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Substrate orientation effects on the nucleation and growth of the $M_{n+1}AX_n$ phase Ti_2AlC

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The $M_{n+1}AX_n$ (MAX) phases are ternary compounds comprising alternating layers of a transition metal carbide or nitride and a third “A-group” element. The effect of substrate orientation on the growth of Ti_2AlC MAX phase films was investigated by studying pulsed cathodic arc deposited samples grown on sapphire cut along the (0001), (10 $\bar{1}0$), and (1 $\bar{1}02$) crystallographic planes. Characterization of these samples was by x-ray diffraction, atomic force microscopy, and cross-sectional transmission electron microscopy. On the (10 $\bar{1}0$) substrate, tilted (10 $\bar{1}8$) growth of Ti_2AlC was found, such that the TiC octahedra of the MAX phase structure have the same orientation as a spontaneously formed epitaxial TiC sublayer, preserving the typical TiC– Ti_2AlC epitaxial relationship and confirming the importance of this relationship in determining MAX phase film orientation. An additional component of Ti_2AlC with tilted fiber texture was observed in this sample; tilted fiber texture, or axiotaxy, has not previously been seen in MAX phase films.

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I. INTRODUCTION

The $M_{n+1}AX_n$ (MAX) phases are a class of ternary compounds, containing a transition metal, an “A-group” element—often silicon or aluminum—and either carbon or nitrogen. Their strongly anisotropic structure results in an unusual combination of properties,¹ prompting research into the synthesis and characterization of both bulk samples¹ and thin films.² Thin film synthesis presents possibilities for controlling the crystallographic orientation of the growing film. This is desirable for basic research into property orientation dependence resulting from the anisotropy of the MAX phase structure. As an example, there are conflicting theories regarding the degree of anisotropy of electrical conductivity in the MAX phases.² This conflict could be resolved with experimental conductivity measurements on films of different orientations. Control of film orientation is also relevant for more directed research into controlling and optimizing the properties of a MAX phase film for a given application. It is highly likely that the tribological properties^{3,4} of MAX phase coatings will be strongly dependent on the coating orientation, for example, as the elastic constants of the MAX phases show strong anisotropy,⁵ and the deformation processes observed to occur in MAX phase materials are a clear consequence of their layered structure.⁶

From the very first publication considering MAX phase growth by physical vapor deposition,⁷ it has been found that a substrate or sublayer presenting a lattice-matched hexagonal template tends to result in epitaxial MAX phase growth such that the MAX phase is aligned with its basal planes parallel to the substrate, and with some specific in-plane orientation. This has been observed to hold for several combi-

nations of MAX phases and substrate.^{8–10} Early investigations reported that a carbide “seed layer” could be used to increase the degree of orientation of the MAX phase deposited onto it.⁷ Later publications demonstrated MAX phase epitaxy could be achieved directly on the substrate surface for a number of MAX phase–substrate combinations,^{10–13} and it is thought that MAX phase nucleation directly on the substrate is possible in general.²

In some reports of MAX phase film growth the basal planes of the MAX phase are tilted, in a defined orientation with respect to the substrate normal and the growth direction.^{13–17} The occurrence of tilted growth has, in some of these cases, been explained as a result of the film growing to maintain the common (111) TiC|| (0001) MAX phase epitaxial relationship, when the MAX phase nucleates on a TiC surface. Emmerlich *et al.*¹⁴ investigated Ti_3SiC_2 deposited on (001) oriented MgO substrates as well as the commonly used (111) orientation. On the (001) MgO substrate, the TiC interlayer was found to be (001) oriented, and the subsequent MAX layer was oriented with its (10 $\bar{1}5$) plane parallel to the substrate. The relative orientation of the film, interlayer and substrate remained fixed with the change from (111) to (001) MgO. Similarly, in an experiment where Ti_3SiC_2 nucleated on TiC grains present at the surface of a polycrystalline substrate,¹⁷ Eklund *et al.* found that the (111) TiC|| (0001) MAX phase epitaxial relationship held, independent of the orientation of these phases with respect to the plane of the substrate surface. From this, Eklund *et al.* proposed that in general, the orientation of a metal carbide or nitride (MX) sublayer would determine the orientation of a subsequently grown corresponding MAX layer.

