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Microstructure and Defects of Wurtzite Structure Thin Films

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Abstract

ZnO and AlN, which exhibit the wurtzite structure, were deposited onto metal coated SiO_2 substrates by sputtering. X-ray diffraction (XRD) indicated that the films contained no second phases and exhibited an [0001] texture. Transmission electron microscopy (TEM) observations confirmed the XRD results and revealed the columnar microstructure of the films. The width of the columnar grains were less than 30 nm for AlN and between 100 and 400 nm for ZnO. In the ZnO grains, a large concentration of defects were identified, which included dislocations and stacking faults that lie on the basal plane. © 1999 Elsevier Science Limited. All rights reserved

Keywords: ZnO, defects, electron microscopy, films.

1 Introduction

ZnO and AlN thin films have been studied for a wide variety of applications including piezoelectric devices.[1,2] It is well known that in general the microstructure and defects of thin films influence macroscopic properties such as the piezoelectric response. In this article, the microstructures of [0001] textured ZnO and AlN thin films are analyzed in order to give more insight into which microstructural features are present that can influence thin film properties. Transmission electron microscopy (TEM) is used to make detailed observations of ZnO and AlN thin film microstructures.

Concerning wurtzite films, recently, a lot of results have been obtained on the microstructure and defects of GaN films deposited epitaxially onto various monocrystal substrates due to the optoelectronic applications associated with the GaN layer.[3,4] In most cases dislocations and stacking faults are observed. For some deposition conditions and substrates, inversion domain boundaries are also present.[3] The wurtzite thin films studied in the literature are mainly single crystal.

Our films are deposited onto a polycrystalline conducting electrode which is deposited onto thermal oxide SiO_2. Therefore the wurtzite films obtained in this study are polycrystalline. They were processed by reactive dc magnetron sputtering. ZnO was deposited on Au at room temperature. The Au electrode was deposited onto a fiber or onto a flat glass substrate. AlN was deposited at 400 °C on $Pt/Ta/SiO_2/Si$ and $Al/SiO_2/Si$. The metal electrodes (Au, Pt and Al) were always [111] oriented. Results from transmission electron microscopy (TEM) are used to characterize film preferred orientation and grain morphology. High resolution transmission electron microscopy (HRTEM) and lattice image simulations are used to identify the types of planar defects that occur in ZnO thin films.

2 Results and Discussion

2.1 Orientation and microstructure

The films are always columnar [Fig. 1(a) and 2(a)]. The diameter of the columns are in the 100–400 nm range for ZnO and in the 10–30 nm range for AlN. XRD indicate that the films exhibit an [0001] preferred orientation. In the case of AlN, the orientation is excellent. Almost all the grains are [0001] oriented as shown by the selected area diffraction pattern (SAED) of Fig. 2(b) which was obtained on a cross section sample. The [0001] orientation is always aligned with the long axis of the columns. For some grains the $\langle 11\text{–}20 \rangle$ or the $\langle 1\text{–}10 \rangle$ are normal to the axis of beam direction and also contributes to the SAED. In the case of ZnO, some grains are far from the [0001] orientation even if this orientation predominates as demonstrated by XRD. The SAED [Fig. 1(c)] was obtained for a plan view sample. The (n n $-2n$ 0) and (n $-n$ 0 0) (n integer) reflections contribute strongly and the other reflections (such as the 000n) are absent. This is in agreement with the fact that some grains have

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an [0001] orientation and none have an orientation such as [11–20] or [1–100], and with the [0001] preferred orientation.

2.2 Interfaces

Figure 3(a) and (b) show lattice images of interfaces. For the Al–AlN interface [Fig. 3(a)], no sign of second phase at the interface can be evidenced. The possible presence of second phase cannot be completely eliminated. First the interface is not completely parallel to the electron beam and a small intermediate layer (in the nanometer range) can be present. Secondly since the substrate is Al it is possible that some oxygen is present at the interface. The grain size is in the 10–30 nm range from the Al–AlN interface to the surface of the AlN film.

For the Au–ZnO heterostructure, the grain size is in the 5–10 nm range close to the interface but the structure becomes very columnar far from the interface and the grain size is between 100 and 400 nm depending on the sample.

2.3 Defects within the grains

2.3.1 Possible defects

2.3.1.1. Planar defects. The wurtzite structure (space group $P6_3mc$) is based on a hexagonal Bravais lattice. The anions (oxygen or nitrogen) stacking is similar to an hcp structure, and the cations (zinc or aluminum) occupy one half of the tetrahedral sites. The stacking sequence along [0001] of the wurtzite structure may be described as AaBbAaB..... where the capital letters designate anions

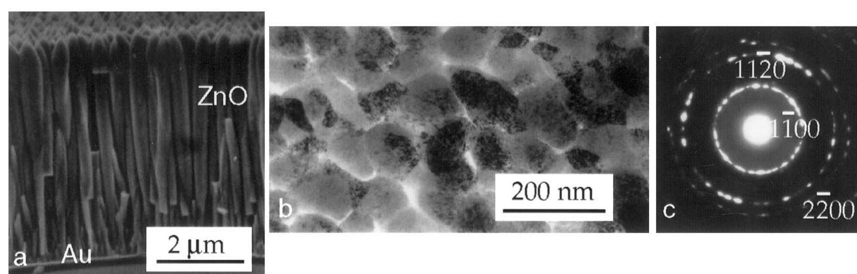

Fig. 1. Electron image of ZnO coating: (a) secondary electron SEM image of the ZnO coating deposited onto a fiber (cross section); (b) plan view TEM image of the ZnO deposited onto flat substrate; (c) corresponding electron diffraction pattern.

