Ti₂AlN thin films synthesized by annealing of (Ti plus Al)/AlN multilayers

Thierry Cabioch, Malaz Alkazaz, Marie-France Beaufort, Julien Nicolai, Dominique Eyidi and Per Eklund

Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:

Thierry Cabioch, Malaz Alkazaz, Marie-France Beaufort, Julien Nicolai, Dominique Eyidi and Per Eklund, Ti₂AlN thin films synthesized by annealing of (Ti plus Al)/AlN multilayers, 2016, Materials research bulletin, (80), 58-63.

<http://dx.doi.org/10.1016/j.materresbull.2016.03.031>

Copyright: Elsevier

<http://www.elsevier.com/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-130056>

Accepted Manuscript

Title: Ti_2AlN thin films synthesized by annealing of (Ti+Al)/AlN multilayers

Author: Thierry Cabioch Malaz Alkazaz Marie-France
Beaufort Julien Nicolai Dominique Eyidi Per Eklund

PII: S0025-5408(16)30139-8
DOI: <http://dx.doi.org/doi:10.1016/j.materresbull.2016.03.031>
Reference: MRB 8724

To appear in: *MRB*

Received date: 4-11-2015
Revised date: 6-3-2016
Accepted date: 23-3-2016

Please cite this article as: Thierry Cabioch, Malaz Alkazaz, Marie-France Beaufort, Julien Nicolai, Dominique Eyidi, Per Eklund, Ti_2AlN thin films synthesized by annealing of (Ti+Al)/AlN multilayers, Materials Research Bulletin <http://dx.doi.org/10.1016/j.materresbull.2016.03.031>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Ti₂AlN thin films synthesized by annealing of (Ti+Al)/AlN multilayers

Thierry Cabioch^{1,*}, Malaz Alkazaz¹, Marie-France Beaufort¹, Julien Nicolai¹, Dominique Eyidi¹, Per Eklund^{1,2,**}

¹ *Institut Pprime, UPR 3346, Université de Poitiers, SP2MI-Boulevard 3, Téléport 2-BP 30179, 86962 Futuroscope Chasseneuil Cedex, France*

² *Thin Film Physics Division, Linköping University, IFM, 581 83 Linköping, Sweden*

* Thierry.cabioch@univ-poitiers.fr

** Perek@ifm.liu.se

Graphical Abstract

Highlights

- Epitaxial thin films of the MAX phase Ti_2AlN are obtained by thermal annealing
- A new metastable (Ti,Al,N) solid solution with the structure of $\alpha\text{-Ti}$ is evidenced
- The formation of the MAX phase occurs at low temperature (600°C)

Abstract

Single-phase Ti_2AlN thin films were obtained by annealing in vacuum of $(\text{Ti}+\text{Al})/\text{AlN}$ multilayers deposited at room temperature by magnetron sputtering onto single-crystalline (0001) 4H-SiC and (0001) Al_2O_3 substrates. In-situ X-ray diffraction experiments combined with ex-situ cross-sectional transmission electron microscopy observations reveal that interdiffusion processes occur in the multilayer at a temperature of $\sim 400^\circ\text{C}$ leading to the formation of a $(\text{Ti},\text{Al},\text{N})$ solid solution, having the hexagonal structure of $\alpha\text{-Ti}$, whereas the formation of Ti_2AlN occurs at $550\text{-}600^\circ\text{C}$. Highly oriented (0002) Ti_2AlN thin films can be obtained after an annealing at 750°C .