Besides alignment of the growing MAX phase with an existing TiC surface, additional driving factors to basal-plane tilted MAX phase growth have been identified. Beckers *et al.*

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extensively investigated tilted growth of Ti_2AlN , deposited with¹⁵ and without¹⁶ a (Ti,Al)N seed layer. In the first case, the growth observed showed a fixed epitaxial relationship $(10\bar{1}2)\text{Ti}_2\text{AlN} \parallel (111) (\text{Ti,Al})\text{N} \parallel (111) \text{MgO}$ for both (111) and (100) MgO substrates, whereas in the second case the final Ti_2AlN film was polycrystalline and without overall texture. Emmerlich *et al.*'s observations of tilted growth were explained through the maintenance of the TiC–MAX epitaxial relationship, and so the minimization of the TiC–MAX interface free energy. In addition, Beckers identifies kinetic effects contributing to the occurrence of tilted growth. At lower substrate temperatures, hence with reduced adatom mobility, tilted growth is advantageous as both Ti and Al atoms incident at the growth surface can be immediately accommodated without the necessity for reconfiguration of the surface layers.¹⁵ Furthermore, as elemental diffusion through the MAX structure is more rapid parallel to the basal planes, tilted growth more easily allows for the correction, through diffusion, of local deviations from the correct MAX stoichiometry.¹⁶ These kinetic effects are also seen influencing nontilted, (000 l) MAX phase growth: for example, the investigation of Ti_2AlC growth by Wilhelmsson *et al.*¹¹ found that diffusion of Al to the surface of a TiC layer occurred until a critical concentration was reached and Ti_2AlC growth commenced, resulting in delayed nucleation of the Ti_2AlC phase.

In this paper, we seek to provide more evidence to support the general principle indicated by Eklund *et al.*,¹⁷ that the crystallographic orientational relationship between the MAX phase and its MX counterpart is an important determinant of the final orientation of MAX phase films. We will do this by comparing the well-known growth mode of Ti_2AlC on (0001) Al_2O_3 with the growth modes of Ti–Al–C films on two orientations of Al_2O_3 not previously investigated in this regard. This will help to assess the relative importance of epitaxy and kinetic effects on MAX phase thin film growth.

II. EXPERIMENTAL METHODS

Ti–Al–C films were deposited using a center-triggered, pulsed cathodic vacuum arc system described elsewhere,¹⁸ fitted with separate Ti, Al, and C elemental cathodes. The system was operated with a peak arc current of 900 A. The arc pulse durations used for the Ti, Al, and C cathodes were, respectively, 350 μs , 300 μs , and 850 μs , chosen to allow for the different radial speed of the arc spots on the different cathode materials. The base pressure of the chamber was 1×10^{-4} Pa.

The substrates used were polished single crystal Al_2O_3 wafers, cut on the (0001), (10 $\bar{1}0$), and (1 $\bar{1}02$) planes. During deposition, the substrate was clamped to a heater held at 900 °C, measured with a thermocouple positioned behind the sample.

X-ray diffraction (XRD) measurements were performed with a PANalytical X-Pert MRD diffractometer, using Ni-filtered $\text{Cu K}\alpha$ radiation. θ – 2θ and grazing incidence measurements were acquired with line focus and an x-ray mirror. Pole figures were acquired with point focus and an x-ray lens.

FIG. 1. (Color online) Grazing incidence XRD diffractograms of Ti–Al–C films deposited on (a) (0001) oriented Al_2O_3 , (b) (10 $\bar{1}0$) oriented Al_2O_3 , (c) (1 $\bar{1}02$) oriented Al_2O_3 . The source of the background peak in (c) was the sample mounting adhesive; this was verified with a separate background scan (not shown).

Cross-sectional transmission electron microscope (TEM) samples were prepared by mechanical grinding and polishing, followed by low angle Ar ion milling using a Gatan PIPS ion miller. The samples were then imaged using an FEI TF20 UT operated at 200 keV for a point resolution of 1.9 Å. Elemental mapping was performed in scanning mode (STEM) by simultaneous acquisition of energy-dispersive x-ray (EDX) and electron energy loss spectra (EELS).

