Characterisation of Dislocations in ZnO by X–Ray Imaging

To cite this article: N Burle et al 2011 J. Phys.: Conf. Ser. 281 012004

View the article online for updates and enhancements.
Characterisation of Dislocations in ZnO by X–Ray Imaging

N Burle1, F Baudin2, A Jonchere2, P Gergaud2 and G Feuillet2
1 IM2NP- CNRS 6242, UPCAM, Campus Scientifique St Jérome, case 262, 13397 Marseille cedex 20 France
2 CEA - LETI, MINATEC, 17 rue des Martyrs, 38054 Grenoble cedex 9, France
e-mail : nelly.burle@im2np.fr ; guy.feuillet@cea.fr

Abstract. Transmission X-Ray topography (X-ray imaging) was used to characterize the density and type of the native dislocations in ZnO substrates. C-oriented ZnO bulk materials from different origins were compared, either high purity Chemical Vapor Transport (CVT) grown or commercial, hydrothermally grown wafers. Elongated dislocations lying within the substrate were found in hydrothermal substrates. In CVT crystals, the density of dislocations was found to be too high for X-ray determination of their Burgers vector. However, in hydrothermal crystals, the density of dislocations were found to be in the range < 10⁴ / cm² and extend mainly within the substrate. Whereas complete Burgers vector identification is not achieved, two kinds of dislocations have been evidenced : grown-in, swirled dislocations ("high" temperature) and linear, gliding dislocations, most probably developed during the cooling steps in (0 1 -1 0) glide planes.

1. Introduction
Quantum well ZnO/ZnMgO heterostructures are promising materials for the realization of electro-luminescent diodes. As for most optical applications, dislocations must be avoided in the emissive materials, where they would act as recombination centers and limit the optical efficiencies of the devices. A strong advantage associated to ZnO is related to the availability of ZnO substrates allowing for homoepitaxial processes. In this case, dislocations could be avoided in the active regions of the devices. But this will be true only if the substrate dislocation density is low enough to prevent replication of threading dislocations in the layers and if no misfit dislocation is developed at the substrate- buffer layer interface due to misfit strain relaxation.

As a substrate for growing emissive structures, the ZnO wafers should combine high chemical purity and good crystalline quality. In this respect, we have compared substrates from two growth techniques : hydrothermal growth which allows to get low dislocation density substrates, with rather high impurity concentrations and Chemical Vapor Transport (CVT) [1] which leads to purer material but with higher dislocation densities.

This paper presents our first results about dislocation imaging in various substrates. High purity CVT wafers were found to exhibit too high dislocation densities to allow their crystallographic characteristics to be determined. However, some hydrothermally grown commercial wafers are of a good enough structural quality to image individual dislocations. The determination of their characteristics could help understanding their origin to prevent them from occurring in CVT crystals, opening the way to the realization of pure and perfectly crystalline wafers for further applications.
2. Experimental results

2.1. Some ZnO Crystallographic data

ZnO exhibits a hexagonal (wurtzite) structure; the lattice constants are a=0.325 nm and c=0.5027 nm; each of the 2 sites \((0, 0, 0)\) and \((\frac{1}{3}, \frac{2}{3}, \frac{1}{2})\) is occupied by 2 atoms: Zn \((0, 0, 0)\) and O \((0, 0, \frac{3}{8})\) (figure 1).

Positions of the compact crystallographic planes expected for dislocations glide are also reported. One must remember that the rule to transform Miller indices between 3 and 4 indices is not the same for planes and for directions: “a” axis is quoted \([100]\) or \([\frac{1}{3} -1 -1 0]\); “m” axis (perpendicular to “a” axis) is quoted \([1 2 0]\) or \([0 1 -1 0]\); more easily, prismatic \((100)\) plane is also quoted \((1 0 -1 0)\) and prismatic \((2 -1 0)\) plane is also called \((2 -1 -1 0)\).

