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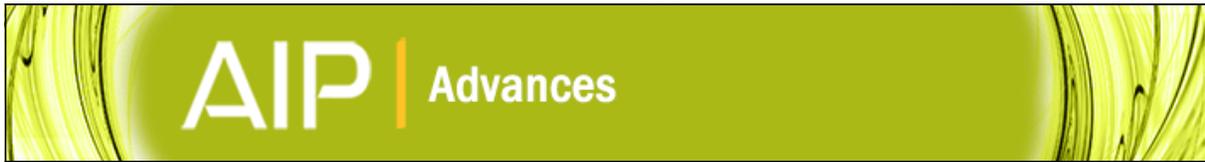
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## Epitaxial growth of $\gamma$ -Al<sub>2</sub>O<sub>3</sub> on Ti<sub>2</sub>AlC(0001) by reactive high-power impulse magnetron sputtering

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Al<sub>2</sub>O<sub>3</sub> was deposited by reactive high-power impulse magnetron sputtering at 600 °C onto pre-deposited Ti<sub>2</sub>AlC(0001) thin films on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) substrates. The Al<sub>2</sub>O<sub>3</sub> was deposited to a thickness of 65 nm and formed an adherent layer of epitaxial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(111) as shown by transmission electron microscopy. The demonstration of epitaxial growth of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> on Ti<sub>2</sub>AlC(0001) open prospects for growth of crystalline alumina as protective coatings on Ti<sub>2</sub>AlC and related nanolaminated materials. The crystallographic orientation relationships are  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(111)//Ti<sub>2</sub>AlC(0001) (out-of-plane) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(2 $\bar{2}$ 0)//Ti<sub>2</sub>AlC(11 $\bar{2}$ 0) (in-plane) as determined by electron diffraction. Annealing in vacuum at 900 °C resulted in partial decomposition of the Ti<sub>2</sub>AlC by depletion of Al and diffusion into and through the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4863560>]

In bulk, Ti<sub>2</sub>AlC is a potential material for applications that require high temperature oxidation resistance, since it forms a dense protective scale of pure Al<sub>2</sub>O<sub>3</sub>, which has virtually the same thermal expansion coefficient as Ti<sub>2</sub>AlC.<sup>1-3</sup> The oxide scale can therefore remain adherent over a wide temperature range (up to at least 1400 °C), and detrimental phenomena like oxide scale spallation are avoided.<sup>4</sup> The minimum temperature for formation of such a continuous protective layer is at least 700 °C.<sup>5</sup> In contrast, the decomposition and oxidation resistance of Ti<sub>2</sub>AlC thin films are relatively unexplored, with only a few studies<sup>6,7</sup> while more studies have been performed on the related phase Cr<sub>2</sub>AlC.<sup>8-10</sup> For the general class of materials known as M<sub>n+1</sub>AX<sub>n</sub> phases ( $n = 1, 2, 3$ , and M = transition metal, e.g., Ti, V, Cr, A = group 12-16 element, e.g., Al, Si, and X=C and/or N) to which Ti<sub>2</sub>AlC belongs, decomposition of thin films typically occurs at lower temperature than in bulk.<sup>11</sup> This is a consequence of the facts that the diffusion length scales and the sensitivity of the analysis methods are different and that the decomposition temperature depends strongly on the environment and on impurities.<sup>12,13</sup>

Recently,<sup>6</sup> we have investigated the low-temperature (500 °C) initial oxidation mechanisms by studying magnetron-sputtered Ti<sub>2</sub>AlC thin films on single-crystal Al<sub>2</sub>O<sub>3</sub>(0001) substrates, a well-defined model system for studying microstructural effects on oxidation. During oxidation at 500 °C, clusters of Al oxide and Ti oxide are formed on the surface. We thus proposed<sup>6</sup> a mechanism in which the locations of the Al-oxide clusters are related to the migration of the Al atoms diffusing out of the Ti<sub>2</sub>AlC. The Al-oxide is initially formed in valleys or on plateaus where the Al atoms have been trapped while the Ti oxide forms by in-diffusion of oxygen into the Al-deficient Ti<sub>2</sub>AlC crystal. At 500 °C, the migration of Al atoms is faster than the oxidation kinetics; explaining this microstructure-dependent oxidation mechanism.

