



How to prevent twin formation in epitaxial ZnO thin films grown on c-plane sapphire

C.S. Steplecaru^a, M.S. Martín-González^{a,*}, J.F. Fernández^b, J.L. Costa-Krämer^a

^a Instituto de Microelectrónica de Madrid, CNM-CSIC, Isaac Newton 8, 28760 Tres Cantos, Madrid, Spain

^b Instituto de Cerámica y Vidrio, CSIC, c/Kelsen 5, 28049 Madrid, Spain

ARTICLE INFO

Available online 6 January 2010

Keywords:

ZnO
PLD
Epitaxy
Twinning
Thin film
Sapphire

ABSTRACT

Epitaxial ZnO thin films have been grown on (0001) sapphire substrates by pulsed laser deposition. The structural and electrical transport properties of the films are measured as a function of the growth temperature and substrate cleaning procedure. The XRD measurements reveal that the cleaning procedure affects drastically the twin formation. Its origin could be attributed to a residual hydrocarbon layer or defects (oh- or O vacancies) at the sapphire surface. The electrical transport characteristics of the films are found to depend moderately on the existence of twinning.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

ZnO is a particularly attractive material because it has a band gap of 3.37 eV at room temperature (RT), which is in the UV range, a large bond strength with a cohesive energy of 1.89 eV, a large mechanical stability with a melting point of about 2200 K, and a high electronic stability due to an exciton binding energy of 60 meV. ZnO can be used for fabrication of electronic and optoelectronic devices such as blue light emitting diodes (LEDs), transparent conducting electrodes in solar cells, oxygen gas sensors, and optical filters. Nevertheless, in order to use ZnO in optoelectronic devices, high quality ZnO films are required.

To obtain high quality ZnO epitaxial layers, sapphire (Al₂O₃) has been extensively used as a substrate because of its hexagonal symmetry and commercial availability [1]. However, defects are easily generated in epitaxial ZnO films grown on the sapphire substrate due to the large lattice mismatch of 18% or 32%, which depends on crystallographic orientation relationships [2].

Most common defects due to the lattice mismatch are misfit dislocations, which have been studied in detail [3–5], and twin domains which are less understood [4]. The electrical properties of ZnO films are affected by film quality, orientation and interface quality, as expected.

The twin formation in ZnO/Al₂O₃ (0001) films has been investigated only by a few groups using growth techniques such as laser molecular beam epitaxy [2], metalorganic chemical vapor deposition [6,7], Pulsed Laser Deposition (PLD) [8], and sputtering [9]. In all these cases, the twinning exhibits the following similarities: a) upon increasing the growth temperature the twinning tends to disappear, b) the relative

intensity of the domains changes from sample to sample when grown at the same conditions and c) the appearance and the intensity of the twinning maxima depend on the deposition rate.

Different theories have been developed to explain the twinning effect in ZnO films. According to Ohkubo et al., the preferential growth of the 30° twisted domains at low temperature is due to kinetic factors. The aligned in-plane oriented (main) domains are thermodynamically more stable than the 30° rotated domains [2]. The improvement of the film alignment has been correlated with the increase of surface mobility of the adatoms at large growth temperatures [8]. Kim et al. performed a study of the twin formation mechanism of sputter-grown epitaxial ZnO/Al₂O₃(001) films, correlating it with the strain evolution. Their study revealed that the twin in the sputter-grown ZnO thin films is a mechanical twin, not a growth twin (indicated by the existence of a transition thickness at which the twin domains nucleate followed by the gradual strain relaxation) [9].

In this study, the PLD technique has been used since it is a suitable method for growing thin oxide films. This is so because of its ability to control oxygen gas pressure in a wide range, thus obtaining oxide films with a good crystalline structure and a preferred c-axis orientation [8]. The twin formation origin of epitaxial ZnO films deposited on (0001) Al₂O₃ substrates by PLD technique is described. Twinning is shown to be affected by the substrate cleaning procedure, and their influence on structural and electrical properties of films obtained under the same conditions, but different cleaning procedures, are presented.