Keywords: Annealing, MAX phases, thin films, multilayer

I. Introduction

The $M_{n+1}AX_n$ phases ($n = 1 - 3$, or ‘MAX phases’) are nanolaminated early transition-metal (M) carbides and nitrides (X) interleaved with a group 12-16 element (A) exhibiting a remarkable combination of metallic and ceramic properties. For reviews, see Refs. 1,2,3,4,5. Thin-film synthesis by physical vapor deposition (especially sputter-deposition) of MAX phases is a relatively mature area [2], where substantial interest is devoted to low-temperature deposition since this is essential for deposition onto many technologically relevant substrates. Among the MAX phases, it is established that [2] M_2AX phases with group-5 or group-6 M elements can be directly deposited from vapor at relatively low substrate temperature, typically around 500 °C. This includes V_2GeC [6], Cr_2GeC [7], and perhaps most importantly Cr_2AlC [8,9,10,11,12,13,14,15], while the Ti-based MAX phases require higher temperatures (see section 4.2.1 in Ref. 2 for a detailed discussion).

An alternative approach to direct deposition of MAX phases is to take advantage of solid-state reactions. For the purpose of thin-film synthesis, these reactions can be categorized into two groups: one based on interdiffusion processes between a film and a substrate during post-deposition thermal annealing and the other based on reaction processes inside the film itself. For MAX phases, the most well-known example of the first category of reactions is Ti_3SiC_2 synthesized by annealing of Ti-based contacts deposited onto SiC substrates, to form ohmic contacts in SiC-based semiconductor devices [16,17,18,19,20,21,22,23]. The second category is deposition of a film containing the three elements M, A, and X in a metastable state, e.g., amorphous [24,25,26] or an artificial multilayer [27,28,29,30], followed by annealing above the deposition temperature, to initiate transformation to the MAX phase. A variation of these approaches is sequential deposition of the three elements at somewhat higher

temperature (~ 650 °C for Ti_3SiC_2), which favors segregation of the elements and enables formation of the complex MAX structure at lower temperature than for direct deposition [31].

In order to fully exploit these approaches, it is important to understand the phase transformation paths, including the role and nature of any intermediate phases. This background is the motivation for the present work, in which we report the synthesis and formation mechanism of Ti_2AlN via intermediate phases from (Ti+Al)/AlN multilayers.

II. Experimental Details

(Ti+Al)/AlN multilayers were deposited at ambient temperature onto 4H-SiC(0001) and Al_2O_3 (0001) substrates by magnetron sputtering in an ultra-high vacuum system (base pressure of $\sim 2.10^{-6}$ Pa) using Ar as the working gas. For (Ti+Al) layers, elemental Ti (99.995% purity) and Al (99.999%) targets were run in DC power-control mode whereas a reactive deposition process was used to achieve AlN layers by introducing N (6.5 sccm) in the deposition chamber during Al deposition (Al target power= 300W). The power applied to the Ti and Al targets and the deposition time of each layer were adjusted to get single-phase Ti_2AlN thin films after thermal annealing (see table 1).

Preliminary ex-situ X-ray diffraction (XRD) θ – 2θ measurements and ω scans (rocking curves) were carried out in a Bruker D8 diffractometer using Cu $K\alpha$ radiation. The instrument was operating at 40 kV and 40 mA for a selected 2θ range (10 – 80°). Steps interval of 0.04° and counting time of 5 s for each step were used. These preliminary measurements (not shown) showed that the main diffraction peaks were observed at $\sim 13^\circ$ for the (0002) diffraction peak of Ti_2AlN and in the 37 – 41° 2θ range for the diffraction peaks of the different phases synthesized after deposition and during annealing.

In situ X-ray diffractograms were acquired in the 25 to 750 °C temperature range under vacuum (2×10^{-4} Pa) in a second diffractometer (X'PERT Philips) operating at 45 kV and 40 mA. The height of the sample was adjusted prior to each X-ray measurement for consistent alignment. An angular step size of 0.04° , with a count time of 1 s for each step, was used for the acquisition of diffractograms in the ranges of $11-15^\circ$ and $37-41^\circ$ (-50° in some cases). The setup is described in more detail elsewhere [32].