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This led to the initial research question behind the present brief report: whether a crystalline  $\text{Al}_2\text{O}_3$  layer can be deposited onto  $\text{Ti}_2\text{AlC}$ . This is interesting both from the point of view of understanding aluminum oxide deposition and growth and as a potential means of improving the resistance to decomposition and oxidation. For the deposition, we use reactive high-power impulse magnetron sputtering (HiPIMS)<sup>14–17</sup> at the relatively low temperature of 600 °C. This technique, like other ionized forms of physical vapor deposition, is known to promote low-temperature growth of crystalline alumina.<sup>18</sup> Additionally, crystallographic templates can be used to promote growth of the crystalline alumina phases, both  $\alpha$ <sup>19–21</sup> and  $\gamma$ .<sup>22,23</sup> Here, the surface of  $\text{Ti}_2\text{AlC}(0001)$  thin films may act as crystallographic template for growth of crystalline alumina, as discussed below.

The synthesis and microstructure of the  $\text{Ti}_2\text{AlC}$  thin films on single-crystal  $\text{Al}_2\text{O}_3(0001)$  substrates is described elsewhere.<sup>6,24</sup>  $\text{Al}_2\text{O}_3$  was deposited by reactive high-power impulse magnetron sputtering (HiPIMS) at 600 °C. The target was pure Al with diameter 50 mm. The power supply was a Melec SPIK 1000A operated at a frequency of 1 kHz, pulse width of 20  $\mu\text{s}$  and a constant average power (manually regulated) of 60 W. During pulse-on, the voltage (square wave) was 540 V and the peak current 13 A. Depositions were performed in an ultrahigh vacuum chamber (base pressure  $<5 \cdot 10^{-8}$  mbar) at a total pressure of 7.5 mTorr in an Ar/ $\text{O}_2$  mixture with an Ar flow of 122.5 sccm and an  $\text{O}_2$  flow of 3.2 sccm. The target-substrate distance was 11 cm. The substrate temperature was  $\sim 600$  °C (referring to a radiative heater calibrated for Si substrate). Vacuum annealing at 900 °C was performed in a water-cooled vacuum chamber with a base pressure of  $10^{-3}$  Pa. Transmission electron microscopy (TEM) imaging was performed with a 200 kV field emission gun microscope (Tecnai G2 F20U-Twin). The cross-sectional TEM specimens were prepared conventionally by gluing two pieces of films face to face together, cutting into slices, polishing, dimpling, and finally ion milling to electron transparency.

Figure 1 shows a TEM overview image and electron diffraction pattern of a 65-nm-thick  $\text{Al}_2\text{O}_3$  layer deposited onto a  $\text{Ti}_2\text{AlC}(0001)$  thin film on a *c*-axis oriented single-crystal sapphire substrate. The electron diffraction pattern identifies the  $\text{Al}_2\text{O}_3$  phase as  $\gamma\text{-Al}_2\text{O}_3$ . Figure 2 is a TEM image of the interface between  $\text{Ti}_2\text{AlC}$  and  $\gamma\text{-Al}_2\text{O}_3$ . The inset shows electron diffraction and a Fourier-filtered lattice image of the  $\gamma\text{-Al}_2\text{O}_3$ . These TEM results show an adherent 65-nm thick layer of epitaxial  $\gamma\text{-Al}_2\text{O}_3(111)$ . From the electron diffraction results, the crystallographic orientation relationships are determined to  $\gamma\text{-Al}_2\text{O}_3(111)/\text{Ti}_2\text{AlC}(0001)$  (out-of-plane) and  $\gamma\text{-Al}_2\text{O}_3(2\bar{2}0)/\text{Ti}_2\text{AlC}(11\bar{2}0)$  (in-plane).