2. Experimental details

The deposition of the ZnO films was carried out in a homemade PLD deposition chamber, using an ArF Excimer laser (Lambda Physics

* Corresponding author. Tel.: +34 918060700; fax: +34 918060701.
E-mail address: marisol@imm.cnm.csic.es (M.S. Martín-González).

Lasertechnik LPX 205i MC) operating at 193 nm in order to ablate the ZnO target. ZnO films were deposited on (0001) sapphire substrates. The excimer laser pulse energy was set at 200 mJ per pulse, repetition rate of 10 Hz and pulse duration of 17 ns. The laser beam was focused on the rotating target into a spot size of 1 mm diameter. The distance between the target and the substrate was 2.5 cm. The target was made from high purity ZnO powders sintered at 1300 °C for 8 h. The deposition chamber was first evacuated by a pump-system (turbo and rotary pumps) to 1×10^{-5} mbar, and then high purity oxygen was introduced through a mass flow controller and maintained at the desired pressure ($\sim 1.2 \times 10^{-2}$ mbar) during the deposition. The sample holder was a heater itself, where the temperature was controlled by the current intensity applied and held constant during the deposition. The temperature was measured by a calibrated thermocouple. The post-growth cooling down to room temperature procedure of the ZnO films was made maintaining the same oxygen pressure.

The ZnO films were deposited on (0001) sapphire substrates at growth temperatures ranging from room temperature (RT) to 600 °C. Furthermore, another set of films was prepared in the same range of temperature, where the substrates were cleaned by a different procedure. For both set of films, in order to remove dust and surface contamination of the substrates, the (0001) sapphire wafers were prepared by ultrasonic cleaning, first in acetone for 10 min and then in isopropanol for 10 min, and finally blown dried with high purity nitrogen gas. For the second cleaning procedure the substrates were additionally immersed in oxygen plasma cleaning at 200 W for 5 min.

The structural properties of the grown films were characterized by X-ray diffraction (XRD) measurements, carried out using a Philips X'Pert four-circle diffractometer system with $\text{CuK}\alpha$ radiation.

The electrical properties of the films were determined by Hall Effect measurements, using van der Pauw configuration. For the van der Pauw four-probe geometry metallic contacts were deposited on top of the films, in the sequence Ti/Al/Pt/Au, each one having a thickness of 150 Å [10,11]. Afterwards they were annealed at 150 °C for 20 min. Before measuring the temperature dependence of the transport properties, the ohmic character of the contacts was verified. Measurements of the electrical resistivity, carrier density and Hall mobility were performed from 33 to 300 K.

3. Results and discussion

3.1. Influence of growth temperature

XRD $2\theta/\omega$ scans measurements for the ZnO films were made (not shown here), in order to analyze the out-of-plane orientation of the films. All the films presented only {000l} diffraction maxima which indicated that the *c*-axis growths perpendicular to the substrate plane.

The coherence length of the films as a function of the growth temperature as calculated from the Scherrer formula using the full-width at half maximum (FWHM) of ZnO (0002) maxima of the $2\theta/\omega$ scan as input is shown in Fig. 1. When plotting the coherence length vs. substrate temperature, two regimes can be observed for the samples where no extra oxygen plasma cleaning was used. This type of behavior is characteristic of two-domain films. It is attributed to the activation of a new adatom surface diffusion process at $T_s > 200$ °C that became dominant at $T_s > 500$ °C.

The epitaxial relationship between ZnO and the sapphire/ Al_2O_3 substrates was determined by asymmetrical XRD measurements. Fig. 2 displays the in-plane ϕ scans for the (1013) plane of the ZnO films and for the (1123) plane of the sapphire substrate. As it can be seen, the epitaxial relationship started at 200 °C. The sample grown at 200 °C presented 6 peaks separated by 60°, characteristic of the six-fold symmetry. These peaks were rotated 30° with respect to the substrate, thus confirming the epitaxial relationship $[11\bar{2}0]_{\text{ZnO}} \parallel$