Atomic force microscopy (AFM) topographic images were acquired in tapping mode using a Molecular Imaging PicoSPM.

Elastic recoil detection analysis (ERDA) measurements were made using 33 MeV Cl^{5+} ions at the STAR tandetron, ANSTO, Lucas Heights, Australia. The angles of both incidence and detection were 67.5° to the sample normal, giving a scattering angle of 45°.

III. EXPERIMENTAL RESULTS

Grazing incidence XRD scans of the samples grown on (0001), (10 $\bar{1}0$), and (1 $\bar{1}02$) oriented Al_2O_3 are shown in Figs. 1(a)–1(c), respectively. All three samples show peaks from polycrystalline Ti_2AlC . The differences in relative peak intensities between the samples are due to differing degrees of texture in the films. The sample grown on (1 $\bar{1}02$) Al_2O_3 also shows peaks from TiC, indicating the presence of polycrystalline TiC in this sample.

XRD scans of these samples in θ – 2θ geometry are shown in Fig. 2. The (0001) oriented substrate sample [Fig. 2(a)] shows (000 l) Ti_2AlC and (l ll) TiC peaks, indicating the out-of-plane orientation (0001) $\text{Ti}_2\text{AlC} \parallel (111)\text{TiC} \parallel (0001)\text{Al}_2\text{O}_3$. The sample on the (10 $\bar{1}0$)-oriented substrate [Fig. 2(b)] shows the TiC (220) peak, indicating the presence of TiC oriented with the (110) plane parallel to the substrate. The sample on the (1 $\bar{1}02$)-oriented substrate [Fig. 2(c)] shows no film peaks in the θ – 2θ scan, suggesting that no significant orientation of any phase relative to the plane of the substrate was present.

These results show that all samples contain both Ti_2AlC

FIG. 2. (Color online) θ - 2θ geometry XRD diffractograms of Ti-Al-C films deposited on (a) (0001) oriented Al_2O_3 , (b) (10 $\bar{1}$ 0) oriented Al_2O_3 , (c) (1 $\bar{1}$ 02) oriented Al_2O_3 .

and TiC. The TiC is strongly textured in the (0001) and (10 $\bar{1}$ 0) Al_2O_3 samples, and not oriented in the (1 $\bar{1}$ 02) Al_2O_3 sample.

XRD ϕ -scans (where the ϕ -axis is parallel to the substrate normal) on off-axis film and substrate reflections of the sample grown on (0001)-oriented Al_2O_3 indicated that the in-plane orientations of the phases present in this sample were $[2\bar{1}\bar{1}0]\text{Ti}_2\text{AlC} \parallel [10\bar{1}]\text{TiC} \parallel [10\bar{1}0]\text{Al}_2\text{O}_3$.

Pole figures were used to identify the orientation distribution in the (10 $\bar{1}$ 0) sample. Fig. 3(a) shows a pole figure taken at $2\theta=39.6^\circ$, corresponding to the (10 $\bar{1}$ 3) and (0006) planes of Ti_2AlC . Three features are present in the higher resolution inset. The high intensity, sharp feature is the substrate (1 $\bar{2}$ 10) pole. The poles at $\psi=35.1^\circ$ and $\psi=24.9^\circ$ are the Ti_2AlC (0006) and (10 $\bar{1}$ 3) poles, respectively. To differentiate the Ti_2AlC (0006) and (10 $\bar{1}$ 3) poles, θ - 2θ scans were made at the ψ and ϕ coordinates of each pole found. A θ - 2θ scan showed the other (000 l) peaks [in particular the strong (0002) peak] when taken at the pole identified as (0006), whereas these peaks did not appear in a θ - 2θ scan

FIG. 3. (Color online) Pole figures of the sample grown on the (10 $\bar{1}$ 0) Al_2O_3 substrate, plotted over the ψ (radial) range 0–80° in equal-area Schmidt projection, with a logarithmic intensity scale. (a) shows a pole figure of the Ti_2AlC (0006) and (10 $\bar{1}$ 3) planes. The inset shows a separate higher-resolution scan of the main peaks. (b) shows a pole figure of the Ti_2AlC (11 $\bar{2}$ 0) plane. The dashed curves overlaid are the patterns expected from the proposed tilted fiber texture, calculated from the geometry of the Ti_2AlC unit cell and the location of the (0006) pole.

