Phase formation of nanolaminated Mo₂AuC and Mo-₂(Au_{1-x}Ga_x)(₂)C by a substitutional reaction within Au-capped Mo₂GaC and Mo₂Ga₂C thin films

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Phase formation of nanolaminated Mo_2AuC and $\text{Mo}_2(\text{Au}_{1-x}\text{Ga}_x)_2\text{C}$ by substitutional reaction within Au-capped Mo_2GaC and $\text{Mo}_2\text{Ga}_2\text{C}$ thin films

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Abstract

Au-containing nanolaminated carbides Mo_2AuC and $\text{Mo}_2(\text{Au}_{1-x}\text{Ga}_x)_2\text{C}$ were synthesized by thermally-induced substitutional reaction in Mo_2GaC and $\text{Mo}_2\text{Ga}_2\text{C}$, respectively. The Au substitution for the Ga layers in the structures was observed using cross-sectional high-resolution scanning transmission electron microscopy. Expansion of c lattice parameters was also observed in the Au-containing phases when compared to the original phases. Energy dispersive spectroscopy detected residual Ga in Au-substituted layers of both phases with a peculiar Ga in-plane ordering for Au:Ga = 9:1 ratio along the Au-Ga layers in $\text{Mo}_2(\text{Au}_{1-x}\text{Ga}_x)_2\text{C}$. These results indicate to a generalization of Au substitution reaction for the A elements in MAX phases.

Keywords: nanolaminate, MAX phase, gold, gallium, molybdenum carbide, thin film

1. Introduction

Nanolaminated carbides comprise thermodynamically stable or metastable crystalline phases, in which transition metal carbide layers are periodically interleaved by layers of another element or another carbide layer. Some common chemical formulae of these carbides have been reported, such as $M_{n+1}AC_n$ (so called MAX phases), $(MC)_n(Al_3C_2)$, and $(MC)_n(Al_4C_3)$, where generally M is a group 3 – 7 transition metal, A is mainly a group 13 – 14 element, and n is 1 – 4.¹⁻³ The inherently nanolaminated carbides are electrically and thermally conductive. They are in general mechanically softer, more resistant to thermal shock, and more damage tolerant compared to the binary carbide counterparts due to the unique layered structure.

At elevated temperature, the A element of the nanolaminated carbides can out-diffuse and chemically react with surrounding materials, forming intermetallic phases or oxides. For example, Ti_3SiC_2 has been reported to react with Cu,^{4,5} Al,^{6,7} and molten cryolite,⁸ resulting in Si-containing intermetallic phases and C-deficient TiC_x . Such carbide reactions can drastically alter the mechanical and electrical properties, which is consequently an issue with respect to high temperature applications.

Most recently, we have reported on synthesis of new nanolaminated carbides, Ti_3AuC_2 and $Ti_3Au_2C_2$, by thermally-induced substitution reaction in Au-capped Ti_3SiC_2 thin films, where the Si in the original structure was fully substituted by Au forming structures with single or double Au layers.⁹ The Ti_3AuC_2 phase was shown to be a long-term high-temperature-stable Ohmic electrical contact to the underlying SiC substrate. Moreover, the $Ti_3Au_2C_2$ sample can further react with an additional Ir capping layer, resulting in the formation of another new nanolaminated phase, Ti_3IrC_2 .⁹ These results imply fully reversible diffusion of Au in the A -element layer of the nanolaminated carbides by the substitutional intercalation mechanism. Apart from Ti_3SiC_2 , the

Au-containing nanolaminated phases, $\text{Ti}_{n+1}\text{Au}_2\text{C}_n$ ($n = 1 - 2$), can also be synthesized from $\text{Ti}_{n+1}\text{AlC}_n$ ($n = 1 - 2$) phases by this reaction.¹⁰ Other previous studies have also shown partial substitution of coinage metals, Cu and Ag, for M and A elements when in contact with MAX phases at elevated temperature.^{11,12} In the reaction with Cu, a preferential substitution on the A sites up to 50 at.% was reported.¹¹

So far, all studies regarding nanolaminated phases from noble metal substitution were based on few Ti-based phases, with Si and Al as the A element.⁹⁻¹² To explore the substitutional intercalation mechanism in the MAX phases, experimental results showing whether the reaction is applicable in other combinations of the M and A elements are important. It is further motivated by the fact that, in the MAX phase family, carbide phases with $M = \text{Mo}$ or Mn were experimentally synthesized only with $A = \text{Ga}$. Studies of the phases with $M = \text{Mo}$ are especially inspiring by the interesting properties of molybdenum carbides, e.g., catalytic properties, superconducting, and thermoelectrical properties in its 2D form.¹³⁻¹⁵

Here, we report on two new nanolaminated phases, Mo_2AuC and chemically in-plane ordered $\text{Mo}_2(\text{Au}_{1-x}\text{Ga}_x)_2\text{C}$, formed by substitutional reaction of Au-capped Mo_2GaC and $\text{Mo}_2\text{Ga}_2\text{C}$ thin films. The latter are two carbides with similar crystal structure, only differing by one Ga versus two Ga layers interspersed between the Mo_2C layers.¹⁶ This is the first report on Au atoms substituting for Ga layers in nanolaminated carbides, and, at the same time, showing an in-plane chemical ordering in the Au-Ga layers of $\text{Mo}_2(\text{Au}_{1-x}\text{Ga}_x)_2\text{C}$ phase.