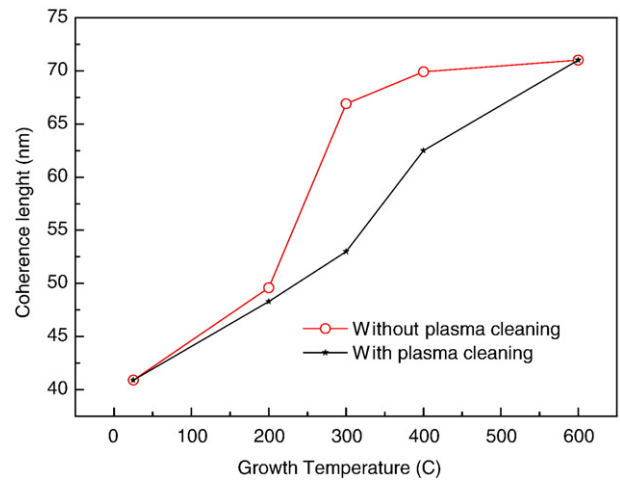


Fig. 1. Crystalline coherence length for films grown at different temperatures.

$[11\bar{2}0]_{\text{sapphire}}$. The sample grown at 400 °C exhibited 12 peaks, which indicated the coexistence of 2 domains: a main domain aligned with the sapphire substrate, and a so-called “twin” domain which was rotated 30° with respect to the main one. The low intensity of the peaks and the relatively high background signal were indicative of both poor in-plane orientation and high contribution of the crystallites with random in-plane orientation. When increasing the growth temperature, the twin peaks intensity decreased and disappeared for the samples grown at 600 °C, which presented just a main domain aligned with the substrate $[10\bar{1}0]_{\text{ZnO}} \parallel [11\bar{2}0]_{\text{sapphire}}$.

3.2. Influence of substrate cleaning

To elucidate the impact of twinning in electrical properties a second set of films was prepared with an extra oxygen plasma cleaning step before deposition. There were indications that the quality of the oxide–oxide interfaces (roughness and interdiffusion) was critical for the final performance. It is, therefore, of great importance to understand the basic principles governing the oxide–oxide growth, which still remains a largely unexplored subject.

XRD $2\theta/\omega$ scans measurement for the substrates cleaned with and without oxygen plasma present the same diffraction pattern. The corresponding ZnO films deposited on top of these substrates exhibit the same {000l} diffraction maxima (not shown here).

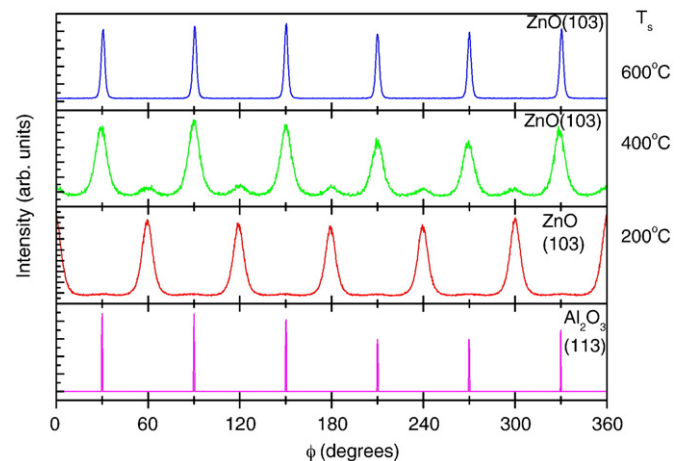


Fig. 2. In-plane ϕ scans for the (1013) plane for the ZnO films grown at 200, 400 and 600 °C and for the (1123) plane of the sapphire substrate for the samples prepared without oxygen plasma.

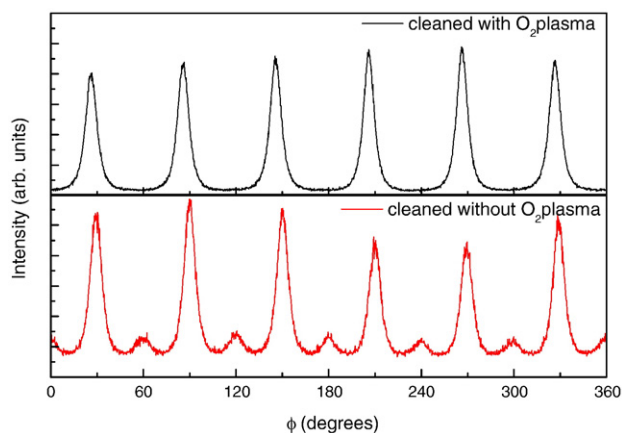


Fig. 3. In-plane ϕ scans for the (1013) plane of the ZnO films grown at 400 °C on substrates cleaned by 2 different procedures (with and without oxygen plasma).