FIG. 4. (Color online) (a) A cross-sectional TEM image of a Ti-Al-C film grown on (10 $\bar{1}$ 0) oriented Al_2O_3 , showing the film morphology. The regions of the sample shown in (c) and (d), and Fig. 5(a) are marked. (b) An AFM topographic map of the sample on (10 $\bar{1}$ 0) Al_2O_3 . (c) A map of the Ti:Al ratio of a selected area of the film, as measured by EDX. (d) A map of the C:Ti ratio of the same area, measured by EELS. In (c) and (d), warmer colors indicate higher values.

taken at the pole identified as (10 $\bar{1}$ 3). A separate partial pole figure (not shown) at the TiC (111) d-spacing found that the TiC (111) poles were coincident with the Ti_2AlC (0006) poles.

Fig. 3(b) shows a pole figure on the (11 $\bar{2}$ 0) plane of Ti_2AlC , taken at $2\theta=61.0^\circ$. Four film (11 $\bar{2}$ 0) poles are present, at $\psi=59.8$ – 60.9° , separated in ϕ by 70.3° .

Together, the positions in ψ and ϕ of the Ti_2AlC (0006), (10 $\bar{1}$ 3), and (11 $\bar{2}$ 0) poles show that an oriented fraction of the Ti_2AlC phase is present, with the orientation (10 $\bar{1}$ 8) $\text{Ti}_2\text{AlC} \parallel (110)\text{TiC} \parallel (10\bar{1}0)\text{Al}_2\text{O}_3$ between the planes parallel to the sample surface, and with the in-plane orientation $[2\bar{1}\bar{1}0]\text{Ti}_2\text{AlC} \parallel [110]\text{TiC} \parallel [0001]\text{Al}_2\text{O}_3$. The basal planes of the Ti_2AlC phase are tilted with respect to the substrate, but the relative orientation of the Ti_2AlC to the TiC phase is the same as that observed in the case of growth on (0001) Al_2O_3 where the basal planes are parallel to the TiC (111) planes.

The pole figures also contain rings centered around the Ti_2AlC (0006) pole. These originate from the Ti_2AlC (10 $\bar{1}$ 3) plane [in Fig. 3(a)] and from the (11 $\bar{2}$ 0) plane [in Fig. 3(b)]. An additional fraction of Ti_2AlC is therefore also present, with a tilted fiber texture such that (0001) $\text{Ti}_2\text{AlC} \parallel (111)\text{TiC}$ but with free rotation of the MAX phase about its C-axis. This is confirmed by the close match between the experimental data and the projected circles calculated assuming this texture, overlaid in Fig. 3.

ERDA compositional data averaged over the film thickness were, in the format Ti:Al:C, 0.56:0.21:0.22 for the (10 $\bar{1}$ 0) Al_2O_3 sample, and 0.47:0.22:0.31 for the (1 $\bar{1}$ 02) Al_2O_3 sample.

An overview cross-sectional TEM image of the film on (10 $\bar{1}$ 0) Al_2O_3 is shown in Fig. 4(a). The film is of average

FIG. 5. A high magnification image of the substrate/film interface region of the $(10\bar{1}0)\text{Al}_2\text{O}_3$ sample. [(b)–(d)] The FFTs of the substrate and the two film regions of Fig. 4(a).

thickness 250 nm, and has inclusions of large pyramidal crystallites that extend above the rest of the film.

The AFM topographic image in Fig. 4(b) shows that these pyramidal crystallites form triangular features when seen in plan view. Each crystallite is aligned in the same direction, implying that a registration exists between crystallites and substrate.