2. Experimental Details

The Mo_2GaC and $\text{Mo}_2\text{Ga}_2\text{C}$ thin film samples, both of ~ 50 nm, were synthesized by direct current magnetron sputtering (DCMS) deposition from 3 elemental targets: Mo (99.95% purity, $\varnothing \approx 7.6$ cm), Ga (99.99999% purity, $\varnothing \approx 5.1$ cm), and C (99.99% purity, $\varnothing \approx 7.6$ cm), onto $\text{MgO}(111)$ substrates. Details about the deposition set-up can be found in Ref. 16 and 17 for Mo_2GaC and $\text{Mo}_2\text{Ga}_2\text{C}$, respectively, and in Ref. 18 for handling Ga sputtering targets. The base pressure of the deposition system was $\sim 10^{-7}$ Pa. with the process pressure was ~ 0.5 Pa of Ar as sputtering gas. During the deposition, the substrates were kept at ~ 590 °C and ~ 560 °C for Mo_2GaC and $\text{Mo}_2\text{Ga}_2\text{C}$, respectively, and rotated at 30 rpm for optimal chemical homogeneity in the films.

The Au capping of the as-grown samples were carried out by DCMS with an elemental Au target (99.99% purity, $\varnothing \approx 5.1$ cm) in another deposition system with a base pressure below 10^{-8} Pa. The Au capping layer is about 200 nm in thickness. The Au target was placed 20 cm above the samples and tilted $\sim 20^\circ$ away from the substrate normal. Right before the sample transfer to the load-lock of the system, the samples were dipped in buffered HF (NH_3F (25 g) + H_2O (50 ml) + HF (10 ml)) for 5 s to remove residual oxides, then thoroughly rinsed with distilled water, and blow-dried in N_2 . Prior to the deposition, the system was filled with ~ 0.24 Pa of Ar sputtering gas. No substrate heating or rotation was applied during the deposition.

The Au-capped samples were thereafter annealed in a horizontal quartz tube, placed in a cylindrical furnace, with a constant nitrogen gas flowing through the tube to avoid oxidation. The temperature was ramped at a rate of ~ 17.6 °C/min. up to 400 °C, where the Au-capped Mo_2GaC and $\text{Mo}_2\text{Ga}_2\text{C}$ samples were annealed for 24 h and 6 h, respectively. For convenience, the Au-capped samples after annealing are hereafter referred to as “annealed samples” in the following text.

Phase composition was analyzed by X-ray diffraction (XRD) patterns acquired by a Philips PW 1820 diffractometer, using Cu K_{α} radiation. Structural and chemical analysis was carried out by high-resolution STEM high angle annular dark field (HRSTEM-HAADF) imaging and STEM-EDX within the Linköping double C_s corrected FEI Titan³ 60-300 microscope operated at 300 kV. HRSTEM-HAADF imaging was carried out using 21.5 mrad probe convergence angle and 0.1 nA beam current. STEM-EDX was acquired using the embedded high sensitivity Super-X EDX detector.

Cross-section samples for STEM investigation were prepared using the traditional “sandwich” and focused ion beam (FIB) approach. The traditional approach includes sample cutting, mounting into a Ti grid, gluing and mechanical polishing from both sides down to ~ 70 μm thickness. Electron transparency of the samples was achieved by Ar^+ ion milling at 5 keV and 5° angle from both sides in the Gatan precision ion polishing system (PIPS). The milling current was reduced to 2 keV at final stages of milling in order to minimize the surface damage. FIB technique employed was on a Carl Zeiss Cross-Beam 1540 EsB system, while the procedure was described elsewhere.¹⁹