Regarding the coherence length of the films as a function of the growth temperature, it can be seen that the samples cleaned with oxygen plasma exhibit an almost linear relationship (see Fig. 1).

The epitaxial relationship between ZnO and the sapphire/ Al_2O_3 substrates was also determined by asymmetrical XRD measurements. For the samples cleaned by oxygen plasma the epitaxial relationship started as low as RT (not shown here), which is lower compared to the temperature of 200 °C for the samples cleaned without oxygen plasma. To the best of our knowledge RT is the lowest growth temperature at which epitaxial films have been obtained.

Fig. 3 shows the in-plane ϕ scans for the (1013) plane of the ZnO films grown at 400 °C, with and without oxygen plasma cleaning procedure. The sample that has been exposed to oxygen plasma cleaning before the deposition was free of twin domains, although it has been grown under the same growth conditions. The deposition onto oxygen plasma pretreated substrates always resulted in films whose ϕ -scans show only six strong peaks separated by 60°. This fact clearly indicated a single-domain in-plane orientation around the c -axis, with the a -axis aligned with respect to the substrate.

The origin of the 30° rotation could be attributed to residual hydrocarbons layer (C–H–O) on the sapphire surface because of the chemical cleaning procedure (see Experimental details section), since by the elimination of this layer during the plasma cleaning procedure

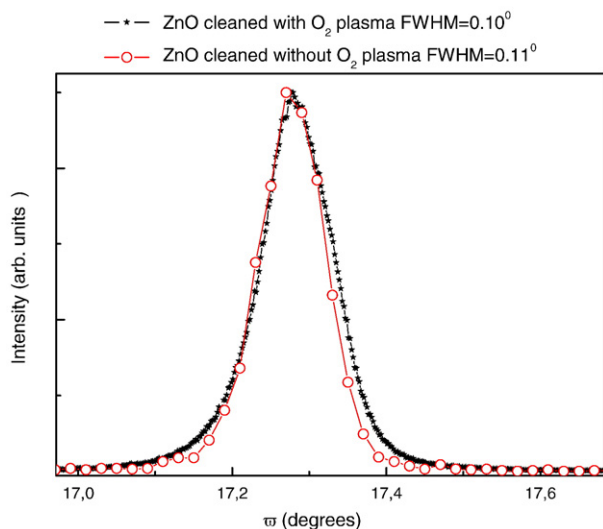


Fig. 4. Rocking curves corresponding to the (0002)–ZnO reflection for films deposited at the same growth temperature of 400 °C, but cleaned by 2 different procedures. The FWHM values of the XRD rocking curves are 0.10 and 0.11, respectively.