Elemental maps were collected in the area of the film indicated by a large box in Fig. 4(a), by EDX for the elements Al and Ti, and EELS for C and Ti. Figure 4(c) shows a map of the Ti:Al ratio in this region, using EDX data. Figure 4(d) shows a similar map of the C:Ti ratio, using EELS data. The elemental ratios were considered in order to accommodate for variations in signal strength caused by the dependence on crystal orientation and associated electron scattering strength (for EELS) and fluorescence yield (for EDX).

The Ti:Al ratio is low and constant through the pyramidal crystallite [the uniform purple region at the top right of Fig. 4(c)], but shows large variations elsewhere in the film. A layer immediately adjacent to the substrate, of approximate thickness 50 nm, shows a low Ti:Al ratio. This layer is also visible in the bright-field TEM image, as a lighter region. The region on the periphery of the large crystallite shows the highest Ti:Al ratio of the measured region. The C:Ti ratio does not show such great variation, but does increase near to the substrate.

Fig. 5(a) shows a higher magnification image of the substrate-film interface. Fast Fourier transforms (FFT) of cropped areas of the image corresponding to the substrate area and the lighter and darker film areas of this image are shown in Figs. 5(b)–5(d), respectively. The periodicities visible in the FFTs indicate that both lighter and darker film regions contain TiC oriented in a manner consistent with the XRD observations, $(110)\text{TiC}\parallel(10\bar{1}0)\text{Al}_2\text{O}_3$ and $[1\bar{1}0]\text{TiC}\parallel[0001]\text{Al}_2\text{O}_3$.

FIG. 6. Cross-sectional TEM images of a Ti–Al–C film deposited on $(1\bar{1}02)$ oriented Al_2O_3 .

The FFT of the lighter region, of higher Al:Ti content, shows evidence of disorder in the blurring of the TiC spots in the vertical direction. This, combined with the EDX data showing increased Al:Ti in this region, suggests that Al is present in this region as a solid solution in TiC. A stoichiometric Al-containing phase would show a fixed Al concentration rather than the varying ratio observed. Such solid solutions of Al in substoichiometric TiC films have been observed previously.¹¹ We conclude that the bulk of the film comprises a solid solution of Al in TiC. This interpretation explains our observation of a high Al concentration layer immediately adjacent to the substrate. The higher concentration near the substrate suggests the occurrence of diffusion of Al into the TiC_x layer from the Al_2O_3 substrate, a phenomenon that is known to occur.^{11,19}

The other distinct phase present in the film forms the pyramidal crystallites, as mentioned earlier. The Ti:Al EDX data [Fig. 4(c)] shows a uniform Ti:Al ratio across the crystallite, suggesting a stoichiometric Ti–Al–C phase rather than another solid solution. It is then likely that these structures are the $(10\bar{1}8)$ oriented Ti_2AlC observed in the XRD measurements. The aligned triangular pyramids seen in the AFM image Fig. 4(b) are consistent with this interpretation: the low-energy (0001) and $(10\bar{1}0)$ surfaces of Ti_2AlC crystallites of this orientation would form the facets of the crystallites observed.

TEM images of the $(1\bar{1}02)$ substrate sample are shown in Fig. 6. The film is of thickness 150 nm. The film structure is polycrystalline, and consists of large grains, mostly spanning the full thickness of the film. These grains meet the substrate with no specific registration and in some cases are etched into the substrate.

IV. DISCUSSION

The observed orientation of the sample on the $(0001)\text{Al}_2\text{O}_3$ substrate, $(0001)\text{Ti}_2\text{AlC}\parallel(111)\text{TiC}\parallel(0001)\text{Al}_2\text{O}_3$ and

$[2\bar{1}\bar{1}0]\text{Ti}_2\text{AlC} \parallel [101]\text{TiC} \parallel [10\bar{1}0]\text{Al}_2\text{O}_3$, agrees with previous results on other MAX phases, including those where TiC was deposited deliberately as an interlayer,⁷ rather than forming spontaneously, as was the case here.