Transmission Electron Microscopy (TEM) was performed in a JEOL 2200FS operating at 200 kV. Tripod polishing was used to mechanically thin cross-sections down to 10 μm before ion milling in a Gatan Precision Ion Polishing System (PIPS) (2.5 keV Ar^+ ion beam at 8° and 4° of incidence with respect to the surface of the sample) to reach electron transparency. STEM images were realized using ADF detector with a camera length which was decreased to 4 cm to ensure that the Bragg electrons do not hit the detector, leading to the formation of a quasi-STEM-HAADF image [33] The STEM image contrast is then predominantly formed by the incoherently scattered electrons and the intensity is proportional to Z^n with n close to 2 [34,35]

The stoichiometry of the different multilayers was determined by Energy Dispersive X-Ray Spectroscopy (EDS) inside a Scanning Electron Microscope (SEM) (JEOL-7001F-TTLS) operated at 10 kV. Pure Ti and AlN samples were used as standards to determine the Ti, Al and N contents in multilayers deposited onto SiC. Due to the quite low energy resolution of the technique (~ 125 eV) and the overlapping Ti-L and N-K peaks, the relative uncertainty for the nitrogen content is estimated to be close to 20%. Both samples studied here have a Ti:Al:N ratio close to 2:0.9:0.8.

III. Results and discussion

Figure 1 shows X-ray diffractograms in θ - 2θ geometry of as-deposited films on 4H-SiC(0001) and *in-situ* annealed films at 300 °C, 400 °C, 500 °C, 550 °C, 600 °C, 650 °C, 700 °C, and 750 °C. The as-deposited films exhibit three broad features due to the multilayered structure of the film. The position of the main peak ($2q=38,22$, labelled with a cross in Fig.1) corresponds to an average distance ($d_0=0.2353$ nm) in the multilayered structure between (0002) planes of an α -Ti structure (Ti+Al layers) and of AlN whereas the other peaks (labelled with a star) are satellites peaks. Figure 2 shows a bright-field TEM image of the as-deposited TiAl/AlN multilayers. As can be seen, (Ti+Al) layers, 12-13 nm thick, are interleaved by thinner (2-3 nm) AlN layers for a total thickness of the film close to 140 nm. HRTEM observations (figure 3) confirm the preferential growth of the Ti-rich layers with the basal planes of the hexagonal structure ((0002) planes) parallel to the surface as indicated by XRD analysis. Brighter AlN layers appear to be less ordered even if (0002) planes of the hexagonal AlN structure, in epitaxy with the Ti (0002) planes, are identified in some areas. It is important to point out that such observations appear to be in contradiction with the average stoichiometry of the thin film (Ti:Al:N ratio close to 2:0.9:0.8). In particular, it is not possible to explain this high nitrogen content by simply considering nitrogen incorporation inside the AlN layers. High-angle annular dark-field imaging (HAADF) of this as-deposited multilayer sheds light on this point (see figure 4) since this technique is highly sensitive to variations in the atomic number of atoms in the sample (the more the layer is bright, the more the average Z is high in the observed area). Instead of uniform contrast inside the Ti-rich layers, the profile is strongly asymmetric, lower intensities being obtained closer to the AlN layers. Even if the influence of strain or defects cannot be totally excluded, their influence is very small with the STEM conditions used here and the evolution of the intensity can then be safely discussed in terms of chemical contrasts. This observation can be explained by considering nitrogen incorporation during the initial stages of the growth of the (Ti+Al) layers. On the basis of our study, it is not possible to definitively determine the origin of this phenomenon, but we propose that it can be attributed to

residual nitrogen inside the vacuum chamber just after the reactive deposition of the AlN layer and/or to poisoning of the Ti and/or Al targets during the AlN deposition.