3. Results and Discussion

Fig. 1 shows XRD patterns of the as-grown and annealed Mo_2GaC sample. In the as-grown case, diffraction peaks resulting from the $\text{Mo}_2\text{GaC}(000l)$ basal planes are dominant, as marked with dashed lines.¹⁷ Consistent with previous reports, minority phases Mo_3Ga and Mo_3C_2 appear as competitive phases for the employed synthesis conditions.¹⁷ For the annealed sample, all Mo_2GaC peaks originally positioned at $2\theta \sim 13.16^\circ$, 26.85° , 40.72° , and 55.30° are reduced in

intensity, while another series of peaks appears at lower angles, $2\theta \sim 12.48^\circ$, 25.70° , 38.71° , and 52.97° . The new peaks share a least common multiple of $\sim 14.29 \text{ \AA}$, which is comparable with the structural periodicity perpendicular to the basal planes in the here discovered nanolaminated phase, Mo_2AuC , observed in the HRSTEM structural analysis presented latter in next paragraph. Hence, we assign the new peaks to the basal plane diffraction $000l$ of the Mo_2AuC phase with a c lattice parameter of $\sim 14.29 \text{ \AA}$, which expands for $\sim 5.9 \%$ from the c lattice parameter of Mo_2GaC ($\sim 13.50 \text{ \AA}$) determined from the Mo_2GaC $000l$ peaks. Such expansion in the c lattice parameter has also been observed in the case of Ti_3AuC_2 phase, as compared to Ti_3SiC_2 , and can be explained by the replacement of Ga or Si atoms by the larger Au atoms. On the contrary, the competing phases, Mo_3Ga and Mo_3C_2 , have no clear shift in their peak positions, showing less reactive behavior to Au upon annealing compared to Mo_2GaC .

Fig. 1. XRD patterns of as-grown and annealed Mo_2GaC samples (black and red lines, respectively). Peak positions of Mo_2GaC and Mo_2AuC phases are marked with dashed and solid lines, respectively.

Fig. 2(a) and (b) shows HRSTEM-HAADF images acquired along the $[11\bar{2}0]$ zone axis of the Mo_2GaC and Mo_2AuC crystals, respectively. The applied HRSTEM-HAADF imaging conditions promote strong STEM image contrast dependence on atomic number Z . In Mo_2GaC , two adjacent rows of atoms with higher intensity, assigned to Mo atoms in the Mo_2C layers, are interleaved by a single row of Ga atoms with lower intensity. The C atoms in the structure, however, cannot be resolved due to very low mass contrast compared to the metal atoms in the applied imaging mode. In the Mo_2AuC crystal (Fig. 2(b)), on the other hand, the Mo atoms have relatively low Z , and therefore intensity, compared to the Au monolayer in the structure. Both Mo_2GaC and Mo_2AuC have the M_2AX crystal structure typical of the MAX phases.¹

Fig. 2. HRSTEM-HAADF images of (a) Mo_2GaC and (b) Mo_2AuC crystals, acquired along the $[11\bar{2}0]$ axis. Several Mo (blue), Ga (red) and Au (yellow) atoms in their respective structure are highlighted on the left-hand side of the images. (c) EDX spectrum acquired from a Mo_2AuC

crystal. The energy region between 0 - 3 keV is expanded in the upper-left inset. The X-ray emission lines and their relative intensities are referenced from Ref. 20 and 21.

Fig. 2(c) shows an EDX spectrum acquired from the Mo_2AuC crystal, where X-ray emission lines are identified and labelled for Mo, Ga, Au, and other impurities from the substrate (Mg and O) and the specimen holder (Ti and Cu). The highest intensity is obtained from Mo and Au, while very low intensity can still be recorded at the position of Ga K and L lines. EDX quantification analysis shows a low concentration of Ga (< 3 at.% in $(\text{Mo} + \text{Au} + \text{Ga})$) on the A sites. The relative intensity of Au and Ga shows that the A sites of the Mo_2AuC phase are almost completely occupied by Au atoms. The signal from the residual Ga is at a similar level of other impurities, e.g., Ti and Cu. The origin of the Ga signal is therefore inconclusive either coming from the original structure or as a result of TEM sample preparation.

Fig. 3 shows XRD patterns of the Au-capped and annealed $\text{Mo}_2\text{Ga}_2\text{C}$ samples. The positions of the diffraction peaks corresponding to the $(000l)$ basal planes of $\text{Mo}_2\text{Ga}_2\text{C}$ are taken from Ref. 22 and marked with dashed lines. The diffraction peak at $2\theta \approx 40^\circ - 41^\circ$ is likely an overlap between the $\text{Mo}_2\text{Ga}_2\text{C}$ 0008 and the binary competing phases, Mo_3Ga , which appears also in the Mo_2GaC sample, see Fig. 1. The relatively high intensity peak at $2\theta \approx 38^\circ$ is assigned to the Au capping layer on top of the $\text{Mo}_2\text{Ga}_2\text{C}$ thin film.

Fig. 3. XRD patterns of the Au-capped and annealed $\text{Mo}_2\text{Ga}_2\text{C}$ samples (black and red lines, respectively). Peak positions of $\text{Mo}_2\text{Ga}_2\text{C}$ and $\text{Mo}_2(\text{Au}_{1-x}\text{Ga}_x)_2\text{C}$ phases are marked with dashed and solid lines. Additional shoulders from the Mo_2AuC phase are indicated by arrows.

