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To cite this article: Chung-Chuan Lai, Andrejs Petruhins, Jun Lu, Michael Farle, Lars Hultman, Per Eklund & Johanna Rosen (2017) Thermally induced substitutional reaction of Fe into Mo₂GaC thin films, Materials Research Letters, 5:8, 533-539, DOI: 10.1080/21663831.2017.1343207

To link to this article: <https://doi.org/10.1080/21663831.2017.1343207>



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Published online: 25 Jun 2017.



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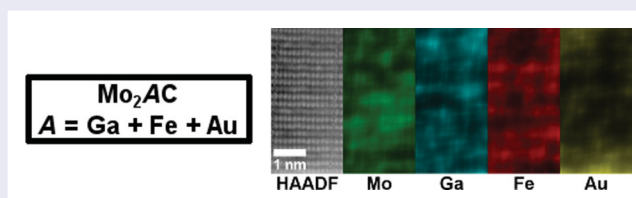
Thermally induced substitutional reaction of Fe into Mo_2GaC thin films

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ABSTRACT

The first Fe-based MAX phase is realized by solid-state substitution reaction of an Fe/Au/ Mo_2GaC thin-film diffusion couple, as determined by X-ray diffraction and scanning transmission electron microscopy. Chemical analysis together with elemental mapping reveals that as much as 50 at.% Fe on the A site can be obtained by thermally induced Au and Fe substitution for Ga atomic layers in Mo_2GaC . One-sixth of the original Ga is also replaced by Au atoms. When annealing Mo_2GaC thin films covered with Fe only, the Mo_2GaC phase remains intact, that is, Au acts as a catalyst for the substitution reaction.



IMPACT STATEMENT

The first direct evidence showing Fe-containing MAX phase, Mo_2AC , with Fe ~ 50 at.% on the A sites is presented, synthesized by thermally induced Fe and Au substitution reaction catalyzed by Au.

ARTICLE HISTORY

Received 3 May 2017

KEYWORDS

MAX phase; nanolaminate; thin film; gold; iron

$M_{n+1}AX_n$ (MAX) phases are a family of nanolaminated transition metal carbides or nitrides ($M_{n+1}X_n$, M = group 3–7 transition metals, X = C or N and n = 1, 2, or 3), where the $M_{n+1}X_n$ laminae are interleaved by A element monolayers typically from groups 13–14 [1–3]. Similar to their binary carbide or nitride counterparts, the MAX phases are chemically inert, and thermally and electrically conductive. However, due to the difference between M –A and M –X bonding, the MAX phases are generally softer but more ductile, and more tolerant to damage and oxidation compared to most ceramics [4,5].

The A layer in the MAX phases is generally more mobile and less chemically inert compared to the adjacent carbide or nitride slabs. Therefore, the A element tends to react with surrounding materials or atmosphere via out-diffusion. For example, Si out-diffuses from Ti_3SiC_2 into molten cryolite [6], Al [7,8], and Cu [9,10], and Al out-diffuses from $\text{Ti}_{n+1}\text{AlC}_n$ (n = 1 and 2) when

exposed to an oxidizing atmosphere [11–13]. The out-diffusion of the A element normally causes collapse and decomposition of the MAX-phase structure, resulting in the formation of porous carbides, intermetallic phases, and transition metal oxides [6,14,15]. It has also been reported on Cu and Ag substitution for both M and A elements in a MAX phase at elevated temperature [16,17], showing the possibility to chemically modify a MAX phase while retaining the nanolaminated structure.

Most recently, we have reported on the synthesis of Au-containing MAX phases, Ti_3AuC_2 and $\text{Ti}_3\text{Au}_2\text{C}_2$, by thermally induced complete replacement of the Si layers in the Ti_3SiC_2 MAX phase by Au [18], indicating a general route for post-synthesis modification of the MAX phases, especially among A layers with high mobility for diffusion. Together with the Au–Fe phase diagram [19] showing that Fe has an increasing solubility with temperature in the face-centered cubic (FCC) Au structure up to ~ 74 at.% at ~ 1446 K, this suggests a possibility

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for Fe incorporation in a MAX phase using substitution reaction.