As seen in Fig. 1, this multilayer structure is initially retained when annealing at 300 °C and the diffraction peak slightly moves towards lower angles due to the thermal expansion. An increase of the temperature to 400 °C results in the disappearance of the satellite peaks, i.e., complete loss of a multilayer structure containing layers with different densities. This clearly indicates that interdiffusion of some of the atomic species occurred at 400°C. Furthermore, a shift of the maximum of the diffraction peak towards a larger angle can be observed in figure 1 when the temperature reaches 400°C. This evolution indicates that an intermediate phase, for which the distance between the diffracting planes is slightly smaller than the one between the (0002) planes in titanium, was formed at this temperature. Only this phase, with a peak position close to that of α -Ti, is observed in XRD. This intermediate phase is retained until 550 °C. Annealing at 600 °C results in a gradual transformation of the intermediate phase into Ti_2AlN , as confirmed by the appearance of the Ti_2AlN (0002) and (0006) peaks at $\sim 13^\circ$ and $\sim 39^\circ$ in 2θ . Further increase in temperature up to 750 °C and/or longer holding time at 600 °C results in the complete transformation of the film into Ti_2AlN .

To identify the intermediate phase, TEM (Fig. 5a) and electron diffraction (Fig. 5b) was performed on the sample annealed at 500 °C, i.e., with only the intermediate phase being observed in XRD. Analysis of the electron diffraction pattern shows that it can be fully indexed as a single-phase material with a hexagonal structure similar to that of α -Ti metal, as indexed in Fig. 4b, but with smaller lattice parameters ($a=0.284(5)$ nm and $c=0.466(5)$) for this intermediate phase than for pure α -Ti ($a=0.29505$ nm; $c=0.46826$ nm)

Other alternative structures for the intermediate phase can be excluded as they would be inconsistent with the electron diffraction results. That excludes the possibility of a tetragonal ε -Ti₂N-like structure (isostructural to (Cr,Al)₂C_x phase which is an intermediate phase when annealing nominally amorphous Cr-Al-C films for transformation into Cr₂AlC [25]) or cubic structures such as the inverse perovskite Ti₃AlN tentatively (and most likely incorrectly) assigned in Ref. 28. The intermediate phase also has a substantial content of Al and N, nominally corresponding to approximately the ratio Ti:Al:N:2:0.9:0.8. The intermediate phase can therefore be identified as a metastable solution of Al and N in hcp-Ti, with higher Al and N content than the equilibrium solubility in Ti (which is ~20% in both cases), enabled by the nonequilibrium low-temperature deposition conditions. The present observations do not allow any definitive confirmation as to the exact positions of the atoms of Al and N, but it is likely that Al is substitutionally dissolved on Ti atomic positions of the hexagonal structure of α -Ti, and the nitrogen atoms are probably interstitially dissolved.

As seen in Fig. 1 for films deposited onto 4H-SiC, increasing the annealing temperature beyond 550 °C results in a transformation into Ti₂AlN. After annealing at 750 °C, the films are fully transformed into Ti₂AlN. Figure 6 shows X-ray diffractograms in θ -2 θ geometry of as-deposited films on Al₂O₃(0001) and *in-situ* annealed films at 300 °C, 400 °C, 500 °C, 550 °C, 600 °C, 650 °C, 700 °C, and 750 °C. Here, the intermediate phase is retained at higher temperature (in coexistence with Ti₂AlN, which starts forming at 550 °C) than for films deposited onto 4H-SiC, suggesting a higher degree of epitaxial stabilization of the intermediate phase on Al₂O₃ than on 4H-SiC. When annealing at 750 °C, the intermediate phase is initially present but fully transforms into Ti₂AlN with time (~75 min). The initial ratio Ti:Al:N:2:0.9:0.8 used here does not exactly match the expected ratio for a 211 MAX phase. Nevertheless, it is now well documented that the Ti₂AlN phase can accommodate substantial amounts of vacancies both on Al and N sites [27,36,37]. This is certainly the case here, especially after

annealing at 750°C (ratio Ti:Al:N:2:0.85:0.6 were obtained by EDS after annealing at 750°C for 1h). Loss of Al and N can thus occur and a progressive transformation of Ti₂AlN into TiN occurs if the sample is maintained at 750°C for several hours.

