Buffer-facilitated epitaxial growth of AlN on Al₂O₃(0 0 0 1)
at room temperature

Yan-Ru Lin ¹, Shinn-Tyan Wu *

Department of Materials Science and Engineering, National Tsing-Hua University, 101, Sec. 2 Kuang Fu Road, Hsinchu 30043, Taiwan, ROC

Received 4 April 2002; accepted for publication 12 June 2002

Abstract

Aluminum nitride (AlN) was deposited on Al₂O₃(0 0 0 1) by direct current magnetron sputtering. It was discovered that the nitride could grow epitaxially near room temperature. A FWHM of 2° was obtained from X-ray rocking curve. A thin compliant buffer of aluminum (Al) was sandwiched between nitride and sapphire. The buffer layer was nitrided before the commencement of AlN deposition. Both electron and X-ray diffraction data are used to support our contention.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Sputter deposition; Epitaxy; Nitrides; Aluminum; Aluminum oxide; Surface relaxation and reconstruction

The ultimate goal of epitaxial growth is to grow a film without dislocations. Achieving this is nearly impossible if the lattice mismatch is present. Previous studies have proposed a compliant substrate to circumvent the difficulty [1,2], by assuming that the strain energy induced by the lattice mismatch can be relieved by plastic deformation of a compliant substrate. Consequently, the driving force behind the creation of dislocations in the film was eliminated or reduced and the perfection of the film was preserved. Several experiments have verified the effectiveness of this approach [3–8]. This study presents a novel application of the perfecting of the film by strain relief. Briefly, the epitaxial growth of an aluminum nitride (AlN) film on a sapphire substrate was sustained down to a very low growth temperature of 333 K if an Al layer of 30 nm was sandwiched between nitride and sapphire. Without a buffer, epitaxial growth was impossible if the growth temperature was lower than 673 K in the system considered here.

The substrate was a mirror-polished sapphire of (0 0 0 1) orientation. No information was available on surface reconstruction. No substrates were plasma cleaned. They were, however, cleaned before they were loaded into the coater according to the following procedure. Acetone and deionized water were sequentially used in ultrasonic baths for degreasing. Acid etching at 343 K for 10 min followed. The etchant was a solution of HCl, H₂O₂.

¹ Corresponding author. Tel.: +886-3-5714386; fax: +886-3-5722366.
E-mail addresses: d867503@oz.nthu.edu.tw (Y.-R. Lin), stwu@mse.nthu.edu.tw (S.-T. Wu).
¹ Tel.: +886-3-571513-3838; fax: +886-3-5722366.

0039-6028/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0039-6028(02)01974-X
and deionized water in the proportion, 1:1:5 by volume. Rinsing in deionized water finished the cleaning. The epitaxial films were deposited using a direct current magnetron sputtering system with a base pressure of $2 \times 10^{-6}$ mbar and a target—substrate separation of 150 mm. The target was aluminum (99.9%). The chamber pressure was maintained at $2 \times 10^{-3}$ mbar during sputtering. The gas was a mixture of argon and nitrogen when AlN films were deposited. The partial pressure of the latter was $5 \times 10^{-4}$ mbar. No nitrogen gas was present during the deposition of the Al buffer. A direct current of 0.7 A and a voltage of 500 V yielded a coating rate of 3 nm/min for AlN, and 15 nm/min for Al. Before coating, the shutter was closed and the target was sputter cleaned for 15 min. The buffer was 30 nm of Al. Since AlN grows on buffer Al, the quality of the nitride is assumed to be markedly affected by the perfection of the buffer layer. Consequently, the buffer was deposited at 873 K, near the melting temperature.

The substrate heater was turned off after the buffer was deposited. The buffer was nitrided by filling the vacuum with nitrogen gas ($1 \times 10^{-3}$ mbar) during the cooling period, to promote the continuous growth of AlN on the metallic buffer. After the substrate temperature was reduced to 303 K, the 300 nm of AlN was deposited on the buffer without breaking the vacuum. A temperature of 303–332 K was detected during AlN deposition. The gradual increase of 29 K might have been caused by the heating of plasma during sputtering.