Inspired by the studies of magnetic properties in the well-defined atomically laminated structure, and consequently potential for, for example, memory storage, there has been a range of studies exploring the development of magnetic MAX phases, and magnetic properties thereof [20]. While most magnetic MAX phases to date are based on $(\text{Cr}, \text{Mn})_2\text{AC}$, where $A = \text{Ge}, \text{Al}, \text{and Ga}$, or $(\text{M}_{0.5}\text{Mn}_{0.5})_{n+1}\text{GaC}_n$, where $M = \text{Mo and V}$ [20], a few attempts have been made on the incorporation of Fe, Ni, and Co into MAX phases. Still, however, there has been no direct evidence of a MAX phase containing Fe, even though formation of such and incorporation of Fe on the M site have been suggested based solely on initial powder mixtures used in MAX phase production [21].

Here, we report an Fe-containing MAX phase, Mo_2AC , where $A = (\text{Ga}, \text{Fe}, \text{Au})$, synthesized by thermally induced substitutional reactions in an Fe/Au-covered Mo_2GaC thin film upon a two-stage annealing process. The structure and composition of the material before and after the reaction were analyzed through X-ray diffractometry (XRD) and scanning transmission electron microscopy (STEM) including energy-dispersive X-ray spectroscopy (STEM-EDX).

Mo_2GaC thin films were deposited on a $\text{MgO}(111)$ substrate by direct current magnetron sputtering (DCMS) from three elemental targets, Mo ($\varnothing \sim 7.6$ cm, 99.95% purity, SCOTECH Ltd.), Ga ($\varnothing \sim 5.1$ cm, 99.99999% purity, 5N Plus UK Ltd.), and C ($\varnothing \sim 7.6$ cm, 99.99% purity, SCOTECH Ltd.), in a deposition system with a base pressure of $\sim 8 \times 10^{-6}$ Pa. Prior to the deposition, Ar was introduced up to a working pressure of ~ 0.64 Pa. A substrate heating of $\sim 590^\circ\text{C}$ was applied during deposition, as well as substrate rotation in order to achieve a homogeneous film composition. More details about the procedures used for materials optimization, and in particular for the synthesis of Mo_2GaC thin films, can be found in [22,23], respectively.

The as-grown Mo_2GaC thin film was sequentially covered with a 100 nm Au layer and a 200 nm Fe layer through deposition from elemental targets (Au, $\varnothing \sim 5.1$ cm, 99.9% purity; Fe, $\varnothing \sim 7.6$ cm, 99.9% purity, SCOTECH Ltd.) by DCMS at room temperature. The Au layer was deposited by a Polaron E5400 coating system for scanning electron microscopy with a base pressure of ~ 10 Pa and an Ar working pressure of ~ 30 Pa, while the Fe layer was deposited in a deposition system with a base pressure below 1×10^{-6} Pa and an Ar working pressure of ~ 0.53 Pa. In order to minimize oxidation of the Fe layer, the sample was immediately transferred into a furnace for subsequent annealing in Ar ambient at atmospheric pressure. According to the Au–Fe phase diagram,

Fe increases its solubility in FCC Au almost linearly from ~ 13 at.% at 600 K up to ~ 74 at.% at 1446 K [19]. Hence, in this work, the Au/Fe-covered sample was initially annealed at 300°C for 12 h to achieve ~ 10 at.% Fe mixing in the Au layer, as that temperature is not high enough for Au to react with the underlying Mo_2GaC phase. Directly afterwards, the sample was annealed at 400°C for another 12 h to initiate the substitution reaction and promote the formation of the Mo_2AC phase.

To confirm the intermixing of the Fe and Au layers at 300°C , two reference samples, one covered with 200 nm Fe on 100 nm Au and one with only 100 nm Au, were deposited on thermal silica, a 500 nm silicon oxide layer produced directly on the surface of silicon wafers by thermally induced oxidation process. These reference samples were subsequently annealed at 300°C for 6 h. Also, to further investigate the role of Au in the substitution reaction, one Mo_2GaC thin-film sample covered only with 200 nm Fe was prepared and annealed at 400°C for 12 h. See Table 1 and Figure 1(a) for the stacking sequences and annealing procedures of all samples.

XRD was performed in a Philips PW 1820 diffractometer, using Cu K_α radiation, to determine the phase composition and the lattice parameters, as well as the solubility of Fe in Au from the reference samples. Structural and chemical analyses were performed using high-resolution STEM for high-angle annular dark field (HRSTEM-HAADF) imaging and STEM-affiliated energy-dispersive X-ray spectroscopy (EDX) with the Linköping double C_s corrected FEI Titan3 60–300 microscope operated at 300 kV. HRSTEM-HAADF imaging was performed using a 21.5 mrad probe convergence angle, while STEM-EDX was recorded with the embedded high-sensitivity Super-X EDX detector.