When compared with the results for Mo_2GaC in Fig. 1, the annealed $\text{Mo}_2\text{Ga}_2\text{C}$ sample exhibits a new series of peaks at $2\theta \approx 9.68^\circ$, 19.43° , 29.92° , 38.96° , and 49.32° . These peaks appear at lower angles compared to the original series of $\text{Mo}_2\text{Ga}_2\text{C}$ peaks, which correspond to a larger c lattice-parameter of $\sim 18.29 \text{ \AA}$ than $\text{Mo}_2\text{Ga}_2\text{C}$ ($\sim 18.08 \text{ \AA}$).²² The new series of diffraction peaks is assigned to the $(000l)$ -basal planes of another new nanolaminated phase, $\text{Mo}_2(\text{Au}_{1-x}\text{Ga}_x)_2\text{C}$. The Mo_3Ga peak, which overlaps with the $\text{Mo}_2\text{Ga}_2\text{C}$ 0008 peak, becomes more easily distinguishable due to the lattice expansion with a resulting left-shift of the $\text{Mo}_2(\text{Au}_{1-x}\text{Ga}_x)_2\text{C}$ 0008 peak. The shoulders (indicated by arrows) at $2\theta \approx 13^\circ$ and 26° are assigned to the Mo_2AuC phase (see Fig. 1) that forms from the Mo_2GaC phase, being one of the phases competing with $\text{Mo}_2\text{Ga}_2\text{C}$.¹⁶

Fig. 4(a) and (b) show HRSTEM-HAADF images of the $\text{Mo}_2\text{Ga}_2\text{C}$ and $\text{Mo}_2(\text{Au}_{1-x}\text{Ga}_x)_2\text{C}$ crystals, respectively. Similar to Fig. 2, the contrast in HRSTEM-HAADF images can mainly be attributed

to the heavier Mo (brighter layers) and the lighter Ga (darker layers) from $\text{Mo}_2\text{Ga}_2\text{C}$, and by Mo (darker layers) and Au (brighter layers) from $\text{Mo}_2(\text{Au}_{1-x}\text{Ga}_x)_2\text{C}$. In Fig. 4(a), the $\text{Mo}_2\text{Ga}_2\text{C}$ phase is structurally distinguished from its double Ga layers, stacking directly on top of each other, between the Mo_2C layers, as compared to the Ga monolayers in the Mo_2GaC phase in Fig 2(a). However, the *A* layers in $\text{Mo}_2(\text{Au}_{1-x}\text{Ga}_x)_2\text{C}$ (Fig 4(b), left image) are in a close-packed stacking as opposed to the simple hexagonal stacking in the double *A* layers of $\text{Mo}_2\text{Ga}_2\text{C}$ (Fig. 4(a)) when observed from the same zone axis, $[11\bar{2}0]$. This finding is in good agreement with previously reported close-packed double Au layers in $\text{Ti}_3\text{Au}_2\text{C}_2$.⁹

Fig. 4. HRSTEM-HAADF images of (a) a $\text{Mo}_2\text{Ga}_2\text{C}$ crystal along $[11\bar{2}0]$ axis, and (b) a $\text{Mo}_2(\text{Au}_{1-x}\text{Ga}_x)_2\text{C}$ crystal acquired along its $[11\bar{2}0]$, $[10\bar{1}0]$, and $[2\bar{1}\bar{1}0]$ zone axes. Some metal atoms in the images acquired along $[11\bar{2}0]$ and $[2\bar{1}\bar{1}0]$ zone axes are highlighted for the ease of comparison.

Unlike the Mo_2AuC crystal for which the A layers have a uniform contrast, an in-plane order is observed in the form of one lighter atom followed by nine heavier atoms along the A layer (horizontal direction in Fig. 4) of $\text{Mo}_2(\text{Au}_{1-x}\text{Ga}_x)_2\text{C}$. According to the HRSTEM-HAADF image contrast and the EDX analysis, the darker and brighter features in the A layers can be assigned to Ga and Au, respectively. This is schematically highlighted in the left image of Fig. 4(b) for $(\text{Au}:\text{Ga}) = (9:1)$. In addition, a shorter-range order along the $[0001]$ direction (vertical direction in Fig. 4) can be found between adjacent Au-Ga layers, where the position of the Ga atoms is regularly shifted in the horizontal direction with respect to each other.

Interestingly, an in-plane periodic misfit can also be identified between an Au-Ga layer and its adjacent Mo layer, where each 10 atoms in the Au-Ga layer (9 Au + 1 Ga) pair up with only 9 atoms in the Mo layer. The insertion of extra atoms in the A layers makes the horizontal distance between atoms different from the $\text{Mo}_2\text{Ga}_2\text{C}$ case, see Fig. 4(a). Specifically, the distance between the A atoms becomes smaller when it is away from the Ga atom, making the positions of Au atoms less resolved.

