### Supplementary information for

## $Ti_2Au_2C$ and $Ti_3Au_2C_2$ formed by solid state reaction of Au

# with Ti<sub>2</sub>AlC and Ti<sub>3</sub>AlC<sub>2</sub>

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#### Supplementary section S1. Materials and methods

#### S1.1 Experimental details

Thin film sputter-deposition of Ti<sub>2</sub>AlC and Ti<sub>3</sub>AlC<sub>2</sub> was performed on single-crystal sapphire (0001) substrates, 10×10 mm in size. Prior to the depositions, the substrates were ultrasonically cleaned by acetone and isopropanol, respectively, finalized by nitrogen blow-dry. The deposition system was an ultra-high-vacuum stainless-steel chamber with a base pressure lower than  $1 \times 10^{-7}$  Pa and a total Ar (99.9999 %) pressure of 0.5 Pa during the deposition. Atomic fluxes were supplied by 3 DC-powered magnetrons, one facing the substrate plane (Al=99.999%, 2 inch in diameter) and two tilted by 35 ° off the substrate normal (Ti=99.99%, C=99.999%, 3 inch in diameter). The following applied powers were chosen for the magnetrons for deposition of Ti<sub>2</sub>AlC (Ti<sub>3</sub>AlC<sub>2</sub>): Ti=110 W (92 W), Al=120 W (26 W), and C=120 W (142 W). A TiC<sub>x</sub> seed layer was deposited prior to each of the deposition of Ti<sub>2</sub>AlC (Ti=106 W and C=138 W for 2 min) and Ti<sub>3</sub>AlC<sub>2</sub> (Ti=92 W and C=142 W for 30 sec). The substrate temperature for the growth of Ti<sub>2</sub>AlC (Ti<sub>3</sub>AlC<sub>2</sub>) and the seed layer was 850 °C (775 °C). The deposition time for Ti<sub>2</sub>AlC and Ti<sub>3</sub>AlC<sub>2</sub> were 10 min and 20 min, respectively, resulting in the thickness of ~60 nm. For the deposition of Au capping-layers on top of  $Ti_2AlC$  and  $Ti_3AlC_2$ , (the intercalation-source for Au), the samples were then transferred ex-situ to another ultrahigh-vacuum stainless-steel magnetron-sputtering chamber with the base pressure lower than 10<sup>-7</sup> Pa. Au-deposition was performed at room temperature powered in DC mode (106 W) for a thickness of ~200 nm.

The annealing procedure was performed in a cylindrical ceramic oven equipped with a quartz tube maintaining nitrogen flow (99.99% of purity) to avoid oxidation. The temperature was controlled during the experiments using a thermocouple placed at the sample position. The temperature of the oven was raised with the ramp of 17.6 °C /min to the annealing temperature of 650 °C.

X-ray diffraction (XRD) was performed using a Philips PW 1820 instrument (Cu (K $\alpha$ ),  $\theta$ -2 $\theta$  scan, aligned with the substrate (0001) peak). Scanning electron microscopy (SEM) was performed in a LEO 1550 for surface imaging and energy dispersive X-ray analysis (EDX). Transmission electron microscopy was performed in the Linköping monochromated double-spherical-aberration-corrected FEI Titan<sup>3</sup> 60–300 operated at 300 kV, equipped with the SuperX EDX system. The corresponding cross-sectional samples were first mechanically polished to a thickness of about 60  $\mu$ m, followed by ion-beam milling with Ar<sup>+</sup> in a Gatan precision ion polishing system at 5 keV with a final polishing step at 1 keV of ion energies.

XPS spectra were recorded with a monochromatic Al K $\alpha$  source (hv = 1486.6 eV) in an Axis Ultra DLD instrument from Kratos Analytical (UK). The base pressure during spectra acquisition was better than  $1.5 \times 10^{-7}$  Pa ( $1.1 \times 10^{-9}$  Torr). All spectra were collected at normal emission angle from the  $0.3 \times 0.7$  mm<sup>2</sup> area centered in the middle of the sputter-etched crater following sample sputter-cleaning with 0.5 keV Ar<sup>+</sup> ions incident at an angle of 70° with respect to the surface normal. Spectra deconvolution and quantification were performed using CasaXPS software package.<sup>1</sup> The binding energy (BE) scale was calibrated against the Fermi

level cut-off,<sup>2</sup> using the procedure described in detail elsewhere,<sup>3</sup> which helps to avoid referencing problems resulting from the fact that C 1s BE depends on the type of surface oxides formed during air exposure,<sup>4</sup> and removes ambiguities related to the use of C 1s as the BE reference.<sup>5</sup>