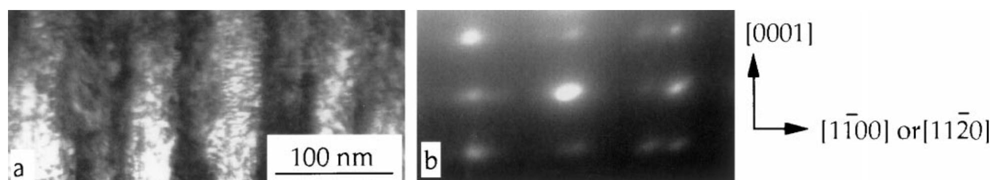

Fig. 2. AlN coating: (a) cross section dark field image showing the columnar structure; (b) corresponding electron diffraction pattern.

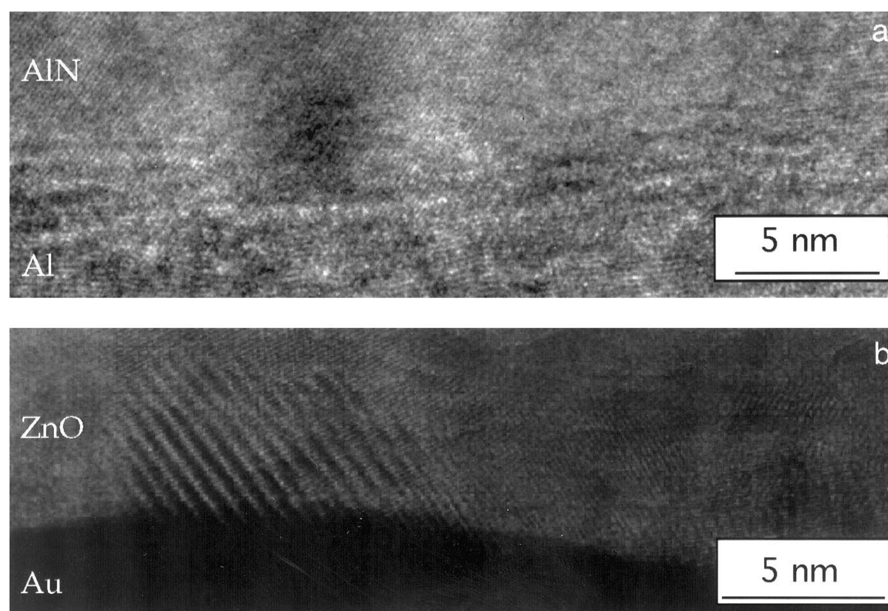

Fig. 3. HRTEM images of interfaces: (a) Al–AlN; (b) Au–ZnO.

and the small letters designate the cations. Locally the hexagonal arrangement may transform to a sphalerite (cubic) structure giving rise to one or two layers having the wrong stacking sequences such as AaBbAaBb/CcBbCc. This defect is a stacking fault and it is important to notice that there is no change in polarity. Two kinds of stacking fault are most often observed : single stacking faults for which the displacement is 1/6⟨2–203⟩ and double stacking faults for which the displacement is 1/3⟨1–100⟩.

Planar defects corresponding to a polarity reversal were also observed in ZnO powder.[5] Since the two crystals on both sides of the defects are related by an inversion, the defect is called an inversion domain boundary (IDB).

In thin films, planar defects lying normal to the substrate are often observed. Most often those wurtzite films are [0001] oriented, and defects lying on the {11–20} and on the {1–100} plane are observed. When a planar defect has only a translation character and does not lie on the basal plane as it is the case for a stacking fault, it has been called a translation domain boundary[3] or a double positioned boundary.[4] Let us first consider planar defects having only a translationnal character (and therefore having no inversion character). Imagine that two regions of a grain nucleate separately with a misfit in the stacking sequence as shown in Fig. 4(a). Such a misfit may be produced by the presence of a step at the interface or of a stacking fault. When the two regions meet, the defect may grow normal to the interface as shown in Fig. 4(b). It has been shown that on the plane, the rigid body displacement is not exactly the same as the one of a stacking fault (1/6[2–203]) but is rather 1/2[1–101]. When a stacking fault changes from the (0001) plane to the (11–20) plane, a partial dislocation of Burgers vector 1/6[1–100] would accommodate the difference in rigid body displacement.[6]

IDB lying normal to the interface were also observed in thin GaN films.[3] Imagine that two regions nucleate epitaxially on the same crystal grain with two opposite polarities [Fig. 5(a)]. This may occur because of difference in surface state of the substrate. As shown in Fig. 5(b), an IDB lying normal to the interface may be present when the two regions meet.