Figure 7 shows TEM images of the resulting Ti₂AlN films. The resulting Ti₂AlN are epitaxially related to the Al₂O₃ or SiC substrates, as evidenced by XRD pole figures (not shown, essentially identical to the insets in Fig. 1 in Ref. 7 and fig 1 in ref. 38) and TEM. On a final note, we also performed current-voltage measurements in the transmission-line geometry for the Ti₂AlN films on SiC (results not shown). These films did not exhibit ohmic behavior and can thus not in as-deposited form be used as ohmic contacts. This is not too surprising given the low temperature and lack of post-annealing at 950 °C -1000 °C, the temperature which is typically required for obtaining a well-ordered interface with ohmic properties [39,40].

To summarize the transformation mechanism, these observations can overall be explained by a gradual transformation from the initial intermixed multilayer into a disordered metastable structure (hexagonal solid solution Ti-Al-N with the α -Ti structure) and further to a more ordered structure (Ti₂AlN) can take place at 550 – 600 °C (considerably lower than the formation temperature for Ti₂AlN in the case of direct deposition from vapor phase by sputtering). This transformation may be enabled by the very short diffusion distance in the presence of nitrogen, a majority of the atomic planes of Ti remaining unchanged. A schematic illustration of this mechanism is shown in Fig. 8.

IV. Summary and Conclusions

We have investigated the synthesis and formation mechanism of Ti₂AlN via intermediate phases from TiAl/AlN multilayers. The as-deposited multilayers show a degree of intermixing and

transform into a single-phase intermediate hexagonal α -Ti-like solid solution with dissolved Al and N, presumably with Al substituting for Ti and N being dissolved interstitially. This intermediate phase is transformed to the more ordered structure of Ti_2AlN at 550 – 600 °C, lower than the formation temperature for Ti_2AlN if directly grown from vapor phase. The short diffusion distances involved explain the occurrence of this phase transformation at this relatively low temperature.

Acknowledgments

The University of Poitiers is acknowledged for funding a Visiting Professor Position for P. E., who also acknowledges support from the European Research Council under the European Community's Seventh Framework Programme (FP/2007-2013) / ERC grant agreement no 335383 and the Swedish Foundation for Strategic Research through the Future Leaders 5 program.

References

-
- ¹ M. W. Barsoum, *Prog Solid State Chem* 28 (2000) 201.
 - ² P. Eklund, M. Beckers, U. Jansson, H. Högberg, L. Hultman, *Thin Solid Films* 518 (2010) 1851.
 - ³ M. W. Barsoum, M. Radovic, *Annu. Rev. Mater. Res.* 41 (2011) 195.
 - ⁴ Z. M Sun, *Int. Mater. Rev.* 46 (2011) 153.
 - ⁵ M. W. Barsoum, *MAX Phases: Properties of Machinable Ternary Carbides and Nitrides*; John Wiley & Sons: New York, 2013.
 - ⁶ O. Wilhelmsson, P. Eklund, H. Högberg, L. Hultman, U. Jansson, *Acta Mater.* 56 (2008) 2563.
 - ⁷ P. Eklund, M. Bugnet, V. Mauchamp, S. Dubois, C. Tromas, J. Jensen, L. Piriaux, L. Gence, M. Jaouen, T. Cabioch, *Phys. Rev. B* 84 (2011) 075424.