In the present work, Ti–Al–C deposition onto the $(10\bar{1}0)$ substrate was found to produce an epitaxial TiC interlayer of (110) orientation spontaneously during deposition. The effects on MAX phase growth of a TiC layer of this orientation have not previously been investigated. Published MAX phase thin film work commonly uses substrate materials presenting a hexagonal surface lattice, such as (0001) Al_2O_3 or (111) MgO, resulting in the formation of (111) oriented TiC. In one publication,¹⁴ where a (001) MgO substrate was used, the TiC interlayer grown was (100) oriented. In each case, the TiC layer is epitaxial with the substrate. The epitaxial (110) layer formed in our work allows investigation of the effect of a third simple orientation of the TiC interlayer on MAX phase nucleation and growth.

The TiC (111) surface is equivalent in structure and orientation to the TiC slab within the MAX phase structure. In the case of growth on (111) TiC, the TiC forms the first basal plane of the MAX phase, resulting in the well-known basal-plane orientation relationship [as observed here on the (0001) Al_2O_3]. In the case of Ti_3SiC_2 on a TiC (100) surface,¹⁴ this relative orientation of the TiC interlayer with the TiC slabs present within the MAX phase is preserved, even though the basal planes are tilted with respect to the substrate surface. In this case, the MAX phase nucleates with its $(10\bar{1}5)$ plane parallel to the substrate, a plane parallel to the faces of the TiC octahedra within the Ti_3SiC_2 structure.

Assuming that the relative orientation of TiC and MAX phase observed in the previous two cases also prevails in the case of a TiC (110) interlayer, the expected Ti_2AlC orientation can be determined. The dihedral angle between a TiC (110) -equivalent plane within the TiC slab of the MAX phase and the basal plane is 33.06° (from the atomic positions in Ref. 1). This plane is almost precisely $\text{Ti}_2\text{AlC}(10\bar{1}8)$, which intersects the basal plane along the same zone axis, $[\bar{1}2\bar{1}0]$, and forms a similar dihedral angle of 32.85° . This is the orientation that we observed experimentally, i.e., $(10\bar{1}8)\text{Ti}_2\text{AlC} \parallel (110)\text{TiC} \parallel (10\bar{1}0)\text{Al}_2\text{O}_3$ and $[2\bar{1}\bar{1}0]\text{Ti}_2\text{AlC} \parallel [110]\text{TiC} \parallel [0001]\text{Al}_2\text{O}_3$. With addition of this result, it has now been experimentally shown that a TiC layer of any of the orientations (100) , (110) , or (111) results in subsequent MAX phase growth such that the TiC slabs of the MAX structure are in the same orientation as the TiC layer itself.

We can draw some conclusions regarding the growth process of the unusual pyramidal crystallites observed in the $(10\bar{1}0)\text{Al}_2\text{O}_3$ sample. In the EDX map [Fig. 4(c)], there is a lower concentration of Al in the TiC region near the crystallite compared to the TiC regions further from the crystallite, suggesting diffusion of Al into the crystallite from the bulk of the film. In the overview TEM image [Fig. 4(a)], the broad, dish-shaped bases of the crystallites are visible. Point nucleation and grain growth only away from the substrate would be expected to produce tapered grains, broadening

toward the surface of the film. Our observations do not support such a growth mode, and suggest that the Ti_2AlC crystallite grows through a solid phase reaction with the solid solution of Al in the epitaxial TiC layer. This is consistent with the observed erosion of the substrate by the film [seen in Figs. 4(a) and 6] and hence release of Al from the substrate into the film, and with the high substrate temperature used during deposition. The fraction of Al in the TiC regions never exceeds that of Ti_2AlC regions, suggesting that when this ratio is reached locally, the Ti_2AlC phase forms. This explanation is supported by other observations of MAX phase nucleation triggered by increasing A-element concentration.¹¹

The growth observed on the final sample, on the $(1\bar{1}02)$ oriented Al_2O_3 substrate, is a polycrystalline mixture of the Ti_2AlC and TiC phases. This growth does not follow the general pattern discussed above, where the relative orientations of the MAX phase with respect to the TiC is fixed. We attribute this to a lack of an adequate template for the TiC layer from the $(1\bar{1}02)$ substrate. The (0001) Al_2O_3 surface provides a reasonable lattice match to the (111) TiC and (0001) Ti_2AlC surfaces. The degree of lattice match between the Al_2O_3 $(10\bar{1}0)$ and TiC (110) surfaces is comparable: the mismatch parameters are 6.4% in the Al_2O_3 $[0001]$ direction and 10.2% in the $[100]$ direction. The Al_2O_3 $(1\bar{1}02)$ surface, however, presents a rhomboidal lattice, which does not register in any straightforward way with TiC or Ti_2AlC , and so polycrystalline growth results.