The temperature of 600 °C is at the border between formation of the  $\gamma$  and  $\alpha$  phases in growth of  $\text{Al}_2\text{O}_3$  with HiPIMS under conditions similar to the present.<sup>18</sup> Furthermore, the in-plane lattice mismatch between  $\gamma(111)$  and  $\text{Ti}_2\text{AlC}(0001)$  is about 7%, considerably less than between  $\text{Ti}_2\text{AlC}(0001)$  and  $\alpha\text{-Al}_2\text{O}_3(0001)$  (10.3%). In conjunction with the relatively low temperature, this epitaxial relation explains the selective formation of  $\gamma$  phase rather than the thermodynamically stable  $\alpha$ .

Vacuum annealing of the  $\gamma\text{-Al}_2\text{O}_3$ -coated  $\text{Ti}_2\text{AlC}(0001)$  thin films was performed for 1 h at 900 °C. The choice of these parameters is motivated by the fact that approximately this temperature is expected to be necessary and sufficient to cause decomposition of  $\text{Ti}_2\text{AlC}$  thin films in vacuum (see discussion below). It is therefore interesting to determine whether decomposition of  $\text{Ti}_2\text{AlC}$  can be prevented or at least delayed because of the presence of a crystalline  $\text{Al}_2\text{O}_3$  layer.

TEM of the annealed samples is shown in Fig. 3. As can be seen, a large fraction of the films has transformed into a twinned TiC, while some  $\text{Ti}_2\text{AlC}$  remains near the substrate. This shows the partial decomposition of the  $\text{Ti}_2\text{AlC}$  by depletion of Al. In general, the release of Al at the temperature of 900 °C is expected in line with what other  $\text{M}_{n+1}\text{AX}_n$  phases show, i.e., the decomposition temperature is related to the chemical potential (or vapor pressure) of the A element with respect to the environment. That is, typical decomposition temperatures for thin-film  $\text{Ti}_3\text{SiC}_2$  is in the vicinity of 1000–1100 °C<sup>12,13</sup> and similar or slightly higher for the Ge-containing MAX phases,<sup>25</sup> while, e.g.,  $\text{Ti}_2\text{SnC}$  or  $\text{Ti}_2\text{InC}$  tend to decompose at lower temperature.<sup>25,26</sup> The presence of a  $\gamma\text{-Al}_2\text{O}_3$  oxide may somewhat retard the decomposition, but not substantially prevent it compared to what is expected for decomposition of unprotected  $\text{Ti}_2\text{AlC}$  thin films.

The surface of the  $\text{Ti}_2\text{AlC}$  films (cf. the SEM images and illustration in Figs. 2, 4, and 6 in ref. 6) exhibits a secondary grain population of tilted (nonbasal-oriented)  $\text{Ti}_2\text{AlC}$  grains, in addition to the