#### S1.2 Computational details

First-principles calculations were based on density functional theory (DFT) and the projector augmented wave method<sup>6,7</sup> as implemented within the Vienna *ab-initio* simulation package (VASP).<sup>8,9,10</sup> Exchange and correlation effects were included within the generalized gradient approximation (GGA) as parameterized by Perdew-Burke-Ernzerhof (PBE).<sup>11</sup> We used a plane-wave energy cut-off of 400 eV and for sampling of the Brillouin zone we used the Monkhorst-Pack scheme.<sup>12</sup> Each considered structure were considered relaxed when forces the relaxation were considered the calculated total energy is converged to within 0.5 meV/atom with respect to k-point sampling. Calculations were performed at zero temperature and pressure and all structures were considered to be relaxed when the forces on each ion converged to below  $10^{-4}$  eV Å<sup>-1</sup>. To determine the dynamical stability of the studied ordered structure, we performed phonon calculations using the small displacement method, with supercell sizes up to 3x3x1 unit cells, along with the code Phonopy.<sup>13</sup>

### Supplementary section S.2 SEM and EDX of Au/Ti<sub>3</sub>AlC<sub>2</sub>/sapphire samples

Au/Ti<sub>3</sub>AlC<sub>2</sub>/sapphire samples were annealed at 650 °C for 10 hours. After the annealing step they were studied using Scanning electron microscopy imaging and energy dispersive x-ray mappings. In contrast to the uniform surface of as-deposited samples prior to the annealing procedure, the annealed samples had distributed clusters on the surface, as shown in Fig. S1, similar to the annealed Au/Ti<sub>2</sub>AlC/sapphire samples. The energy dispersive x-ray mappings of one of such clusters revealed them to contain Al while being deficient in Au. This result indicates out-diffusion of Al from the Ti<sub>3</sub>AlC<sub>2</sub> sublayer.



**Fig. S1.** Scanning electron microscopy image of annealed Au/Ti<sub>3</sub>AlC<sub>2</sub>/sapphire sample and the corresponding energy dispersive x-ray mappings of Al (Kα) and Au (Mα).

Supplementary section S.3 X-ray Photoelectron Spectroscopy

Figure S2 shows intensity-normalized Au 4f and Ti 2p spectra recorded from  $Ti_2Au_2C$ . The XPS measurements were made on the Au layer, followed by further sputtering to reach the  $Ti_2Au_2C$  layer before XPS was performed on  $Ti_2Au_2C$ . These results show a significant change in the valence charge state of Au atoms in the nanolaminate compared to pure Au. The Au 4f peaks are shifted by 0.4 eV towards higher binding energy (BE) with respect to the signal from metallic Au capping layer, while Ti 2p core levels move 0.2 eV to the lower BE than measured for a reference TiC. This indicates a negative charge transfer from Au to Ti atoms.



Figure S2. Intensity-normalized Au 4f and Ti 2p spectra recorded from Ti<sub>2</sub>Au<sub>2</sub>C.

#### Supplementary section S4. Ab initio calculations

Calculations on Ti<sub>2</sub>Au<sub>2</sub>C was performed by assuming different candidate structures which are based on observations from STEM and previously determined structure of Ti<sub>3</sub>Au<sub>2</sub>C<sub>2</sub>. Fig. S2 shows six unit cells that fully or in part denote certain crystallographic requirements of the structure of Ti<sub>2</sub>Au<sub>2</sub>C discussed in the main text. Table S1 lists the parameters of the candidate structures together with the corresponding total energy values, energy comparison between the different candidate structures, and stating the structural similarities to the experimental results. As can be noted, only two of the six lattices fully match the structures obtained by STEM, P3m1 (Z = 2) and P-3m1 (Z = 6), where the one with P-3m1 symmetry having the lower total energy of the two. Fig. S3 illustrates the phonon frequency calculations for each of the assumed candidate structures. The results show that one candidate structure, within the P6<sub>3</sub>/mmc symmetry, possesses negative frequencies, denoting dynamical instability. The candidate structure fulfilling both conditions of zig-zag Ti<sub>2</sub>C stacking and zig-zig Au<sub>2</sub> stacking and is lowest in energy is the one with the space group P-3m1, which is concluded to best description of the crystal structure of Ti<sub>2</sub>Au<sub>2</sub>C.