The additional, fiber-textured Ti_2AlC component identified in the $(10\bar{1}0)$ film has its $[0001]$ zone axis parallel to that of the completely oriented component, but with free rotation of the basal planes around this direction. Fiber texture where the fiber axis is perpendicular to a specific in the substrate, rather than being perpendicular to the substrate surface, was first observed, and designated “axiotaxy,” by Detavernier *et al.*²⁰ in films formed through solid phase reaction of a metal film with a semiconductor substrate.

In our sample, the process of nucleation of the fiber-textured fraction of the film is related to the mechanism that governs the formation of the fully oriented fraction. This can be seen in the pole figures [Fig. 3] by the gaps in the rings that appear immediately adjacent to the poles of the main oriented component. These gaps suggest that sufficiently close alignment of a growing Ti_2AlC crystallite causes the crystallite to “snap” into the full orientation relationship. There are, then, two related energetic considerations involved in the growth of Ti_2AlC on the (110) TiC surface. While the lowest energy interface results from the complete in- and out-of-plane orientation relationship, there is an energetic advantage merely in the single-axis alignment resulting from the Ti_2AlC basal planes being parallel to the TiC (111) planes. The presence of intensity variations and gaps around the arcs shows that all angles of rotation which maintain the single-axis alignment are not equally advantageous; similar variations can be seen in the axiotaxy literature.^{20–22}

In the case of tilted fiber texture growth, the film lattice planes perpendicular to the fiber axis will meet the substrate at the same angle and spacing regardless of the angle of

rotation around the fiber axis. Detavernier *et al.* proposed that the cause of the axiotaxy they observed was alignment of the edges of these film lattice planes with the substrate. We note that matching of the plane edges at an interface would be more difficult for the basal planes of the MAX phases, given that the alternating stacking sequence of the MX layers within the MAX phase structure would mean only every second TiC slab in the Ti₂AlC layer would align with the TiC sublayer. Another possible cause is that the Ti₂AlC growth nucleates as for conventional (nontilted) fiber texture, but on tilted (111) facets of the TiC sublayer. If fiber texture nucleation on (111) TiC facets was possible, though, one might expect to see conventional nontilted fiber texture in MAX phase films grown on the TiC (111) surface, which has not been reported. Nontilted fiber textured MAX phase growth has been demonstrated recently,²³ but this required a specific processing sequence in which the Ti₂AlC texture was inherited from the Ti layers of an annealed multilayer stack. The mechanism causing the tilted fiber texture we observe would seem to be an interesting topic for future work.

V. CONCLUSION

In this study, films containing Ti₂AlC were deposited onto Al₂O₃ substrates of different crystallographic orientations. Where the substrate provides a suitable lattice-matched template to TiC, film growth proceeds by nucleation of TiC and Ti₂AlC, with a fixed relative orientation between these two phases. This orientational relationship holds regardless of the orientation of the TiC with respect to the substrate normal, and on the (10 $\bar{1}$ 0) substrate used, results in basal plane tilted (10 $\bar{1}$ 8)Ti₂AlC growth. On the (1 $\bar{1}$ 02) oriented substrate, which does not provide a suitable template for TiC, polycrystalline growth occurs. A component of Ti₂AlC with tilted fiber texture was observed in the sample grown on (10 $\bar{1}$ 0)Al₂O₃. This tilted fiber texture, also referred to as axiotaxy, has not previously been found in MAX phase growth.

Our observations provide further evidence for the robustness of the MX–MAX orientation relationship with respect to changes in overall orientation of the two phases with respect to the substrate surface. Consideration of the epitaxial relationship between TiC and the substrate provides a valuable means for prediction and experimental control of the orientation of titanium carbide MAX phase films.

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