Both transmission electron microscopy (TEM) and X-ray pole figures were considered to analyze the structure of the film. Nitriding was suspected to result in a very thin AlN layer on the buffer’s surface. Accordingly, another specimen was prepared, in which AlN was replaced with capping Al of 60 nm. The cross-sectional TEM of this specimen was obtained with atomic resolution. The analytic tools were the JEOL-4000EX HRTEM and the MAC Science MXP18 X-ray Diffractometer (Cu Kα).

Fig. 1 shows a plane-view electron diffraction pattern of the multilayer on a sapphire substrate. Fig. 1(b) is a computed pattern for indexing Fig. 1(a). The close match between the two figures strongly supports the hypothesis on which the calculation is based. The extra spots in Fig. 1(a), which are absent from Fig. 1(b) are due to double diffraction by the sapphire substrate. Some important crystal planes are numbered: $(11 \overline{2}0)$sapphire, $(220)_\text{Al}$, $(10 \overline{1}0)_\text{AlN}$ and $(1120)_\text{AlN}$ at the bottom of the figure. Corresponding spots are indicated by arrows. The calculation assumes that the zone axes are [0001]AlN, [111]Al and [0001]Al$_2$O$_3$, for over-
layers and substrate respectively. Furthermore there is a rotation of $-9^\circ$ ($\gamma$) between 2 (or 4) and 1. Mathematically these two assumptions are expressed by the equations:

$$\langle 0001 \rangle_{\text{AIN}} \parallel \langle 111 \rangle_{\text{Al}} \parallel \langle 0001 \rangle_{\text{Al}_2\text{O}_3}$$

(1)

and

$$\langle 11\bar{2}0 \rangle_{\text{AIN}} \parallel \langle 1\bar{1}0 \rangle_{\text{Al}} \parallel R \pm 9^\circ \langle 1\bar{1}\bar{2}0 \rangle_{\text{Al}_2\text{O}_3}.$$  

(2)

The filled squares and triangles are mirror images of open ones. Hence a rotation of $+9^\circ$ is also present in Eq. (2). Accordingly, the diffraction pattern implies the existence of two kinds of buffer Al with different in-plane orientations. Both have closed-packed planes parallel to $\text{Al}_2\text{O}_3(0001)$. One (▼) has a close-packed row $\langle 1\bar{1}0 \rangle_{\text{Al}}$ rotated by $+9^\circ$ away from $\langle 1\bar{1}\bar{2}0 \rangle_{\text{Al}_2\text{O}_3}$ and the other (▲) is rotated in the other direction. A nitride film grows epitaxially on top of each of these two differently oriented buffers. In summary, the diffraction pattern consists of sub-patterns of $\text{Al}_2\text{O}_3$, Al ($\pm 9^\circ$) and AlN ($\pm 9^\circ$), five in total and satisfying the relationships of Eqs. (1) and (2). Epitaxial growth is well established by the close match between the calculation and measurement.

Fig. 2 shows a rocking curve of AlN(0002) from which FWHM of $2^\circ$ is obtained. Therefore the nitride film is not so perfect and substantial mosaic spread is expected.

Fig. 3 is a pole figures of X-ray diffraction by AlN(10\bar{1}1). Calculations give $\chi = 61.58^\circ$, which is the angle subtended between AlN(0001), the center pole, and AlN(10\bar{1}1). Bragg’s law yields

$$2\theta = 37.916^\circ (\lambda = 0.15405 \text{ nm, Cu } K\alpha_1).$$

The concentration of diffraction intensity into singular poles implies that the film is single crystalline over a macroscopic area. In fact, only two orientations correspond to the $\pm 9^\circ$ rotation in Fig. 1. Together, the two figures show that epitaxial relationships on a macro scale are confidently established. These relationships are not accidental as they are identical to the famous $(\sqrt{3}1 \times \sqrt{3}1)R \pm 9^\circ$ of reconstructed $\text{Al}_2\text{O}_3(0001)$ [9–17]. The buffer plausibly grows “homo-epitaxially” on the metallic bilayer of $(\sqrt{3}1 \times \sqrt{3}1)R \pm 9^\circ$ so that the $\pm 9^\circ$ rotation is inherited, since the buffer Al is deposited at a temperature at 873 K. This is in complete agreement with previous report [12] where depositing between 1 and 2 monolayer of aluminum on top of $\text{Al}_2\text{O}_3(0001)-(1 \times 1)$ surface resulted in $(\sqrt{3}1 \times \sqrt{3}1)R \pm 9^\circ$ reconstruction. As the AlN is deposited it inherits the structure by “homo-epitaxial” growth. The buffer is nitrided during the period of cooling by filling the vacuum with nitrogen gas, to enhance this inheritance. If this “nitriding” is omitted, then AlN turns polycrystalline, as determined by X-ray diffraction. A thin layer of nitride is suspected to have appeared on the buffer’s surface.