Figure 1. a) Atoms in the hexagonal cell (Largest atoms are Zn, smallest are O); b) Positions of basal plane \((0 0 1)\), prismatic planes \((0 1 -1 0)\) and \((2 -1 -1 0)\), pyramidal plane \((2 -1 -1 2)\) in the hexagon; c) Stereographic projection on \((001)\): poles of the prismatic planes are plotted by respect with basal vectors \(a, b,\) and \(u = -(a+b)\) and with usual indications of “a” axis and “m” axis.

2.2. Dislocation densities depending on the type of substrate

Samples from various providers have been imaged: CVT wafers grown at LETI, and commercial hydrothermal wafers from CrysTec GmbH (referred to as CT) and Tokyo Denpa (TD). All samples are \((001)\) oriented, their sizes are about 10 x 10 mm\(^2\) and thicknesses between 0.5 mm and 1 mm.

X-ray images have been recorded on Ilford L4 nuclear plates with \(\lambda K_\alpha Ag\) provided by a rotating anode Rigaku generator, using Lang (transmission) laboratory setting.

In CVT and CT samples dislocation densities are too high to be measured on X-Ray topograms, which means they are over than \(10^4\), in accordance with the values estimated from etch pit density counting (EPD): \(10^2\) cm\(^3\) in MOVPE and between \(10^4\) and \(10^5\) cm\(^3\) in CT samples; in TD samples, the density is found under \(10^3\) cm\(^3\) both by EPD and X-ray imaging (figure 2).

Figure 2. a) CVT sample 77-A, \(g = (1 0 -1 0)\); b) CVT sample 79-A, \(g = (-2 1 1 0)\); c) sample CT4, \(g = (-2 1 1 0)\); d) sample TD 2, \(g = (-2 1 1 0)\); scale 0.5 mm.
2.3. Geometrical characteristics of dislocations in TD wafers.

Two kinds of dislocations can be observed in the lowest density samples (Tokyo Denpa, \( [D] < 10^3 \text{ cm/cm}^3 \)): few very linear lines and some swirled dislocations. Nevertheless the general directions of the dislocation lines are along the crystallographic directions \( \mathbf{a}, \mathbf{b} \) and \( \mathbf{u} = -(\mathbf{a}+\mathbf{b}) \) (figure 3).

The directions correspond to the trace of the \{10-10\} type prismatic planes of the hexagonal cell in the \( \mathbf{c} \) plane. This is in good accordance with previous X-ray or TEM observations \([2, 3]\) where such slip lines in the basal plane are frequently observed even if Burgers vectors are not always determined.

The images obtained with the 3 possible \{2 -1 -1 0\} diffracting conditions lead to intense, or weak contrasts for the various dislocations. It is obvious from large scale images that the swirled lines follow roughly the same three directions, but seem to be pinned at the emerging points or at several points along the lines; they look like typical “high temperature” dislocation structures observed after cooling in Semiconductors. \([4]\)

![Figure 3](image_url)

**Figure 3**: Transmission X-Ray topographies of the same area in ZnO sample TD-2

- a) \( g = (2 -1 -1 0) \)
- b) \( g = (-1 2 -1 0) \)
- c) \( g = (1 1 -2 0) \)

\( \lambda = K_{\alpha} A_{g} = 0.056 \text{ nm} \)

3. Discussion and conclusion

Observations of dislocation contrasts on several images usually allow one to determine the Burgers vector \( \mathbf{B} \) using the extinction rule “\( g \cdot \mathbf{B} = 0 \)”, if two extinctions are obtained; if the glide systems are well known, one single extinction could give a good indication of the vector \( \mathbf{B} \). Unfortunately, this rule is not always powerful enough since it is only a simplified criterion. It is the case in our samples, as it can be noticed in figure 3.