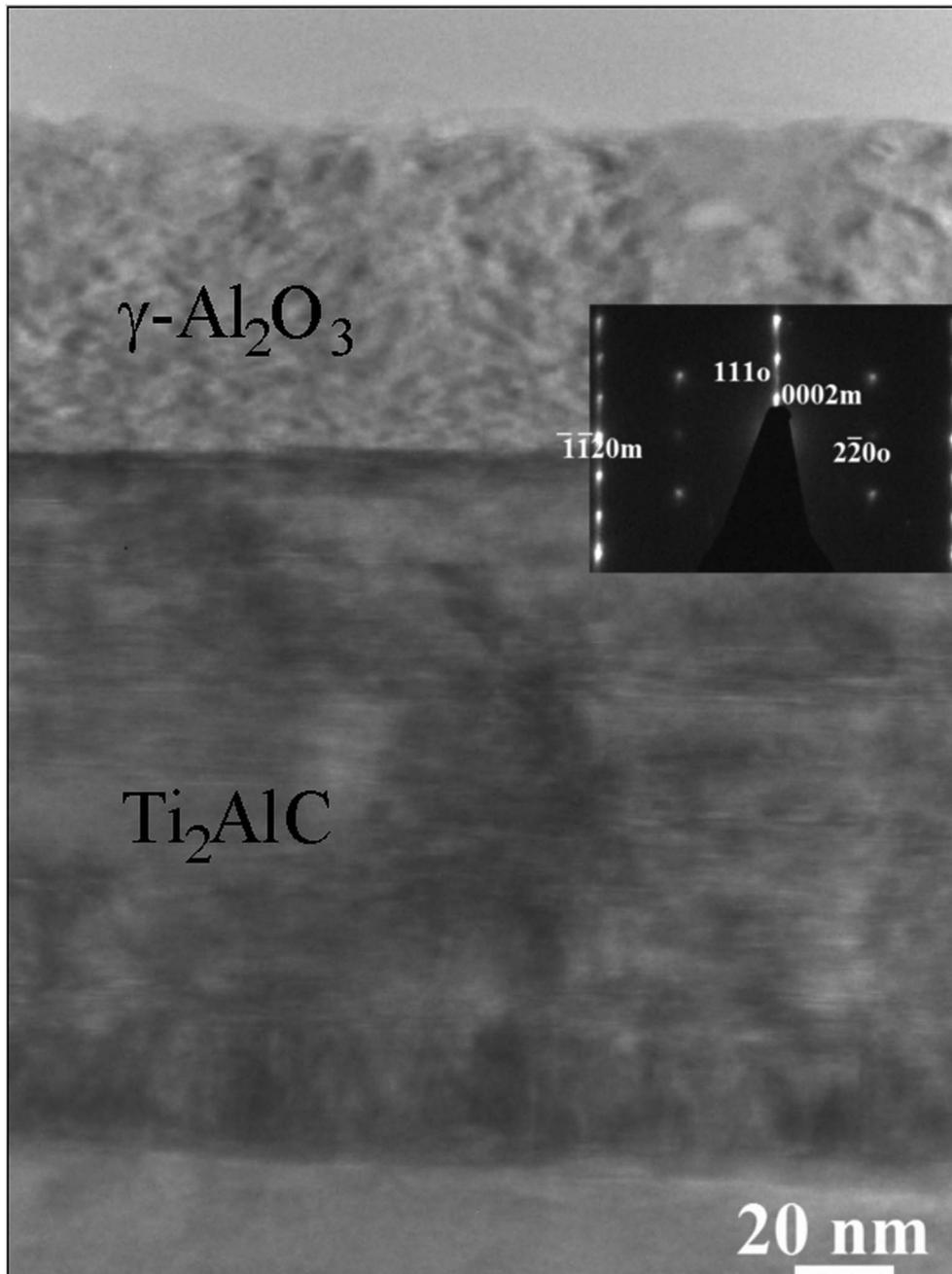


FIG. 1. TEM overview image and electron diffraction pattern of a 65-nm-thick  $\text{Al}_2\text{O}_3$  layer (marked 'o' in diffraction pattern) deposited onto a  $\text{Ti}_2\text{AlC}(0001)$  thin film (marked 'm' in diffraction pattern) on a *c*-axis oriented single-crystal sapphire substrate.

dominant (0001) orientation. This microstructure is explained by and should be viewed in parallel to other studies. In general, the growth of thin film  $M_{n+1}AX_n$  phases is dependent on the substrate temperature, with basal-plane-oriented  $\text{Ti}_2\text{AlC}$  growth obtained at  $\sim 900^\circ\text{C}$ . Reduced temperatures tend to yield additional growth orientations with tilted grains<sup>6,27</sup> and even basal planes perpendicular to the substrate surface, as has been observed for  $\text{Ti}_2\text{AlN}$  and  $\text{Cr}_2\text{GeC}$ ,<sup>28,29</sup> and also for  $\text{Cr}_2\text{AlC}$  onto polycrystalline substrates.<sup>30,31</sup> These growth modes are consequences of the incomplete coverage due to the limited mobility of the adatoms and the higher growth rate of nonbasal grains than parallel