-
- ⁸ R. Mertens, Z.M. Sun, D. Music, J.M. Schneider, *Adv. Eng. Mater.* 6 (2004) 903.
- ⁹ C. Walter, D.P. Sigumonrong, T. El-Raghy, J.M. Schneider, *Thin Solid Films* 515 (2006) 389.
- ¹⁰ J. M. Schneider, D. P. Sigumonrong, D. Music, C. Walter, J. Emmerlich, R. Iskandar, J. Mayer, *Scripta Mater.* 57 (2007) 1137.
- ¹¹ Q.M. Wang, A. Flores Renteria, O. Schroeter, R. Mykhaylonka, C. Leyens, W. Garkas, M. to Baben, *Surf. Coat. Technol.* 204 (2010) 2343.
- ¹² J. J. Li, L. F. Hu, F. Z. Li, M. S. Li, Y. C. Zhou, *Surf. Coat. Technol.* 204 (2010) 3838.
- ¹³ J.J. Li, M.S. Li, H.M. Xiang, X.P. Lu, Y.C. Zhou, *Corros. Sci.* 53 (2011) 3813.
- ¹⁴ Q.M. Wang, R. Mykhaylonka, A. Flores Renteria, J.L. Zhang, C. Leyens, K.H. Kim, *Corros. Sci.* 52 (2010) 3793.
- ¹⁵ M. R. Field, P. Carlsson, P. Eklund, J. G. Partridge, D. G. McCulloch, D. R. McKenzie, M. M. M. Bilek, *Surf. Coat. Technol.* 259 (2014) 746.
- ¹⁶ B. Pécz, L. Tóth, M.A. di Forte-Poisson, J. Vacas, *Appl. Surf. Sci.* 206 (2003) 8.
- ¹⁷ T. Abi-Tannous, M. Soueidan, G. Ferro, M. Lazar, B. Toury, M.F. Beaufort, J.F. Barbot, J. Penuelas, D. Planson, *Appl. Surf. Sci.* 347 (2015) 186.
- ¹⁸ A. Drevin-Bazin, J.F. Barbot, M. Alkazaz, T. Cabioch, M.F. Beaufort, *Appl. Phys. Lett.* 101 (2012) 021606.
- ¹⁹ M. Gao, S. Tsukimoto, S.H. Goss, S.P. Tumakha, T. Onishi, M. Murakami, L.J. Brillson, *J. Electron. Mater.* 36 (2007) 277.
- ²⁰ S. Tsukimoto, K. Nitta, T. Sakai, M. Moriyama, M. Murakami, *J. Electron. Mater.* 33 (2004) 460.
- ²¹ Z. Wang, S. Tsukimoto, M. Saito, Y. Ikuhara, *Phys. Rev. B* 79 (2009) 045318.
- ²² Z. Wang, S. Tsukimoto, M. Saito, K. Ito, M. Murakami, Y. Ikuhara, *Phys. Rev. B* 80 (2009) 245303.
- ²³ Z. Wang, M. Saito, S. Tsukimoto, Y. Ikuhara, *Adv. Mater.* 21 (2009) 4966.
- ²⁴ V. Vishnyakov, O. Crisan, P. Dobrosz, and J. S. Colligon, *Vacuum* 100 (2014) 61.