Images along two additional zone axes, $[10\bar{1}0]$ and $[2\bar{1}\bar{1}0]$, of $\text{Mo}_2(\text{Au}_{1-x}\text{Ga}_x)_2\text{C}$ are shown in the middle and the right images of Fig. 4(b), respectively, where no in-plane order of the A layers or misfit between the A layers and the Mo layers is resolved. This indicates that the residual Ga atoms in the A layers form arrays along the $[11\bar{2}0]$ direction, and are overlapped with Au atoms when observed along other zone axes, i.e. it is a one-dimensional in-plane chemical order. This is different from the in-plane-ordered nanolaminated phase, $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$, where two-dimensional in-plane order in both M and A layers can be observed in HR-STEM images acquired along zone axes $[010]$ and $[110]$ with 60° in between.²³

Based on the results from Fig. 4(b), in the chemical formula for the new phase $\text{Mo}_2(\text{Au}_{1-x}\text{Ga}_x)_2\text{C}$ can be estimated to $x \sim 0.1$. Note that the $[11\bar{2}0]$ and the $[2\bar{1}\bar{1}0]$ directions are equivalent in the $\text{Mo}_2\text{Ga}_2\text{C}$ phase, but not in the $\text{Mo}_2(\text{Au}_{1-x}\text{Ga}_x)_2\text{C}$ phase. Although the (9 Au + 1 Ga) ratio is similar to the stoichiometry of reported intermetallic $\text{Au}_{0.875}\text{Ga}_{0.125}$ (α) and Au_7Ga_2 (β) phases,²⁴ the in-plane chemical order of the $\text{Mo}_2(\text{Au}_{1-x}\text{Ga}_x)_2\text{C}$ phase has not been observed in these intermetallic phases. This indicates that the structure in the *A* layers is also affected by the Mo_2C laminates, in order to lower the free energy of the entire system, and should not be considered as a separate metallic phase.

Thus, we propose a mechanism for the substitution, or exchange-intercalation, reaction taking place in between Au atoms in the capping layers and Ga atoms in the Mo_2GaC and $\text{Mo}_2\text{Ga}_2\text{C}$ crystals as following. The reaction can be separated into two steps: (1) Creating vacancies in the *A* layers of a nanolaminated carbide by out-diffusion of the original *A* element, and (2) backfilling the vacancies in the *A* layers of the carbide with a new element, denoted as *A'*. It is initiated by step (1), while formation of a nanolaminated carbide that is different from the original one is accomplished by step (2).

The proposed mechanism is based on the fact that the relatively mobile *A* element in nanolaminated carbides, compared to the *M* element, can be attracted to out-diffuse from the structure in presence of another high affinity element/compound. In our case, a high chemical affinity between Ga and Au is supported by experimental observations on room-temperature interdiffusion at Au/Ga interfaces,^{25,26} on Au gettering by elemental Ga in semiconductors,²⁷ and on fast dissolution of Ga from GaAs into Au contact without melting.^{28,29} On the whole, the reaction of Ga layers in the nanolaminated carbides is likely initiated by attracting Ga atoms into

the Au capping layer. This is also supported by Au-Ga binary phase diagram, where a Ga solubility of ~12 at.% in face-center cubic Au may be the driving force for such attraction.²⁴

In fact for step (1), there has already been several reports on out-diffusing *A* element from a nanolaminated carbide either in oxidizing atmosphere or in contact with another element. For example, crack healing of Ti_2AlC and Cr_2AlC can be introduced primarily by formation of Al_2O_3 while exposing the cracked carbides to oxidizing ambient (e.g. air, water vapor...).^{30,31} It has also been shown that Si from Al-alloy can diffuse into Ti_2AlC crystals during infiltration process, forming either $\text{Ti}_2(\text{Al},\text{Si})\text{C}$ solid solution or $\text{Ti}_2\text{AlC} + \text{Ti}_2\text{SiC}$ two phase regions.³² Another example is that Ti_3SiC_2 can decompose when in contact with powder or molten Al at a temperature above 600 °C, due to out-diffusing Si dissolved in the Al matrix.^{6,7} The mechanisms for this out-diffusion in vacuum or in oxidizing ambient has been reported on Ti_3SiC_2 and Ti_2AlC systems, where the substoichiometric MAX phases eventually collapsed and decomposed into binary carbide, intermetallic phases, and oxides, as applicable.^{33,34}

