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Epitaxial growth and electrical-transport properties of Ti$_7$Si$_2$C$_5$ thin films synthesized by reactive sputter-deposition

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Abstract

Epitaxial predominantly phase-pure Ti$_7$Si$_2$C$_5$ thin films were grown onto Al$_2$O$_3$(0001) by reactive magnetron sputtering. The c-axis lattice constant is ~60.2 Å; the Ti$_7$Si$_2$C$_5$ unit cell comprising alternating Ti$_3$SiC$_2$-like and Ti$_4$SiC$_3$-like half-unit-cell stacking repeated three times. Elastic recoil detection analysis showed a few percent of nitrogen in the films from the acetylene gas used. The nitrogen-induced stabilization mechanism for Ti$_7$Si$_2$C$_5$ relative to Ti$_3$SiC$_2$ and Ti$_4$SiC$_3$ is discussed. Electrical-transport measurements showed metallic temperature dependence and a room-temperature resistivity of ~45 $\mu\Omega$cm.
MAX phases are a group comprising ~60 ternary compounds with a general composition of $M_{n+1}AX_n$ ($n=1, 2, or 3$) where $M$ is a transition metal, $A$ is an A-group element, and $X$ is carbon or nitrogen [1,2,3]. Usually, the MAX phases are classified into three groups based on their $n$ values, i.e., “211” for $n = 1$, “312” for $n = 2$, and “413” for $n = 3$. The archetypical $Ti_{n+1}SiC_n$ phases are in existing applications as ohmic contacts to SiC [4,5,6,7] and of potential interest in a range of other applications [2]. They have been synthesized in single crystal form as thin films [2] and very recently $Ti_3SiC_2$ bulk single crystals have been made [8,9]. Further, in the Ti-Si-C system, Palmquist et al. [10] first demonstrated the “intergrown structures” $Ti_3Si_2C_3$ and $Ti_3SiC_3$. These “523” and “725” phases comprise alternating layers of “211” and “312” or “312” and “413”, respectively. The same phases were also demonstrated in the Ti–Ge–C system [11]. Zhou et al. [12] later reported another “523” phase, (V,Cr)$_3$Al$_2$C$_3$. These compounds have only been observed as minority phases in samples consisting primarily of $M_2AC$ and $M_3AC_2$ (for “523” phases) or $M_3AC_2$ and $M_4AC_3$ (for “725” phases). In has even been debated whether it is appropriate to describe them as phases, since they only existed in small quantities and never in macroscopic amounts. Here, we resolve this issue by synthesizing epitaxial virtually single-phase $Ti_7Si_2C_5$ thin films. Our results suggest a nitrogen-induced physical mechanism for the stabilization of this complex phase relative to a simple mixture of $Ti_3SiC_2$ and $Ti_4SiC_3$.

$Ti_7Si_2C_5$ thin films were synthesized in a custom-built ultra-high vacuum magnetron sputtering chamber with an ultimate base pressure of $10^{-7}$ mbar [13]. Films were deposited at a substrate temperature of 850 °C (determined by optical pyrometer
and calibrated with a thermocouple) in a mixture of high-purity argon (99.999%) and industrial-grade acetylene (C₂H₂) gas at a total pressure of 2.7 Pa (20 mTorr). The argon flow was maintained at 40 sccm while the acetylene was varied from 3.5-4.0 sccm. Two 50-mm cathodes positioned directly over a rotating table contained the titanium (99.95%) and silicon (99.999%) targets. A direct current (DC) power source varied from 135-160 W was used for titanium while a radio frequency (RF) power source varied from 400-500 W was used on the silicon, yielding a deposition rate of ~1-1.2 μm/h. The substrate rotation rate was approximately 18 rpm with a substrate-cathode distance of 10 cm. All depositions were performed on (0001)-oriented polished sapphire (Al₂O₃) wafers and were at floating potential. X-ray diffraction (XRD) was performed on a Panalytical Empyrean configured in standard 0-2θ Bragg-Brentano geometry with Cu-Kα radiation. Electron microscopy was performed with a LEO 1530VP scanning electron microscope (SEM) and a FEI Tecnai G2 TF 20 UT field emission gun transmission electron microscopy (TEM) operated at 200 kV acceleration voltage. Cross sectional TEM samples were prepared by mechanical polishing down to a thickness of ~50 μm, and ion milling in a Gatan Precision Ion Polishing System (PIPS) with Ar ions with energy of 5 keV with a final polishing step with 2 keV Ar ions. Sample composition and thickness were measured with a Rigaku ZSX Primus II wavelength dispersive x-ray fluorescence (WDXRF) spectrometer with RhKα radiation. Elemental depth profiles of as-deposited films were obtained from time-of-flight elastic recoil detection analysis (ToF-ERDA) with a 40 MeV ¹²⁷I⁺ ion beam at Uppsala University [14]. The recoil angle was 45° while the incident angle of primary ions and the exit angle of recoils were both set to 67.5° relative to the surface normal. All spectra were analyzed using the CONTES code
[15] to obtain relative atomic concentration profiles from the recoil energy of each element. Electrical transport measurements were carried out on microbridges 400 μm wide and 1600 μm long. The bridges were defined by standard photolithographic techniques followed by a wet etch. The resistivity was measured as a function of temperature $T$ for $2 \text{ K} \leq T \leq 300 \text{ K}$ range with a Quantum Design Physical Properties Measurement System (PPMS) by a four-probe technique. Details can be found elsewhere [16].