2.3.1.2. Dislocations. Perfect dislocations are the ones which are translation of the Bravais Lattice. The possible Burgers vectors are 1/3⟨11–20⟩, [0001] and 1/3⟨11–23⟩. Partial dislocations are also often observed. Possible Burgers vectors include 1/3⟨1–100⟩ and 1/2[0001]. A partial dislocation may terminate one translation boundary (such as a stacking fault) or separate two different planar defects.

2.3.2 Observation of defects

Due to the very small size of the AlN grains, it was not possible to make a detailed study of the defects in the AlN films. This could be done in the ZnO films. The HRTEM images (Fig. 6) reveal a very high density of defects. Those defects are planar defects and dislocations.[8] The HRTEM image and the associated simulation of Fig. 6(c) is in perfect agreement with a double stacking fault. The parameters of the simulation introduced in EMS[7] are the following: thickness, 6·5 nm; defocus, −60 nm, Cs = 1·1 mm and accelerating voltage: 300 kV. Single stacking faults were also observed [Fig. 6(a)]. The density of dislocations is very high (about 10^{12} cm^{-2})[8] and the distance between the stacking faults is about 10 nm. Shifts in the lattice image of about 1/2[0001] are often observed, those may correspond to the presence of a translation domain boundary.

The ZnO films studied are [0001] oriented and show a large peak width associated with the (0002) reflection. The peak width was estimated to be about 0.3°.[8] This confirms results of other studies[9] on ZnO films deposited at room temperature for which similar peak width was found. This may come from non uniform strain or lattice imperfections. Those lattice imperfections include large and low angle grain boundaries, planar defects and dislocations. The structure is very columnar and therefore the influence of the large angle grain boundaries on the (0002) peak width is negligible. The stacking faults do not affect the (0002) spacing and do not contribute. Most of the dislocations

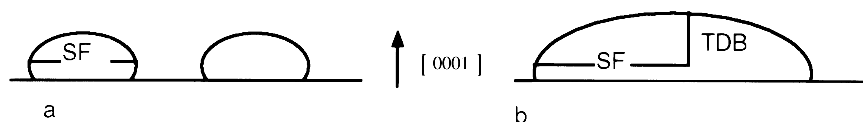

Fig. 4. Possible mechanism of formation of a translation domain boundary (TDB).

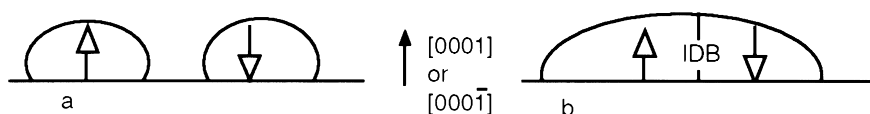

Fig. 5. Possible mechanism of formation of a inversion domain boundary in thin films.

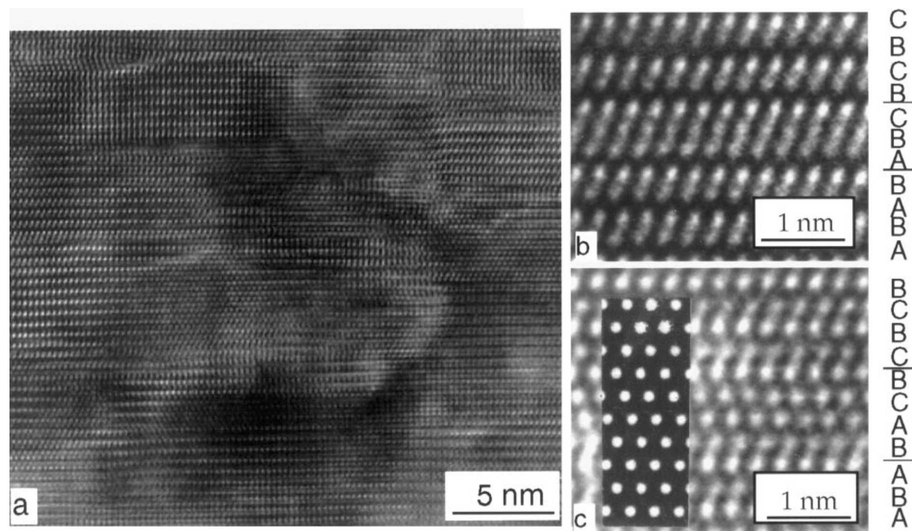

Fig. 6. HRTEM image of the ZnO coating: (a) general view; (b) single stacking fault; (c) double stacking fault.

affect the (0002) spacing and the orientation and are likely to contribute to the large (0002) peak width.

The resistivity of our ZnO films measured normal to the fiber axis is high at low voltage and decreases abruptly above a certain voltage[1] and it is of interest to know the type of defects and microstructure which may be associated to this behavior. Important features include the grain boundaries that separate the columns, the high concentration of dislocations and stacking faults, point defects, the low crystallinity closed to the Au interface and the Au/ZnO interface.

Acknowledgements

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