XRD patterns between $2\theta = 30^\circ$ and 40° of the Au/Fe and Au reference samples (see Table 1) are shown in Figure 1. The well-known Si 002 forbidden reflection at $\sim 33^\circ$ [24] in both patterns is lined up, indicating that the systematic error on the peak position from different scans is negligible and the discussion on peak position is reasonable. The position of the Au 111 peak for the Au/Fe and the Au reference samples is at 38.554° and 38.256° , which correspond to lattice parameters of 4.044 and 4.076 Å, respectively, for the same FCC structure. The peak position and the calculated lattice parameter of the

Table 1. Stacking sequence and annealing procedures of all samples presented in this work.

Sample ID	Stacking	Annealing
Au/Fe Reference	Fe/Au/silica/Si(001)	300°C (6 h)
Au Reference	Au/silica/Si(001)	300°C (6 h)
$\text{Mo}_2\text{GaC} + \text{Au/Fe}$	Fe/Au/ $\text{Mo}_2\text{GaC}/\text{MgO}(111)$	300°C (12 h) + 400°C (12 h)
$\text{Mo}_2\text{GaC} + \text{Fe}$	Fe/ $\text{Mo}_2\text{GaC}/\text{MgO}(111)$	400°C (12 h)

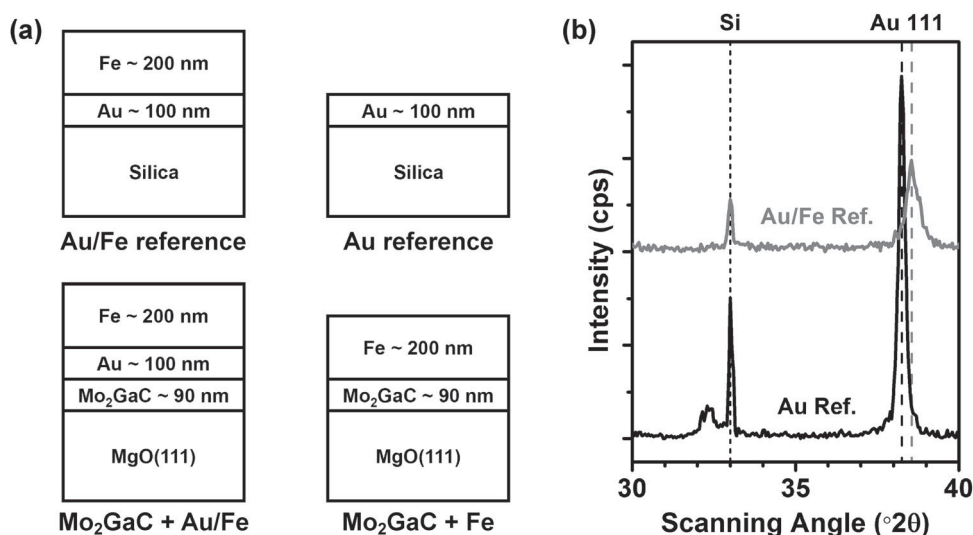


Figure 1. (a) Schematic illustrations of the layer stacking of all samples presented in this work. (b) XRD θ - 2θ patterns between $2\theta = 30^\circ$ and 40° of the Au/Fe and Au reference samples after annealing at 300°C for 6 h.

Au reference sample are very close to tabulated numbers from a powder diffraction file of pure Au (ICDD-PDF 00-004-0784 (Au): $2\theta \sim 38.185^\circ$ or lattice parameter $\sim 4.079 \text{ \AA}$). Furthermore, the change in the lattice parameter between the two reference samples can be interpreted as about 10–15 at.% of Fe dissolved in the FCC Au structure, based on observations in [25]. Notice that the FCC Au–Fe solid solution has a positive deviation from the Vegard law, which yields an underestimated Fe content $< 10 \text{ at.}\%$ [19,25]. The calculated Fe–Au concentration agrees well with the Au–Fe phase diagram, which shows an Fe solubility of about $\sim 13 \text{ at.}\%$ at 600 K (327°C) [19]. Considering the fact that the volume of the Fe layer is twice that of the Au layer, the Au–Fe mixture is unable to accommodate all Fe atoms, leaving undissolved Fe behind in an Fe layer. The undissolved Fe is most likely residing on top of the Au–Fe mixture, with the topmost surface layer being oxidized during annealing, as it has been shown in the literature that Fe tends to diffuse toward an oxidative atmosphere [26]. This is supported, and at the same time explains, the appearance of Fe_2O_3 later on in the XRD patterns.