The mechanism for step (1) is consistent with observation in Ref. 9 and 10, showing the reaction of Au for the Si layers in Ti_3SiC_2 and for the Al layers in $\text{Ti}_{n+1}\text{AlC}_n$ ($n = 1$ and 2), respectively. Diffusion between Au/Si and Au/Al interfaces are both classic cases for studying metallization of semiconductors. Similar to the case of Au/Ga, Au/Si interface can interdiffuse on a scale of tens of nanometers when heating up to ~100 °C in air,³⁵ a temperature much lower than the eutectic temperature of Au-Si system (~363 °C).³⁶ While for Au/Al interface, the interdiffusion takes place upon formation of intermediate phases and ceases when either of the elemental materials is totally reacted. The reason why the Au-Al intermediate phases were not observed in Ref. 10 may be due to a too small amount of Al, and oxidation of the intermediate phase.^{37,38}

Step (2) in the reaction has an interdependent driving force with step (1). That is, to equilibrate the chemical potential of Ga and Au in the nanolaminates and the capping layer by replacing the vacancies in the *A* layers with Au atoms. Since the capping layer in this case can be seen as a semi-infinite Au reservoir, a major part of Ga in the *A* layers is replaced by Au, resulting in a nearly complete reaction.

Moreover, step (2) can also be achieved in the condition where the carbide slabs of the nanolaminated carbides are chemically inert to the additional element *A*'. It has been shown in Ag-on-Ti₂AlC wetting experiments that Ag can react with Ti₂AlC by substituting on both *M* and *A* sites.¹² Upon further increasing the amount of Ag, it will start to nucleate into Ag grains inside the nanolaminated structure, and eventually, lead to decomposition of Ti₂AlC phase. Another example is afore mentioned decomposition of Ti₃SiC₂ when in contact with Al.^{6,7} It shows that, upon Si out-diffusing from Ti₃SiC₂ into Al matrix, the remaining TiC_{*x*} (*x* ~ 0.67) would react with Al, forming TiAl₃ and Al₄C₃ phases. Hence, the inertness of Au to the carbide slabs may be the essential characteristic in order for the Au-containing nanolaminated carbides to form.

4. Conclusions

Mo₂AuC and Mo₂(Au_{1-*x*}Ga_{*x*})₂C were synthesized by substitutional solid state reactions between Au and Mo₂GaC and Mo₂Ga₂C, during annealing at 400 °C. The lattice parameters expand along the *c*-axis upon Ga-Au exchange, from 13.50 Å to 14.29 Å (+5.85 %) for Mo₂AuC and from 18.08 Å to 18.29 Å (+1.16 %) for Mo₂(Au_{1-*x*}Ga_{*x*})₂C. The Ga-Au substitution between the Mo₂C layers is close to complete with only residual Ga in Mo₂AuC. For Mo₂(Au_{1-*x*}Ga_{*x*})₂C, 10 at. %

retained Ga forms in-plane chemical order along $[11\bar{2}0]$ with correlated Au-Ga double layers consisting of repeated one Ga separated by nine Au atoms, where this correlation consists in Ga atoms in adjacent A layers. These results suggest a generalization of Au substituting for A elements in MAX phases.

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References

- ¹ M. W. Barsoum, The $M_{N+1}AX_N$ Phases: A New Class of Solids; Thermodynamically Stable Nanolaminates, *Prog. Solid St. Chem.*, 2000, **28**, 201-281.

- ² P. Eklund, M. Beckers, U. Jansson, H. Högberg, and L. Hultman, The $M_{n+1}AX_n$ phases: Materials science and thin-film processing, *Thin Solid Films*, 2010, **518**, 1851-1878.
- ³ Y. C. Zhou, L. F. He, Z. J. Lin, and J. Y. Wang, Synthesis and structure–property relationships of a new family of layered carbides in Zr-Al(Si)-C and Hf-Al(Si)-C systems, *J. Euro. Ceram. Soc.*, 2013, **33**, 2831-2865.
- ⁴ Y. C. Zhou and W. L. Gu, Chemical reaction and stability of Ti_3SiC_2 in Cu during high-temperature processing of Cu/ Ti_3SiC_2 composites, *Z. Metallkd.*, 2004, **95**, 50-56.
- ⁵ J. R. Lu, Y. Zhou, Y. Zheng, H. Y. Li, and S. B. Li, Interface structure and wetting behaviour of Cu/ Ti_3SiC_2 system, *Adv. Appl. Ceram.*, 2015, **114**, 39-44.
- ⁶ T. El-Raghy, M. W. Barsoum, and M. Sika, Reaction of Al with Ti_3SiC_2 in the 800–1000°C temperature range, *Mater. Sci. Eng.*, 2001, **A298**, 174-178.
- ⁷ W. L. Gu, C. K. Yan, and Y. C. Zhou, Reactions between Al and Ti_3SiC_2 in temperature range of 600–650°C, *Scripta Mater.*, 2003, **49**, 1075-1080.
- ⁸ M. W. Barsoum, T. El-Raghy, L. Farber, M. Amer, R. Christini, and A. Adams, The topotactic transformation of Ti_3SiC_2 into a partially ordered cubic $Ti(C_{0.67}Si_{0.06})$ phase by the diffusion of Si into molten cryolite, *J. Electrochem. Soc.*, 1999, **146**, 3919-3923.
- ⁹ H. Fashandi, M. Dahlgqvist, J. Lu, J. Rosen, L. Hultman, M. Andersson, A. Lloyd Spetz, and P. Eklund, Synthesis of Ti_3AuC_2 , $Ti_3Au_2C_2$ and Ti_3IrC_2 by noble metal substitution reaction in Ti_3SiC_2 for high-temperature-stable Ohmic contacts to SiC, *Nat. Mater.*, 2017, **16**, 814-818.