Fig. 2. The X-ray rocking curve of the (0 0 0 2) diffraction peak of AlN. The thickness of AlN is 300 nm. The growth temperature is near room temperature.

Fig. 3. The pole figures of AlN(10\bar{1}1) from the same specimen as that of Fig. 1. The sixfold symmetry originates from the HCP structure of AlN.
following nitriding. Fig. 4 is a TEM photograph of a cross-section of a nitrided buffer capped with Al. The overlayer is changed to demarcate the buffer/overlayer interface. After nitriding, the buffer layer composition near the interface can be reasonably assumed to be similar to the AlN. Omit the changing of the overlayer, the cross-sectional TEM cannot be easily used to decide whether the nitriding affects the composition of the buffer’s surface. Notice the bright stripe of ≈2 nm in Fig. 4. The crystal structure is in perfect registry with Al. It is quite tempting to identify this as a nitride layer on the buffer’s surface, which is responsible for transmitting structural information to the overlayer. This assertion is supported by the fact that the cubic phase of AlN has a lattice constant of 0.40450 nm (JCPDS 46-1200, rock-salt structure, r-AlN), which value is very close to 0.40494 nm for Al. Furthermore, an insulator such as AlN tends to be brighter under TEM due to charge accumulation. If the capping metal is restored with AlN, then the continuity may be thought to remain. However, suggestion requires experimental verification in the future. Yet another indirect support is shown in Fig. 5 in which two pole figures are shown. Fig. 5(b) shows diffraction by the same specimen as that of Fig. 4, which consists of a nitrided buffer sandwiched between substrate and capping Al. Fig. 5(a) concerns a specimen whose buffer was not nitrided. Clearly, the capping film grows epitaxially on the buffer if nitriding is omitted, proven by the threefold symmetry of the fcc lattice. However, Fig. 5(b) depicts a sixfold symmetry, which implies that a stacking sequence of the buffer (A–B–C–A...) has been switched to (A–C–B–A...) in half of capping.

---

Fig. 4. High resolution cross-sectional transmission electron micrograph of a nitrided buffer. The top layer is aluminum rather than AlN to demarcate the buffer/overlayer interface.

---

Fig. 5. X-ray pole figures of Al(2 0 0) from Al (60 nm)/Al (30 nm)/Al2O3. The nitriding of buffer Al (30 nm) changes the symmetry from (a) threefold to (b) sixfold. The Bragg angle (θ) is taken as 22.369° for Al(2 0 0). Poles of Al2O3(11 2 2) marked by “S” also appear because its Bragg angle is 21.681°.
layer, creating a stacking fault at the interface between the buffer and the capping. Therefore, the nitriding alters the surface of the buffer layer, as depicted in Fig. 4, facilitating the epitaxial growth of AlN at room temperature. If the buffer layer is absent, the epitaxial nitride deposited at a temperature above 773 K, the epitaxial relationship is identical to that already reported [18–21], and AlN films become polycrystalline if the growth temperature is under 673 K.

In summary, this study has demonstrated the feasibility of epitaxial growth of AlN on sapphire at room temperature by interposing an Al buffer layer. The process of nitriding the buffer’s surface is vital. This fact is highly significant in view of the expected low adatom mobility at a temperature, which in absolute temperature scale is only one tenth of the melting temperature of AlN [22]. According to the current wisdom [23,24], the film should be highly defective. The diffraction data in this study establish that an epitaxial film can be grown despite low mobility.

Acknowledgements

The study has been supported by the National Science Council of the Republic of China under contract no. NSC89-2216-E-007-033. The authors would like to thank Dr. Xing-Jian Guo for his excellent instruction on the use of TEM.

References