The results from the reference samples confirm the intermixing between the Au and the Fe layers at 300°C and provide a rough estimate of the composition in the resulting Au–Fe mixture. With this information in mind, we can move on to the experiment of having an Au–Fe mixture with at least 13 at.% of Fe reacting with the underlying Mo₂GaC thin film. We know from a separate experiment that the substitution reaction of Au for the Ga layers in Mo₂GaC requires a temperature above 400°C , where no reaction took place after 12 h of annealing at 300°C . Since the Au–Fe mixture can be prepared

at a lower temperature than the required temperature for the reaction, we can conclude that the experiment on Mo₂GaC + Au/Fe displays a reaction between the Mo₂GaC phase and the Au–Fe mixture.

Figure 2(a) shows the XRD patterns of the as-grown and covered/annealed Mo₂GaC + Au/Fe sample. In the as-grown sample, the peaks at around 13° and 27° are assigned to the major phase, Mo₂GaC, in the film, while the peaks at around 36° and 45° are identified as a competing binary phase, Mo₃Ga, as reported previously [22]. The asymmetric peak at 40° is an overlap of the Mo₂GaC 103 and 006 peaks, together with peaks from the competing phases Mo₃Ga and Mo₂C (ICDD-PDF 00-042-0112 and 00-035-0787, respectively).

Comparing the peak position of the as-grown Mo₂GaC phase to the covered/annealed Mo₂GaC + Au/Fe sample, there is no clear peak shift, that is, no change in lattice parameters in between the two patterns. This is different from the previously reported formation of Ti_3AuC_2 from Au-capped Ti_3SiC_2 , where a 5.3% lattice expansion of the basal planes was observed [18]. The XRD results in Figure 2(a) suggest that either the Mo₂GaC did not react with the Au–Fe mixture, or the substitution of Ga is more complex than in the case of Ti_3AuC_2 , where the lattice expands due to a complete Au replacement for Si, as will be shown below.

Figure 2(b) shows the XRD patterns of the as-grown and the covered/annealed Mo₂GaC + Fe thin film (see Table 1). The XRD pattern for the as-grown sample is similar to the one in Figure 2(a), except that the Mo₂C peak at around 38° is much more intense. This is possibly due to fluctuations in the sputter yield of the liquid Ga target, where a lower Ga flux to the substrate

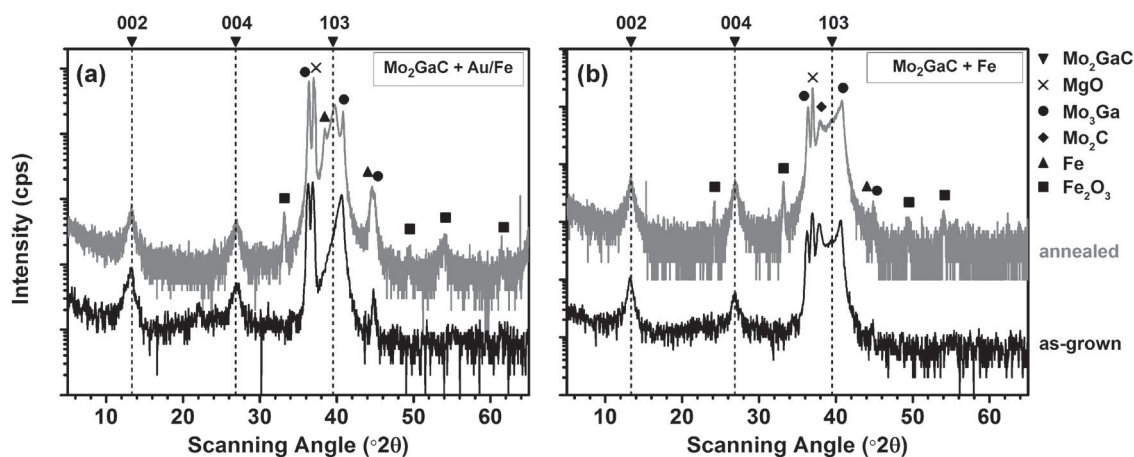


Figure 2. XRD patterns of the as-grown (bottom) and the capped/annealed (top) (a) $\text{Mo}_2\text{GaC} + \text{Au/Fe}$ sample and (b) $\text{Mo}_2\text{GaC} + \text{Fe}$ sample. The positions of the Mo_2GaC diffraction peaks are indexed with vertical dashed lines.

can promote non-Ga-containing secondary phases, for example Mo_2C . Similar to the $\text{Mo}_2\text{GaC} + \text{Au/Fe}$ sample in Figure 2(a), no drastic change can be observed by comparing the as-grown and the covered/annealed $\text{Mo}_2\text{GaC} + \text{Fe}$ sample, besides the appearance of Fe_2O_3 .