Figure 1 shows an X-ray diffractogram of a virtually phase-pure (000 $\bar{\ell}$)-oriented Ti$_7$Si$_2$C$_5$ thin film. The minute peaks not indexed in Fig. 1 originate from a very small amount of Ti$_4$SiC$_3$; no TiC or Ti$_3$SiC$_2$ can be detected. Figure 2 is a high-resolution TEM image showing the hexagonal layered structure with the “725” structure formed by interleaving half-unit-cell layers of “312” and “413”. From the XRD results, the $c$-axis lattice constant is determined to 60.2 Å. Note that this refers to a unit cell with a $c$ axis three times the average of the Ti$_3$SiC$_2$ and Ti$_4$SiC$_3$ unit cells. The description of Ti$_7$Si$_2$C$_5$ as alternating half-unit-cell layers of Ti$_3$SiC$_2$ and Ti$_4$SiC$_3$ repeated twice to form a “725” supercell is a good first approximation but not completely accurate as it would yield a $c$ axis twice the average of Ti$_3$SiC$_2$ and Ti$_4$SiC$_3$, i.e., the sum of the two $c$ axes. Rather, the alternating stacking of even and odd numbers of Ti layers induces a lateral translation of the Si position in the lattice (c.f., Fig. 2), i.e., the Si atoms are not positioned above each other until after three repetitions [2,10]. The indexes of the 000$\ell$ reflections in the θ–2θ diffractogram (Fig. 1) are therefore $\ell=3n$ ($n=1, 2, 3\ldots$).
Figure 3 shows the depth profile of composition as determined by ToF-ERDA. The composition is essentially constant with depth and is Ti:Si:C = 7:2:5 within the error bars of the measurement. However, most notable is the presence of nitrogen in the films. The source of the nitrogen is likely the acetylene, only being industrial grade. Ti-Si-C films (with Ti:Si:C = 7:2:5 composition) deposited from elemental targets of carbon, titanium, and silicon contained less than 0.3 at. % nitrogen as indicated by WDXRF (not shown). These films were not pure Ti$_7$Si$_2$C$_5$, but contained large amounts of Ti$_3$SiC$_2$ and/or Ti$_4$SiC$_3$ (not shown, very similar to films described in, e.g., Ref. 10). In contrast, deposits in acetylene showed 1.4-2.5 at. % nitrogen (confirmed by both ERDA and WDXRF).

Thus, both in the present work and previous work [10], deposition of Ti-Si-C films from elemental targets of carbon, titanium, and silicon (with Ti:Si:C = 7:2:5 composition) yield a Ti$_3$SiC$_2$/Ti$_4$SiC$_3$ phase-mixture with Ti$_7$Si$_2$C$_5$ as a minority phase; while the present reactively sputtered nitrogen-containing films are virtually phase-pure Ti$_7$Si$_2$C$_5$. The $c$-axis lattice parameter of ~60.2 Å is somewhat lower than the value of 60.62 Å suggested by Palmquist et al. [10] (again, referring to three times the average of the pure Ti$_3$SiC$_2$ and Ti$_4$SiC$_3$ unit cells). The effective stabilization of the Ti$_7$Si$_2$C$_5$ phase by the introduction of a few percent of nitrogen in the reactive gas might be explained by N hindering the known stable Ti$_3$SiC$_2$ and Ti$_4$SiC$_3$ from forming. The otherwise expected step-flow mechanism [2,7,10] may be intermittently blocked by N at surface steps (forming a tetrahedrally coordinated Si-N bond). Instead, a self-organizing process would
be operating with TiC<sub>x</sub> slabs terminated by monolayers of segregating Si in a 413+312 repetitive manner corresponding to the set composition. Another possible explanation is that the N incorporation might offset the energy of the competing compounds in favor of the 725 phase. While this possibility can be tested by *ab initio* calculations (cf., e.g., Refs. 17,18), it is less likely as no Ti-Si-N MAX phases exist because of the preference for TiN and Si<sub>3</sub>N<sub>4</sub> phase separation.