**Fig. S2**. Ti<sub>2</sub>Au<sub>2</sub>C crystal structure with six different atomic stacking configurations of space group (a)  $Cmc2_1$ , (b) P3m1 with Z = 2, (c) P3m1 with Z = 3, (d) P-3m1 with Z = 6, (e) P-3m1 with Z = 1, and (f)  $P6_3/mmc$ . Detailed crystallographic information are given in Table S1.



**Fig. S3.** Phonon dispersion of Ti<sub>2</sub>Au<sub>2</sub>C for space group (a)  $Cmc2_1$ , (b) P3m1 with Z = 2, (c) P3m1 with Z = 3, (d) P-3m1 with Z = 6, (e) P-3m1 with Z = 1, and (f)  $P6_3/mmc$ . All five structures are depicted in Figure S2.

**Table S1**. Calculated crystallographic information for different stackings of  $Ti_2Au_2C$  using the GGA-PBE exchange-correlation functional. Wyckoff positions are given for each unique crystallographic site. The candidate structure fulfilling both conditions of zig-zag  $Ti_2C$  stacking and zig-zig  $Au_2$  stacking and is lowest in energy is the one with the space group P-3m1, which is concluded to best description of the crystal structure of  $Ti_2Au_2C$ .

Space group	<i>Cmc</i> 2 <sub>1</sub> (#36)	P3m1 (#156)	P3m1 (#156)	<i>P</i> -3 <i>m</i> 1 (#164)	<i>P</i> -3 <i>m</i> 1 (#164)	P6 <sub>3</sub> /mmc (#194)
zig-zag Ti <sub>2</sub> C	yes	yes	no	yes	no	yes
zig-zig Au <sub>2</sub>	no	yes	yes	yes	yes	no
Z (fu/uc)	2	2	3	6	1	2
E (eV/fu)	-33.9612	-33.8798	-33.9829	-33.9626	-33.9396	-33.7394
energy rank	3	5	1	2	4	6
a (Å)	3.08336	3.08562	3.08433	3.08253	3.07906	3.06775
b (Å)	5.34056	3.08562	3.08433	3.08253	3.07906	3.06775
<i>c</i> (Å)	18.1272	18.1221	27.1490	54.3857	9.09815	18.9933
α (°)	90	90	90	90	90	90
β (°)	90	90	90	90	90	90
γ (°)	90	120	120	120	120	120
Ti	4a (0, 0, 0.75271) 4a (0, 1/3, 0.88023)	1a (0, 0, 0.06438) 1a (0, 0, 0.56272) 1b (1/3, 2/3, 0.43686) 1c (2/3, 1/3, -0.06221)	1a (0, 0, 0.37587) 1a (0, 0, 0.62411) 1b (1/3, 2/3, 0.04258) 1b (1/3, 2/3, 0.29071) 1c (2/3, 1/3, -0.04257) 1c (2/3, 1/3, 0.70922)	2c (0, 0, 0.18791) 2c (0, 0, 0.35461) 2d (1/3, 2/3, -0.02128) 2d (1/3, 2/3, 0.14542) 2d (1/3, 2/3, 0.52124) 2d (1/3, 2/3, 0.68795)	2d (1/3, 2/3, 0.87282)	4f (1/3, 2/3, 0.56151)
Au	4a (0, 0, 0) 4a (0, 2/3, 0.13233)	1a (0, 0, 0.81691) 1b (1/3, 2/3, 0.18403) 1c (2/3, 1/3, 0.31589) 1c (2/3, 1/3, 0.68368)	1a (0, 0, 0.21076) 1a (0, 0, 0.78928) 1b (1/3, 2/3, 0.45594) 1b (1/3, 2/3, 0.87738) 1c (2/3, 1/3, 0.12264) 1c (2/3, 1/3, 0.54402)	2c (0, 0, 0.10532) 2c (0, 0, 0.27213) 2d (1/3, 2/3, 0.06120) 2d (1/3, 2/3, 0.22802) 2d (1/3, 2/3, 0.60547) 2d (1/3, 2/3, 0.43865)	2d (1/3, 2/3, 0.36693)	4f (1/3, 2/3, 0.17482)
С	4a (0, 2/3, 0.81638)	1b (1/3, 2/3, 0) 1c (2/3, 1/3, 0.49990)	1a (0, 0, 0) 1b (1/3, 2/3, 0.66667) 1c (2/3, 1/3, 0.33329)	1a (0, 0, 0) 1b (0, 0, 1/2) 2d (1/3, 2/3, 0.33333) 2d (1/3, 2/3, 0.83333)	2a (0, 0, 0)	2a (0, 0, 0)

#### References

- <sup>1</sup> Kratos Analytical Ltd.: library filename: "casaXPS KratosAxis-F1s.lib"
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