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Growth, structural and electrical properties of polar ZnO thin films on MgO (100) substrates

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ABSTRACT

ZnO films have been grown on (100) oriented MgO substrates by pulsed-electron beam deposition in the room temperature to 500 °C range. Highly (00·2) textured films are obtained for a growth temperature higher than 200 °C, and epitaxial films are formed at 500 °C with the following epitaxial relationships: $(1\text{-}1\cdot0)_{ZnO}$ // $(110)_{MgO}$ and $(11\cdot0)_{ZnO}$ // $(110)_{MgO}$, despite the difference in symmetry between film and substrate. The low temperature resistivity curves evidenced a metal–semiconductor transition for the ZnO films grown in the 300 to 500 °C range which has been interpreted in the frame of the model of conductivity in disordered oxides.

1. Introduction

While the growth of c-axis epitaxial ZnO films on crystalline substrates like sapphire presenting the rhomboedral symmetry has been and is nowadays the subject of numerous works [1], the formation of ZnO films on single crystal substrates presenting a different structural symmetry is not so well documented. The formation of non polar ZnO films, i.e. ZnO films with their c-axis in the plane parallel to the substrate, would however lead to interesting applications [2,3]. Motivated by this aspect, the growth of ZnO films on cubic substrates has been studied, in particular on $SrTiO_3$ single crystal substrates according to the fact that a high density, two dimensional electron gas with unique electrical and thermal properties forms at the interface between $SrTiO_3$ and other oxides [3,4]. The growth of non polar m oriented (11·0) ZnO films on (001) $SrTiO_3$ substrates has been thus reported [3,4], while the classical polar (00·2) ZnO growth is observed on (111) oriented $SrTiO_3$ [5].

In the case of ZnO films on MgO single crystal substrates, the situation appears rather confusing, with results which in terms of film orientation not only depend upon the substrate orientation, but also on the growth method, and experimental conditions. Indeed, films with multiple textures, or m-axis or c-axis oriented ZnO films can be obtained depending upon growth parameters [2,6–8]. This underlines the difficulties to obtain high crystalline quality ZnO thin films with a single epitaxial relationship with the MgO single crystal substrate. The epitaxial growth is not trivial, due to differences in crystallographic symmetries of the hexagonal ZnO network (a = 0.3249 nm and c = 0.5206 nm) and the cubic MgO (a = 0.421 nm).

We have studied the formation, structure and electrical properties of ZnO films grown on (100) oriented single crystal MgO substrates, by the pulsed-electron beam deposition method (PED). This thin film growth technique [9–13], conceptually similar to the pulsed laser deposition, differs by the use of an intense pulsed electron beam to ablate the target material instead of a laser beam. Oxide films are easily grown by PED, with a good control of the surface morphology, cationic composition, oxygen stoichiometry and crystalline structure of the films [9–14]. Our main objective was to determine the pertinent parameters governing the ZnO film orientation and epitaxial relationships with MgO substrates, and to correlate their structural characteristics with their electrical properties. We evidenced the (00·2) ZnO growth on (100) MgO substrates, as well as the heteroepitaxial growth of ZnO films. Depending on the growth temperature, variations in the electrical properties were observed for the ZnO films grown on (100) MgO substrates. The resistivity curve shows a semiconducting behaviour for the films grown at room temperature, while the films grown in the 300 to 500 °C range show a metallic conductivity at room temperature followed at lower temperatures by a metal–semiconductor transition (MST), as was already observed in epitaxially ZnO films on Al_2O_3 single crystal substrates grown by PED [14]. This behaviour was interpreted in the frame of the quantum corrections to conductivity in a disordered medium [15].

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2. Experimental details

The ZnO films were grown on (100) oriented MgO substrates by the PED method [9,16,17]. The PED set-up consists of a pulsed electron beam source in the channel-spark discharge configuration and a vacuum chamber for the thin film growth. The channel-spark discharge configuration consists of a hollow cathode, a dielectric capillary tube (6 mm diameter and 100 mm length) and the vacuum chamber as the grounded anode.

A pulsed intense electron beam is produced when an external capacitor of 16 nF, charged at 15 kV, is discharged between the hollow cathode and the anode. The pulsed electron beam has 100 ns full width at half maximum (FWHM), a fluence of 2.5 J/cm^2 and a repetition rate of 1 Hz. The electron beam interacts at an angle of 45° with the ZnO target, in Ar gas at a pressure of 1 Pa and a residual oxygen pressure equal to 10^{-3} Pa. The MgO (100) substrates were placed parallel to the target at a distance of 40 mm. ZnO thin films were grown under a controlled substrate temperature in the room temperature to 500 °C range. After deposition the films were cooled down under the argon pressure used for the growth.

The thickness and composition of the films were measured by Rutherford backscattering spectrometry (RBS) using the 2 MeV Van de Graaff accelerator at the Institut des Nanosciences de Paris (Université Paris 6). The structural characterizations of the ZnO films were carried out by X-ray diffraction (XRD) analyses using a four-circle diffractometer (Philips Xpert MRD) with the Cu Kα radiation (λ = 0.154 nm) at the Laboratoire d'Ingenierie des Materiaux (Ecole Nationale Supérieure des Arts et Métiers). Analyses in the symmetric Bragg–Brentano geometry were used to determine the axis parameters and possible textures of the films. The in-plane epitaxial relationships between the ZnO films and MgO substrates were studied by asymmetric X-ray diffraction from the measurements of pole figures for selected XRD peaks of the films and substrate. The resistivity of ZnO films as a function of temperature (from room T down to liquid He) was obtained by the standard dc four-probe measurements.