Figure 3(a) shows the STEM-HAADF images of the Mo_2AC phase ($A = \text{Ga, Fe, Au}$) from the annealed $\text{Mo}_2\text{GaC} + \text{Au/Fe}$ sample, acquired along the $[11\bar{2}0]$ and $[10\bar{1}0]$ zone axes of the crystal. Along the vertical direction of both images, it can be observed that two adjacent layers of brighter spots (the M elements) are interleaved by one layer of less resolved, dimmer spots (the A elements). Carbon is typically not visible because of its low contrast compared to the heavier M and A atoms. Except for the relative intensity between different elements, the presented images are comparable with STEM images of other M_2AX phases, especially the characteristic zig-zag stacking of the $M_{n+1}X_n$ slabs along $[11\bar{2}0]$ zone axes (see Figure 3 in [27]). The A layers of the Mo_2AC phase in Figure 3 are less resolved in the in-plane direction compared to the M layers, which is consistent with the recently reported Ti_3AuC_2 phase, where the Au atoms in the A layers are also blurred [18]. This may be due to the weakened M – A interlayer bonding after the substitution of the A elements, allowing more movement of the new A elements around an equilibrium position. According to previous reports, the A element has a much higher atomic motion with respect to the M and the X elements in MAX phases due to weaker bonding of the A element [28,29]. In addition, both experimental and theoretical results indicate an anisotropic atomic displacement of the A element, which has a higher amplitude along the basal plane than along the $[0001]$ direction [28].

The STEM-EDX analysis on single-phase regions of Mo_2AC from the annealed $\text{Mo}_2\text{GaC} + \text{Au/Fe}$ sample

shows a relative atomic composition of ($\text{Mo} : \text{Ga} : \text{Fe} : \text{Au}$) $\sim (67 \pm 3 : 11 \pm 1 : 17 \pm 2 : 5 \pm 1)$ at.%, based on calculated average and standard error from five quantification results. The ($M : A$) ratio consequently equals $(67 : 33) = (2 : 1)$, which is consistent with the composition of Mo_2AC , where $A = (\text{Ga, Fe, Au})$. It can, therefore, be assumed that the A layers are occupied by a mixture of Ga, Fe, and Au, while the M layers are occupied by Mo only. This is supported by STEM-EDX elemental mapping (see Figure 3(b)) indicating the primary position of the different elements in the structure. It is shown that the Mo layers do not line up with the layers of Ga, Fe, or Au in their respective panels. That is, the Fe and Au atoms in the Mo_2AC phase are most likely localized in the A layers (original Ga sites), while the Mo layers remain intact as in the original Mo_2GaC phase. Notably, the formation of the Mo_2AC phase with $A = (\text{Ga, Fe, Au})$ is homogeneous throughout the 90 nm Mo_2GaC thin film in the growth direction.

Figure 3(c) shows a HAADF-STEM image of an annealed $\text{Mo}_2\text{GaC} + \text{Fe}$ sample acquired along the $[10\bar{1}0]$ zone axis, together with respective STEM-EDX elemental mapping from the same region. Compared to the Mo_2AC in Figure 3(a), there is more contrast between the brighter Mo layers and the darker Ga layers, with no Au substitution for Ga. An intergrown layer of Mo_2C can be observed at the bottom of the image, which is consistent with the XRD analysis in Figure 2(b), where the Mo_2C 002 diffraction peak at $2\theta \sim 38^\circ$ is much more intense in this sample. EDX quantification in a single-phase Mo_2GaC region shows a relative atomic composition of ($\text{Mo} : \text{Ga}$) $\sim (67 : 33)$ at.% with an Fe content below 1 at.%, consistent with the initial Mo_2GaC stoichiometry. Hence, the EDX results indicate that no Fe enters the Mo_2GaC phase upon annealing.