-
- ²⁵ A. Abdulkadhim, T. Takahashi, V. Schnabel, M. Hans, C. Polzer, P. Polcik, J.M. Schneider, Surf. Coat. Technol. 206 (2011) 599.
- ²⁶ A. Abdulkadhim, M. to Baben, V. Schnabel, M. Hans, N. Thieme, C. Polzer, P. Polcik, J. M. Schneider, Thin Solid Films 520 (2012) 1930.
- ²⁷ V. Dolique, M. Jaouen, T. Cabioch, F. Pailloux, Ph. Guérin, V. Pélosin, J. Appl. Phys. 103 (2008) 083527.
- ²⁸ C. Höglund, M. Beckers, N. Schell, J. v. Borany, J. Birch, L. Hultman, Appl. Phys. Lett. 90 (2007) 174106.
- ²⁹ A. Abdulkadhim, T. Takahashi, D. Music, F. Munnik, J. M. Schneider, Acta Materialia 59 (2011) 6168.
- ³⁰ R. Grieseler, T. Kups, M. Wilke, M. Hopfeld, P. Schaaf, Mater. Lett. 82 (2012) 74.
- ³¹ V. Vishnyakov, J. Lu, P. Eklund, L. Hultman, J. Colligon, Vacuum 93 (2013) 56.
- ³² J. Emmerlich, D. Music, P. Eklund, O. Wilhelmsson, U. Jansson, J. M. Schneider, H. Högberg, L. Hultman. Acta Mater 55 (2007) 1479.
- ³³ Transmission electron microscopy: a textbook of materials science, D.B. Williams, C.B. Carter, Springer (second edition) (2009)].
- ³⁴ E. J. Kirkland, R. F. Loane, J. Silcox, Ultramicroscopy 23 (1987) 77.
- ³⁵ S. J. Pennycook, Ultramicroscopy 30, 58-69 (1989).
- ³⁶ T. Cabioch, P. Eklund, V. Mauchamp, M. Jaouen, J. Eur. Ceram. Soc, 32 (2012) 1803.
- ³⁷ M.A. Pietzka, J.C. Schuster, J. Amer. Ceram. Soc 79 (1996) 2321.
- ³⁸ P. Eklund, M. Dahlgqvist, O. Tengstrand, L. Hultman, J. Lu, N. Nedfors, U. Jansson, J. Rosén, Phys. Rev. Lett. 109 (2012) 035502.
- ³⁹ K. Buchholt, R. Ghandi, M. Domeij, C.-M. Zetterling, J. Lu, P. Eklund, L. Hultman, and A.Lloyd Spetz, Appl. Phys. Lett. 98 (2011) 042108.

⁴⁰ H. Fashandi, M. Andersson, J. Eriksson, J Lu, K. Smedfors, C-M Zetterling, A. Lloyd Spetz, P. Eklund, *Scripta Mater.* 99 (2015) 53.

Table 1 : Deposition parameters for (Ti+Al)/AlN multilayers.

	Substrate	4H-SiC (0001)	Al ₂ O ₃ (0001)
(Ti+Al) layer	Ti target power (W)	300	400
	Al target power (W)	30	30
	Deposition time (s)	46	30
AlN Layer	Al target power (W)	300	300
	N flow (sccm)	6.5	6.5
	Deposition time (s)	15	20

Figure captions

Figure 1. XRD θ - 2θ scans of (Ti+Al)/AlN multilayer as-deposited on 4H-SiC(0001) and annealed in-situ at 300 °C, 400 °C, 500 °C, 550 °C, 600 °C, 650 °C, 700 °C, and 750 °C. The different holding times at each temperature from 600 °C and above are marked for each scan with the label ' for minutes (eg 15' = 15 minutes holding time)

Figure 2. TEM micrograph of (Ti+Al)/AlN multilayer film (as-deposited) with 10 bilayers; total thickness ~140 nm.

Figure 3. High-resolution TEM of (Ti+Al)/AlN multilayer film (as-deposited) and SAED pattern (inset) obtained on the multilayer

Figure 4. HAADF STEM image (a) of (Ti+Al)/AlN multilayer film (as-deposited) and corresponding intensity profile (b)

Figure 5. TEM micrograph of (Ti+Al)/AlN multilayer film with 10 bilayers annealed at 500 °C and electron diffraction pattern (insert) showing a hexagonal structure (similar to α -Ti) of the intermediate phase

Figure 6. XRD θ - 2θ scans of as-deposited (Ti+Al)/AlN films on Al₂O₃(0001) and films annealed in-situ at 300 °C, 400 °C, 500 °C, 550 °C, 600 °C, 650 °C, 700 °C, and 750 °C. The different holding times at

each temperature from 550 °C and above are marked for each scan with the label ' for minutes (eg 15' = 15 minutes holding time)

Figure 7. TEM of annealed film at 750 °C, fully transformed into Ti_2AlN (BF observation (right) and HRTEM of the interface (left))

Figure 8. Schematic illustration of the transformation from the intermediate α -Ti-like phase into Ti_2AlN .

Figure 1

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.