth of *m*-axis ZnO on a substrate [33]. Actually, in the ZnO wurtzite structure, the (001) plane is a polar plane consisting in either Zn or O plane, along the *c*-axis. According to theoretical calculations [34], the surface free energy of such polar planes is infinite [34]. On the other hand, the non-polar prismatic planes of ZnO present a lower surface free energy [34]. The ZnO film growth will occur in such a way that the surface free energy would be minimum. It follows that the polar (00l) plane has thus to represent the minimum surface area, while the prismatic planes have to represent the maximum surface area in order to have the minimum surface free energy for the crystallites. This will lead to the growth of elongated (00l) oriented ZnO crystallites. For films presenting the *m*-axis texture, *c*-axis elongated stripes are formed as shown in Fig. 2a and b, while in the case of a *c*-axis texture a columnar growth is observed [5] leading to a very different surface morphology which evidences the top of the columnar grains (Fig. 2c).

In the SEM images, different domains can be observed according to the directions of the stripes. These elongated stripes are along the $[001]_{ZnO}$ direction and they clearly indicate the existence of well-defined in-plane specific orientations between the ZnO crystalline domains and the MgO substrate. In what follows we use, as it is commonly admitted in the literature, the term “epitaxial films” to characterize such films. This does not mean that our films are single crystalline ZnO films, but this characterizes the fact that such films are composed of crystalline domains presenting well defined in-plane epitaxial relationships with the substrate.

Pole figure measurements were carried out on these films and a typical result is presented in Fig. 3, *via* the pole figure recorded for the (103) ZnO diffraction peak (2θ = 62.8°) of a pure (100) ZnO film on MgO grown at 500 °C under 1 Pa. This pole figure shows 8 very well-defined poles at a declination angle ψ = 59° which corresponds to the angle between the (100) ZnO plane (parallel to the substrate) and the (103) ZnO plane film. The presence of 8 poles has been already reported in previous studies [8,15–18] on ZnO films grown on MgO substrates by molecular beam epitaxy or other methods. These 8 poles are due to the respective 4-fold and 2-fold symmetries of the (001) MgO and (100) ZnO plane respectively.

As indicated in Fig. 3, the position of the (103) ZnO poles allows the determination of the angle α between the $[001]_{ZnO}$ and $[100]_{MgO}$ axess. In the present case this angle α is equal to about 14°. The same value was obtained for the doped (Nd and Fe) (100) ZnO films grown under 1 Pa oxygen and at temperatures ≤ 500 °C. Differently, for pure ZnO, a α value in the 14.5–15° range was obtained for films grown under 10^{-2} or 10^{-5} Pa whatever the substrate temperature, the film grown at 500 °C and 1 Pa, being the sole presenting the α value around 14°.

The pole figures were obtained by scanning along the two angles φ and Ψ. To avoid a too long time measurement, the step size for the φ scan was 1°. With such a step size the accuracy on the pole determination (± 0.5°) is not sufficient to draw reliable conclusions on the