3. Results

The parameters of the PED method were optimized in order to obtain dense and smooth ZnO films free from any particulates at their surface, as it has been previously established [9], with the film thickness in the 50–100 nm range. Fig. 1 represents a typical RBS spectrum which shows the formation of a stoichiometric and uniform ZnO film. However, due to the accuracy of the RBS analysis for the determination of the content in light elements (like oxygen), i.e. about 5%, we cannot exclude a slight oxygen deficiency in the ZnO films. Such a possible deviation in stoichiometry could be due to the fact that these films are grown under a quite low oxygen pressure that usually involves an unbalanced incorporation of cations and oxygen atoms into the film [18,19]. This RBS spectrum does not show the presence of elements other than Zn, O and Mg, i.e. the incorporation during the PED growth of foreign atoms which could play an important role in the transport properties of the films [20,21] is not evidenced by RBS.

X-ray diffraction patterns were recorded for the ZnO films grown on (100) MgO substrates at room T, 300 and 500 °C. Films grown at T<200 °C were found amorphous. Fig. 2 shows typical XRD patterns for films grown at 300 and 500 °C and for the MgO substrate, respectively. The scan shows the presence of the (00·2) reflection peak and its harmonics characteristic of the ZnO wurtzite structure, along with the (100) MgO substrate reflections, indicating that the ZnO film is highly c-axis oriented, a very small (10·0) ZnO peak being observed only at 2θ = 31.7°. Note that the (111), (200), (220) and (311) Au peaks observed in the XRD pattern of the ZnO film are due to the Au contacts deposited on the film for resistivity measurements.

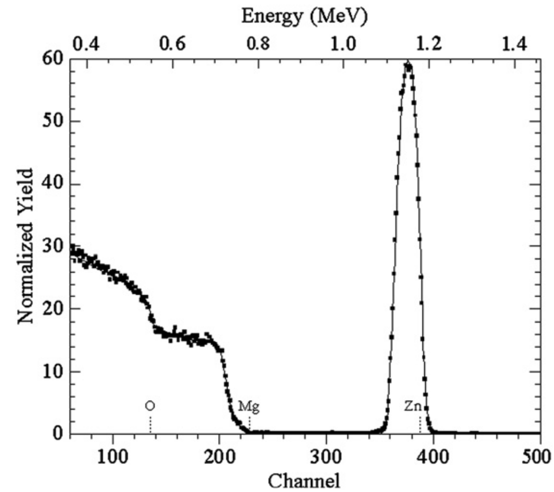

Fig. 1. A typical RBS spectrum recorded for a ZnO film grown by PED on the (100) MgO substrate at 300 °C.

Moreover, the absence of any additional peaks in the XRD patterns rules out the presence of spurious crystalline phases in the ZnO films.

The c-axis parameters obtained from the XRD patterns, the values of crystallite size d (coherence length) deduced from the (00·2) ZnO line width (the Scherrer formulae) and the FWHM values of the rocking curves of the (00·2) reflection peaks are presented in Table 1 for the ZnO films grown on MgO substrates at 300 and 500 °C substrate temperatures. The FWHM of the (00·2) ZnO rocking curves show a decrease from 4.8° at 300 °C to 2.4° at 500 °C. Moreover, the ZnO c axis values are larger than the bulk value (0.5206 nm), the difference decreasing with increasing growth temperature, which could be explained by a decreasing defect density in the films as the growth temperature increases. All these results prove an enhancement of the crystalline quality of the ZnO films with T, i.e. a decrease of the defect density in films with increasing growth T, as it is generally observed in the case of ZnO film growth [1,14,22].

XRD pole figures were observed only for films grown at T>300 °C. Fig. 3 represents a typical pole figure of the (10·3) ZnO plane, recorded for 2θ = 62.8°, for a ZnO thin film grown on the (100) MgO substrate at 500 °C. Twelve well-defined poles are observed at a declination angle ψ equal to 31.6°, i.e. the value expected for the (10·3) plane of the ZnO wurtzite structure in the case of a (00·2) texture. In addition, the poles located at ψ = 45° with a four fold

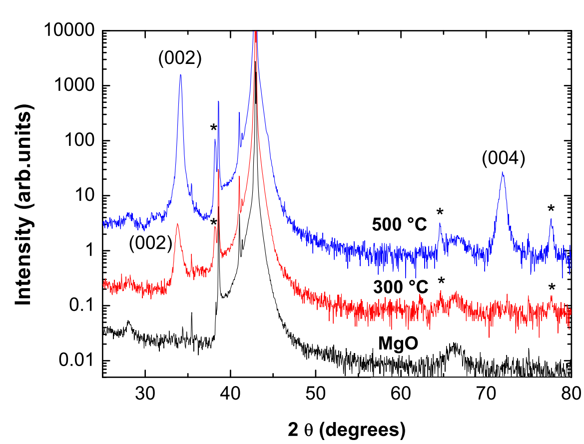

Fig. 2. X-ray diffraction patterns for the ZnO thin films grown on the (100) MgO substrate at 300 and 500 °C and the (100) MgO substrate, respectively. The (111), (200), (220) and (311) Au peaks are marked by *.