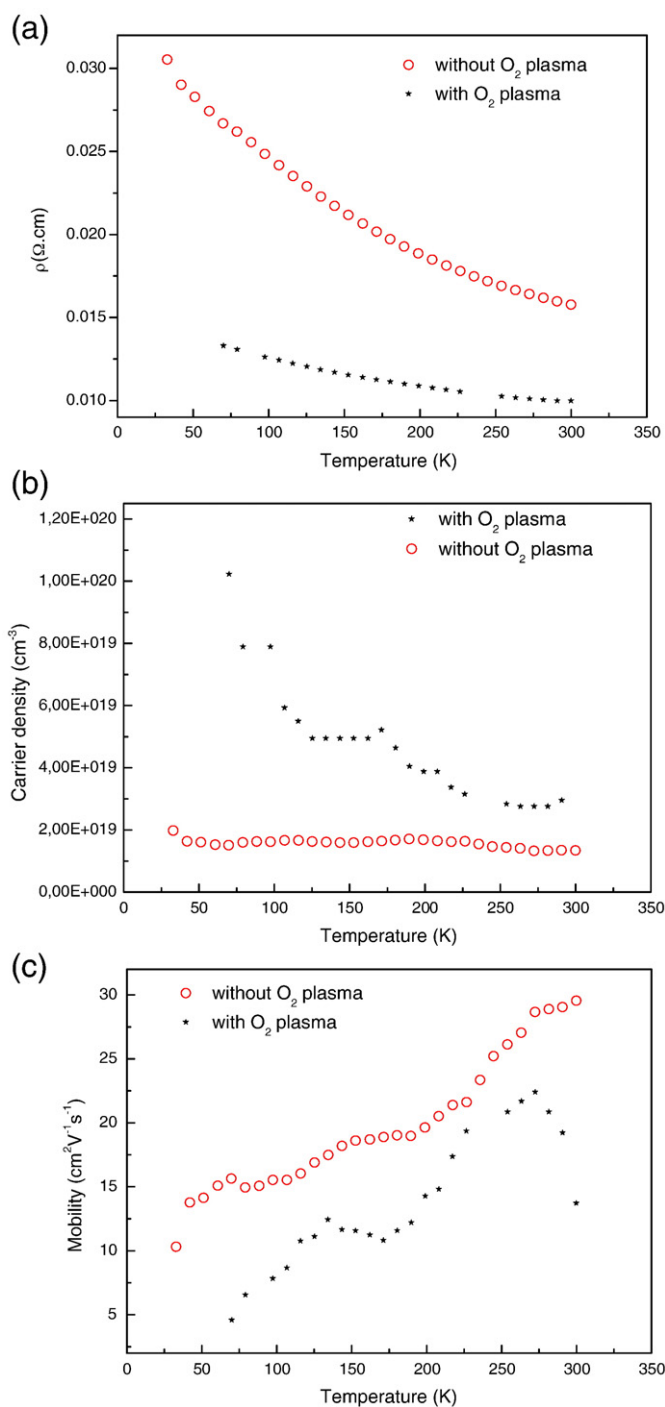


Fig. 5. Measurements of electrical properties for films grown at 400 °C on substrates cleaned by 2 different procedures (a) resistivity versus temperature; (b) carrier density versus temperature; (c) mobility versus temperature.

Table 1

Electrical properties (resistivity, carrier density and mobility) measured at RT for films grown at the same temperature of 400 °C, but prepared by different cleaning procedures: with and without oxygen plasma.

T (°C)	Cleaning procedure	Resistivity (Ω cm)	Carrier density (cm ⁻³)	Mobility (cm ² V ⁻¹ s ⁻¹)
400	With oxygen plasma	10×10^{-3}	3×10^{19} n-type	12
400	Without oxygen plasma	15×10^{-3}	1.2×10^{19} n-type	30

the formation of twin domains was avoided. The appearance of a new adatom surface diffusion process detected at $T_s > 300^\circ\text{C}$ (see Fig. 1) could be related to the temperature at which the hydrocarbons layer started to desorb from the sapphire surface in vacuum. This hydrocarbon layer was completely eliminated when heating the substrate at temperature $> 500^\circ\text{C}$ in vacuum conditions. At 300 and 400°C the desorption of the hydrocarbon layer was inhomogeneous, therefore the aligned domain appeared where the hydrocarbon layer was removed, while the rotated domain originated where the hydrocarbon layer was still present when ZnO film started to grow. This fact was confirmed by the variation of the domains intensity between different series of samples.

On the other hand, in a previous study of ZnO grown on sapphire by atomic layer epitaxy it was concluded that cleaning of sapphire with oxygen plasma increased the density of hydroxyl group on the substrate surface [12]. Different density of hydroxyl groups will produce a different concentration of reactive surface sites, therefore increasing the nucleation rate of the film.

Fig. 4 shows an example of rocking curves corresponding to the (0002)–ZnO reflection for the samples grown at 400°C , but cleaned by different procedure. The FWHM value of the XRD rocking curves was similar for both samples, indicating that the cleaning procedure did not affect the film quality along the [0001] direction.