For example, the straight line \( \circ \) is visible with \( g = (2 -1 -1 0) \) (figure 3a) or \( (-1 2 -1 0) \) (figure 3b) and vanishes with \( g = (1 1 -2 0) \) (figure 3c); the line direction is \( \mathbf{u} = -(\mathbf{a}+\mathbf{b}) \) which is perpendicular to \( \{11 -2 0\} \) plane, so it would be a pure edge dislocation. Whereas edge growth dislocations have already been observed in some cases \([5]\), such straight lines in semiconducting materials evocate “low” temperature glide along Peierls directions, and would be screw or 60° dislocations, so the expected vector would be one of the basal plane, \( \mathbf{a} = [1 0 0] = 1/3[2 -1 -1 0] \) or \( \mathbf{b} \) or \( \mathbf{u} \).

The swirled line \( \& \) vanishes with \( g = (2 -1 -1 0) \) or \( g = (1 1 -2 0) \), which should lead to a Burgers vector \( \mathbf{c} \) perpendicular to the basal plane; if true, this dislocation would also vanish with \( g = (-1 2 -1 0) \) (figure 3b) where it is in contrast.
These two examples illustrate clearly that in these samples the simplified rule \( g \cdot B = 0 \) cannot lead to complete identification of Burgers vectors by X-ray imaging. It can be due at least partially, to the diffracting conditions, as the samples are quite thick so Bormann effect is not negligible. As it is well known, the complete extinction rule is \( g \cdot R = 0 \) where \( R \) is the displacement vector around the dislocation, and the expression of \( g \cdot R \) contains several terms including not only \( g \) and \( B \) but also the line vector \( t \). This line vector can be determined in the case of straight dislocations so the contrast of dislocations could be calculated and compared with images. In the case of the swirled dislocations this would be more problematic.

Moreover, the glide planes of these non linear dislocations are not obvious: primary glide and cross-slip have already been reported in ZnO and similar wurtzite materials depending on the deformation method [6, 7] and the dislocations in ZnO are reported to be easily mobile, with low activation energy [8], and not dissociated, which would favour cross-slip events [9]. Easy slip occurs in basal or prismatic (01-10) planes but (2-1-10) prismatic planes and various pyramidal planes have been observed in wurtzite semiconducting materials [2, 5, 6, 8, 9].

Optimization of the experimental conditions, as thinning samples to get Bragg diffracting conditions instead of Bormann, will render the images easier to be interpreted; comparison with contrast calculations would lead to an easier determination of Burgers vectors.

It has been shown that the dislocation density in ZnO wafers as well as their characteristics is highly dependant on the growth method. Correlation with EPD and cathodoluminescence measurements is in progress. Controlled, low temperature plastic deformation will also be undertaken in low dislocation density samples to allow glide mechanisms to be precise.

References

[1] Santailler J C G, Audouin C and Chichignoud G 2010 J. Crystal Growth to be published
[2] Zheng Y, Boulliard J C, Demaille D, Bernard Y and Petroff J F 2005 J. Crystal Growth 274 156
[3] Yoshino K, Yoneta M and Yonenaga I 2008 J Mater Sci: Mater Electron. 19 199
[4] Pichaud B, Burle-Durbec N, Minari F and Duseaux M 1985 J. Crystal Growth 71 648
[5] Dhanaraj G, Dudley M, Bliss D, Callahan M and Harris M 2006 J. Crystal Growth 297 74
[6] Bradby J E, Kucheyev S O, Williams J S, Jagadish C, Swain M V, Munroe P and Phillips M R 2002 Appl. Phys. Lett. 80 (24) 4537
[7] Kucheyev S O, Bradby J E, Williams J S, Jagadish C and Swain M V 2002 Appl. Phys. Lett. 80 956
[8] Yonenaga I, Ohno Y, Taishi T and Tokumoto Y 2009 Physica B 404 4999
[9] Suzuki K, Ichihara M, Takeuchi S, Nagakawa K and Maeda K 1984 Philos. Mag. A 49 451