- ¹⁰ H. Fashandi, C.-C. Lai, M. Dahlqvist, J. Lu, J. Rosen, L. Hultman, G. Greczynski, M. Andersson, A. Lloyd Spetz, and P. Eklund, $\text{Ti}_2\text{Au}_2\text{C}$ and $\text{Ti}_3\text{Au}_2\text{C}_2$ formed by solid state reaction of gold with Ti_2AlC and Ti_3AlC_2 , *Chem. Commun.*, 2017, **53**, 9554-9557.
- ¹¹ M. Nechiche, V. Gauthier-Brunet, V. Mauchamp, A. Joulain, T. Cabioc'h, X. Milhet, P. Chartier, and S. Dubois, Synthesis and characterization of a new $(\text{Ti}_{1-x}\text{Cu}_x)_3(\text{Al,Cu})\text{C}_2$ MAX phase solid solution, *J. Euro. Ceram. Soc.*, 2017, **37**, 459-466.
- ¹² C. Lu, G. Wang, G. Yang, G. Fan, J. Zhang, and X. Liu, Substitution behavior of Ag atoms in the Ti_2AlC ceramic, *J. Am. Ceram. Soc.*, 2017, **100**, 732-738.
- ¹³ W.-F. Chen, C.-H. Wang, K. Sasaki, N. Marinkovic, W. Xu, J. T. Muckerman, Y. Zhu, and R. R. Adzic, Highly active and durable nanostructured molybdenum carbide electrocatalysts for hydrogen production, *Energy Environ. Sci.*, 2013, **6**, 943-951.
- ¹⁴ C. Xu, L. Wang, Z. Liu, L. Chen, J. Guo, N. Kang, X.-L. Ma, H.-M. Cheng, and W. Ren, Large-area high-quality 2D ultrathin Mo_2C superconducting crystals, *Nat. Mater.*, 2015, **14**, 1135-1141.
- ¹⁵ M. Khazaei, M. Arai, T. Sasaki, M. Estili, and Y. Sakka, Two-dimensional molybdenum carbides: potential thermoelectric materials of the MXene family, *Phys. Chem. Chem. Phys.*, 2014, **16**, 7841-7849.
- ¹⁶ C.-C. Lai, R. Meshkian, M. Dahlqvist, J. Lu, L.-Å. Näslund, O. Rivin, E. N. Caspi, O. Ozeri, L. Hultman, P. Eklund, M. W. Barsoum, and J. Rosen, Structural and chemical determination of the new nanolaminated carbide $\text{Mo}_2\text{Ga}_2\text{C}$ from first principles and materials analysis, *Acta*

Mater., 2015, **99**, 157-164.

- ¹⁷ R. Meshkian, A. S. Ingason, M. Dahlqvist, A. Petruhins, U. B. Arnalds, F. Magnus, J. Lu, and J. Rosen, Theoretical stability, thin film synthesis and transport properties of the $\text{Mo}_{n+1}\text{GaC}_n$ MAX phase, *Phys. Status Solidi RRL*, 2015, **9**, 197-201.
- ¹⁸ A. Petruhins, A.S. Ingason, M. Dahlqvist, A. Mockute, M. Junaid, J. Birch, J. Lu, L. Hultman, P.O.Å. Persson, and J. Rosen, Phase stability of $\text{Cr}_{n+1}\text{GaC}_n$ MAX phases from first principles and Cr_2GaC thin-film synthesis using magnetron sputtering from elemental targets, *Phys. Status Solidi RRL*, 2013, **7**, 971-974.
- ¹⁹ R. M. Langford and A. K. Petford-Long, Preparation of transmission electron microscopy cross-section specimens using focused ion beam milling, *J. Vac. Sci. Technol. A*, 2001, **19**, 2186-2193.
- ²⁰ J. A. Bearden, X-ray wavelengths, *Rev. Mod. Phys.*, 1967, **39**, 78-124.
- ²¹ M. O. Krause and J. H. Oliver, Natural widths of atomic K and L levels, $\text{K}\alpha$ X-ray lines and several K L L Auger lines, *J. Phys. Chem. Ref. Data*, 1979, **8**, 329-338.
- ²² C. Hu, C.-C. Lai, Q. Tao, J. Lu, J. Halim, L. Sun, J. Zhang, J. Yang, B. Anasori, J. Wang, Y. Sakka, L. Hultman, P. Eklund, J. Rosen, and M. W. Barsoum, $\text{Mo}_2\text{Ga}_2\text{C}$: A new ternary nanolaminated carbide, *Chem. Commun.*, 2015, **51**, 6560.
- ²³ Q. Tao, M. Dahlqvist, J. Lu, S. Kota, R. Meshkian, J. Halim, J. Palisaitis, L. Hultman, M. W. Barsoum, P. O. Å. Persson, and J. Rosen, Two-dimensional $\text{Mo}_{1.33}\text{C}$ MXene with divacancy ordering prepared from parent 3D laminate with in-plane chemical ordering, *Nat. Commun.*,