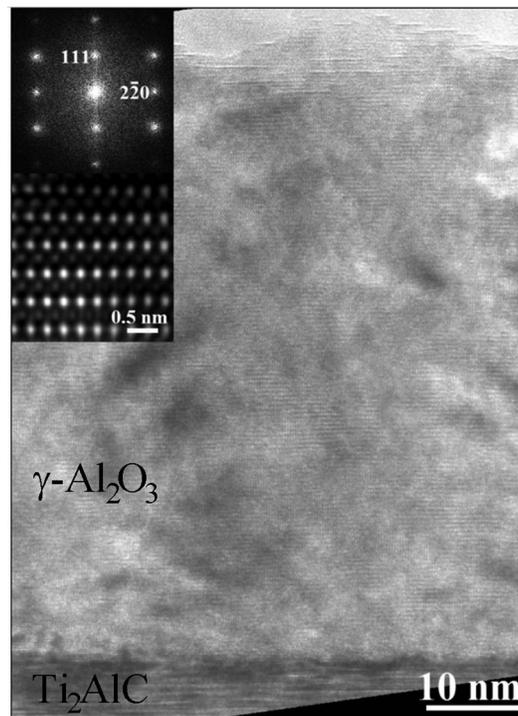


FIG. 2. TEM image of the interface between  $\text{Ti}_2\text{AlC}$  and as-deposited  $\gamma\text{-Al}_2\text{O}_3$ . Insets: (top) electron diffraction and a (bottom) Fourier-filtered lattice-resolved image of the  $\gamma\text{-Al}_2\text{O}_3$ .

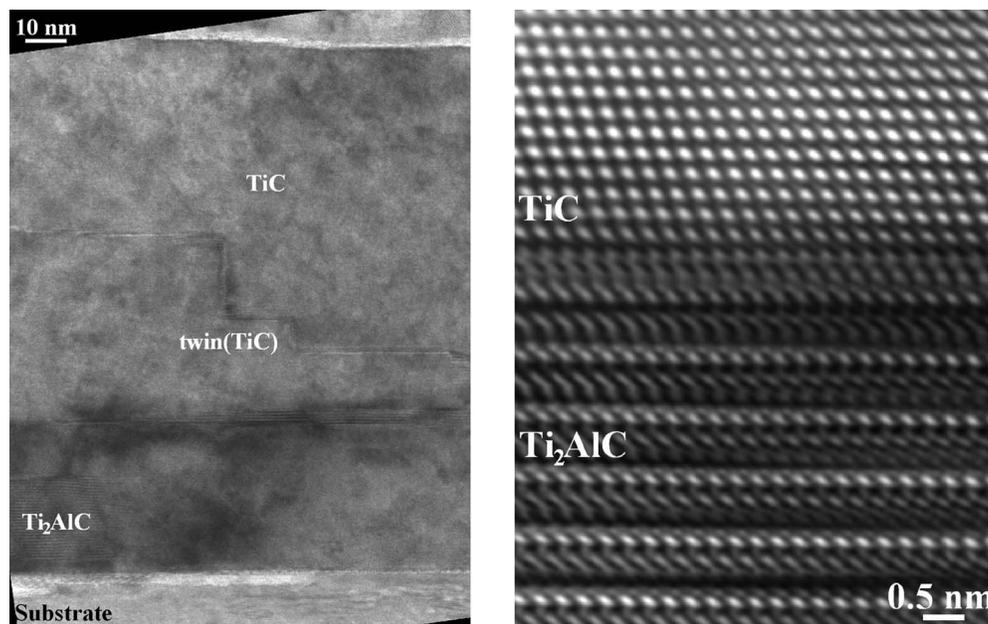


FIG. 3. (left) TEM of annealed  $\gamma\text{-Al}_2\text{O}_3(111)/\text{Ti}_2\text{AlC}(0001)$  showing formation of a twinned structure and partial decomposition of the  $\text{Ti}_2\text{AlC}$ , (right) high-resolution TEM of the  $\text{Ti}_2\text{AlC}/\text{TiC}$  interface.

to the surface. The explanation for the limited to no enhancement in resistance to decomposition is thus likely found in the underlying microstructure of the  $\text{Ti}_2\text{AlC}$  leading to an incomplete or uneven coverage of the alumina coating.

Nevertheless, the present study demonstrates epitaxial growth of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> on Ti<sub>2</sub>AlC(0001) by high-power impulse magnetron sputtering and thus open prospects for growth of crystalline alumina as coatings on Ti<sub>2</sub>AlC or M<sub>n+1</sub>AX<sub>n</sub> phases in general.

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