Measurements of the electrical resistivity, carrier density and Hall mobility have been also performed. As an example of such a measurement Fig. 5 (a–c) shows the behavior of the electrical resistivity, carrier density and Hall mobility versus temperature, in the range of 33–300 K, for films grown at 400°C . Table 1 shows the values of these electrical properties at room temperature for the ZnO films prepared by both cleaning procedures. It can be seen that the electrical transport characteristics of the films are not very influenced by twinning. Both samples present n-type conductivity and have almost the same resistivity; the only significant difference was the higher mobility values of the sample un-exposed to the oxygen plasma cleaning.

4. Conclusions

Epitaxial ZnO films have been grown on (0001) sapphire substrates using the PLD technique. Two different substrate cleaning

procedures have been demonstrated to affect drastically the twin formation. Cleaning the substrate by oxygen plasma after a conventional organic solvent cleaning procedure is demonstrated to eliminate the appearance of the twin domains. The origin of the twin domains has been tentatively correlated with the existence of the residual hydrocarbons on the substrate surface prior to the PLD growth, although the twinning did not affect the grain size. Electrical transport measurements of the films show that there is no significant influence due to the existence of twinning.

Acknowledgments

This work was financially supported by CYCYT MAT2007-66845-C02-01, CSIC 2006-50F0122, CSIC 2007-50I015 and MAT2008-06330. We also thank to Raquel Álvaro and Mariana Köber for cooperation.

References

- [1] F. Vigué, P. Vennéguès, C. Deparis, S. Vézian, M. Laügt, J.-P. Faurie, *J. Appl. Phys.* 90 (2001) 5115.
- [2] I. Ohkubo, A. Ohtomo, T. Ohnishi, Y. Matsumoto, H. Koinuma, M. Kawasaki, *Surf. Sci.* 443 (1999) L1043.
- [3] D.M. Hwang, S.A. Schwarz, T.S. Ravi, R. Bhat, C.Y. Chen, *Phys. Rev. Lett.* 66 (1991) 739.
- [4] J. Narayan, K. Dovidenko, A.K. Sharma, S. Oktyabrsky, *J. Appl. Phys.* 84 (1998) 2597.
- [5] W.-Y. S. C.-Y. C. S.-C. Chin, C.-F. Huang, T.-Y. Tang, Y.-C. Lu, Y.-L. Lin, L. Hong, F.-Y. Jen, C.C. Yang, B.-P. Zhang, Y. Segawa, *J. Appl. Phys.* 99 (2006) 054301.
- [6] S.-H. Park, S.-Y. Seo, S.-H. Kim, S.-W. Han, *Appl. Phys. Lett.* 88 (2006) 251903.
- [7] B. Zhang, L. Manh, K. Wakatsuki, K. Tamura, T. Ohnishi, M. Lippmaa, N. Usami, M. Kawasaki, H. Koinuma, Y. Segawa, *Jpn. J. Appl. Phys. Part 2* 42 (2003) L264.
- [8] R.D. Vispute, V. Talyansky, Z. Trajanovic, S. Choopun, M. Downes, R.P. Sharma, T. Venkatesan, M.C. Woods, R.T. Lareau, K.A. Jones, A.A. Iliadis, *Appl. Phys. Lett.* 70 (1997) 2735.
- [9] I.-W. Kim, K.-M. Lee, *Thin Solid Films* 516 (2008) 4921.
- [10] S.J. Pearton, D.P. Norton, K. Ip, Y.W. Heo, T. Steiner, *Prog. Mater. Sci.* 50 (2005) 293.
- [11] E. López-Ponce, J.L. Costa-Krämer, M.S. Martín-González, F. Briones, J.F. Fernández, A.C. Caballero, M. Villegas, J. de Frutos, *Phys. Stat. Sol. (a)* 203 (6) (2006) 1383.
- [12] Jongmin Lim, Kyoungchul Shin, Hyounwoo Kim, Chongmu Lee, *Thin Solid Films* 475 (2005) 256.