2017, DOI: 10.1038/ncomms14949.

- ²⁴ B. Predel and O. Madelung, *Eds.*, Au-Ga (Gold-Gallium). In: Landolt-Börnstein - Group IV Physical Chemistry 5A (Ac-Au - Au-Zr) [Online]. Berlin Heidelberg: Springer-Verlag; 1991. Available from: https://link.springer.com/chapter/10.1007%2F10000866_277. (accessed Apr 10, 2017).
- ²⁵ V. Simic and Z. Marinkovic, Thin film interdiffusion of Au and Ga at room temperature, *Thin Solid Films*, 1976, **34**, 179-183.
- ²⁶ S. Nakahara and E. Kinsbron, Room temperature interdiffusion study of Au/Ga thin film couples, *Thin Solid Films*, 1984, **113**, 15-26.
- ²⁷ N. Momma, H. Taniguchi, M. Ura, and T. Ogawa, Gettering of gold and copper in silicon during gallium diffusion, *J. Electrochem. Soc.*, 1978, **125**, 963-968.
- ²⁸ D. C. Miller, The alloying of gold and gold alloy ohmic contact metallizations with gallium arsenide, *J. Electrochem. Soc.*, 1980, **127**, 467-475.
- ²⁹ V. G. Weizer and N. S. Fatemi, The interaction of gold with gallium arsenide, *J. Appl. Phys.*, 1988, **64**, 4618-4623.
- ³⁰ H. J. Yang, Y. T. Pei, J. C. Rao, J. Th. M. De Hosson, S. B. Li, and G. M. Song, High temperature healing of Ti₂AlC: On the origin of inhomogeneous oxide scale, *Scripta Mater.*, 2011, **65**, 135-138.
- ³¹ L. Shen, D. Eichner, S. van der Zwaag, C. Leyens, and W. G. Sloof, Reducing the erosive wear rate of Cr₂AlC MAX phase ceramic by oxidative healing of local impact damage, *Wear*, 2016,

358-359, 1-6.

- ³² L. Hu, M. O'Neil, V. Erturun, R. Benitez, G. Proust, I. Karaman, and M. Radovic, High-performance metal/carbide composites with far-from-equilibrium compositions and controlled microstructures, *Sci. Reports*, 2016, **6**, 35523.
- ³³ J. Emmerlich, D. Music, P. Eklund, O. Wilhelmsson, U. Jansson, J. M. Schneider, H. Högberg, and L. Hultman, Thermal stability of Ti_3SiC_2 thin films, *Acta Mater.*, 2007, **55**, 1479-1488.
- ³⁴ J. Frodelius, J. Lu, J. Jensen, D. Paul, L. Hultman, and P. Eklund, Phase stability and initial low-temperature oxidation mechanism of Ti_2AlC thin films, *J. Euro. Ceram. Soc.*, 2013, **33**, 375-382.
- ³⁵ A. Hiraki, Low temperature reactions at Si/metal interfaces: What is going on at the interfaces?, *Surf. Sci. Report*, 1984, **3**, 357-412.
- ³⁶ B. Predel and O. Madelung, *Eds.*, Au-Si (Gold-Silicon). In: Landolt-Börnstein - Group IV Physical Chemistry 5A (Ac-Au - Au-Zr) [Online]. Berlin Heidelberg: Springer-Verlag; 1991. Available from: https://link.springer.com/chapter/10.1007%2F10000866_318. (accessed Apr 10, 2017).
- ³⁷ C. Xu, C. D. Breach, T. Sritharan, F. Wulff, and S. G. Mhaisalkar, Oxidation of bulk Au-Al intermetallics, *Thin Solid Films*, 2004, **462-463**, 357-362.
- ³⁸ F. Wulff, C. W. Tok, and C. D. Breach, Oxidation of Au_4Al in gold ballbonds, *Mater. Lett.*, 2007, **61**, 452-456.