Figure 4 shows the electrical resistivity curves in the temperature range 2-300 K of Ti<sub>7</sub>Si<sub>2</sub>C<sub>5</sub> thin films along with Ti<sub>3</sub>SiC<sub>2</sub> and Ti<sub>4</sub>SiC<sub>3</sub> reference samples (the latter two grown from elemental targets of carbon, titanium and silicon). The room-temperature resistivity ρ of Ti<sub>7</sub>Si<sub>2</sub>C<sub>5</sub> of ~45 μΩcm is intermediate between Ti<sub>4</sub>SiC<sub>3</sub> (~67 μΩcm) and Ti<sub>3</sub>SiC<sub>2</sub> (~31 μΩcm). The numbers for Ti<sub>4</sub>SiC<sub>3</sub> and Ti<sub>3</sub>SiC<sub>2</sub> are consistent with but systematically slightly higher than previously reported thin-film values [19]. The residual resistivity ratios (RRR, i.e., ρ(300 K)/ρ(2 K)) are 5.9 (Ti<sub>3</sub>SiC<sub>2</sub>) and 1.9 (Ti<sub>4</sub>SiC<sub>3</sub>) and 2.5 (Ti<sub>7</sub>Si<sub>2</sub>C<sub>5</sub>). Since the residual resistivity (ρ(2 K)) depends on defect and impurity scattering, the RRR is indicative of sample quality and defects. It is therefore somewhat surprising that the RRR of Ti<sub>7</sub>Si<sub>2</sub>C<sub>5</sub> is higher than the Ti<sub>4</sub>SiC<sub>3</sub> sample despite the incorporation of several percent of nitrogen; this fact indicates that the virtually phase-pure Ti<sub>7</sub>Si<sub>2</sub>C<sub>5</sub> is of high crystalline quality. The temperature coefficient of resistivity (TCR) of Ti<sub>7</sub>Si<sub>2</sub>C<sub>5</sub> is ~0.1 μΩcm/K; the same as for Ti<sub>3</sub>SiC<sub>2</sub>. Note also that the TCR for Ti<sub>3</sub>SiC<sub>2</sub> is slightly higher than the literature values of ~0.08 μΩcm/K for bulk polycrystalline samples [20,21], suggesting some degree of anisotropy in electron-phonon coupling (cf., Ref. 22).
Variations in the relative composition of Ti and Si or in the Ar/acetylene ratio (results not shown) resulted in films containing Ti$_7$Si$_2$C$_5$, but with substantial fractions of Ti$_3$SiC$_2$, Ti$_4$SiC$_3$, and binary phases (TiC, Ti$_5$C$_3$). Thus, the process window with respect to reactive gas partial pressure for the synthesis of phase-pure Ti$_7$Si$_2$C$_5$ is relatively narrow, but apparently less sensitive than results for Ti$_2$AlN, which is the only previously reported MAX-phase synthesized by reactive sputtering in Ar/N$_2$ [2]. In contrast, since the MAX-phase carbides can be easily grown by elemental- and compound-target sputter-deposition there has not been much interest in reactive deposition of carbide MAX phases until now. The present results show that it is time to reevaluate this opinion.

In conclusion, phase-pure Ti$_7$Si$_2$C$_5$(0001) films have been fabricated by reactive sputter epitaxy and their electrical properties determined. The method is suitable to make large and complex inorganic crystal structures in a fast and inexpensive fashion. Our proposition of self-assembled nanolaminate crystals by segregation and monolayer precipitation of Si with a fourth element blocking lateral step-flow growth have far-reaching implications concerning the synthesis of compounds with any conceivable stacking order. Other yet more complex structures than the Ti$_7$S$_2$C$_5$ phase can thus be envisioned.

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References

FigureCaptions

**Fig. 1** X-ray diffractogram of Ti$_7$Si$_2$C$_5$ thin films grown on Al$_2$O$_3$(0001). The minute peaks not indexed in the figure originate from a very small amount of the secondary phase Ti$_4$SiC$_3$.

**Fig. 2** High-resolution TEM image of Ti$_7$Si$_2$C$_5$ thin film; tilted bars in the left are guides for the eye indicating the alternating “312” and “413” stacking.

**Fig. 3** ERDA depth profile of a phase-pure Ti$_7$Si$_2$C$_5$ thin film, showing no significant variation in composition with depth and a constant nitrogen content of ~2%.

**Fig. 4** Electrical resistivity of Ti$_7$Si$_2$C$_5$ in the temperature range 2-300 K along with Ti$_3$SiC$_2$ and Ti$_4$SiC$_3$ reference samples.