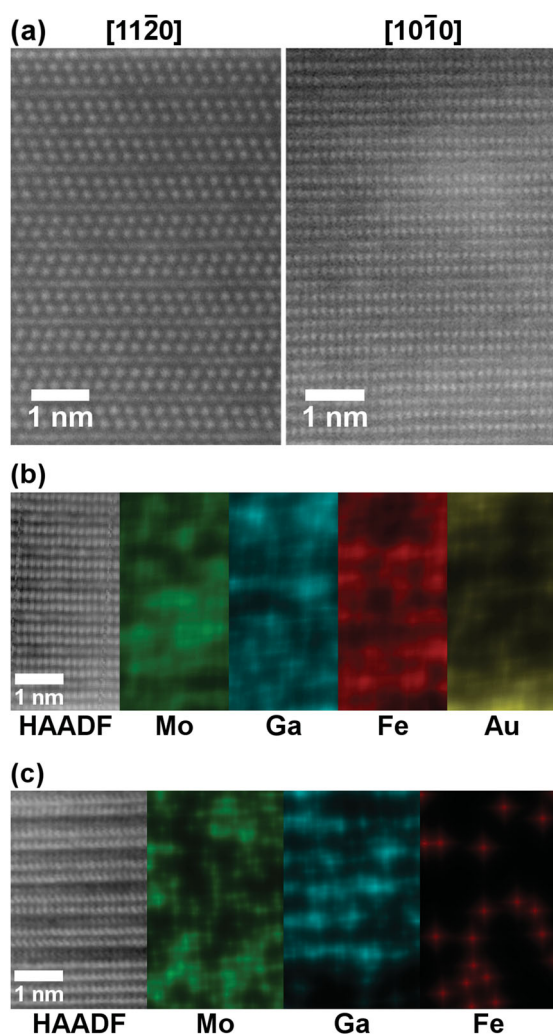


Figure 3. (a) STEM-HAADF images acquired from a Mo_2AC crystal, $A = (\text{Ga}, \text{Fe}, \text{Au})$, along the $[11\bar{2}0]$ and $[10\bar{1}0]$ zone axes and (b) STEM-EDX elemental mapping acquired along the $[10\bar{1}0]$ zone axis of a Mo_2AC crystal from the annealed $\text{Mo}_2\text{GaC} + \text{Au/Fe}$ sample. (c) STEM-EDX elemental mapping acquired along the $[10\bar{1}0]$ zone axis of a Mo_2GaC crystal intergrown with Mo_2C in the annealed $\text{Mo}_2\text{GaC} + \text{Fe}$ sample.

From the presented results, we can conclude that a complex substitution reaction has taken place in the annealed $\text{Mo}_2\text{GaC} + \text{Au/Fe}$ sample, in which about two-thirds of the Ga atoms in the original A layers of the Mo_2GaC phase are replaced by Fe and Au atoms. The relative atomic ratio of $(\text{Ga} : \text{Fe} : \text{Au}) \sim (2 : 3 : 1)$ in the A layer of Mo_2AC with $A = (\text{Ga}, \text{Fe}, \text{Au})$ shows a much higher Fe-to-Au composition than the composition of the Au-Fe mixture, that is, ~ 13 at.% of Fe, from the reference samples. In addition, the low occupancy ($\sim 1/6$) of Au in the A layer is fundamentally different from the previously discovered Au-containing MAX phase Ti_3AuC_2 , where the Si atoms are fully replaced by Au atoms [18]. This is consistent with the XRD analysis, where no peak

shift can be observed, as shown in Figure 2(a) and (b). The lack of expansion in the lattice parameter of the Mo_2AC phase from the Mo_2GaC phase can be explained by a smaller difference in the atomic radius of Fe and Ga, compared to the difference in the atomic radius of Au and Ga. This can be compared to the Ti_3AuC_2 phase, where replacement of the original Si atoms by the larger Au atoms gives a significant increase ($+5.3\%$) in the lattice parameter [18].

Together with the annealed $\text{Mo}_2\text{GaC} + \text{Fe}$ sample, where the Mo_2GaC phase remains intact and shows no indication of the Ga being substituted, it is clear that Au has an important role for catalyzing the reaction of Fe, while being a less competitive substituent than Fe. Formation of the MAX phases assisted by an additional element has been reported in, for example, the synthesis of Ti_3SnC_2 , which is difficult to form in bulk without the addition of Fe [30,31]. Other examples can be found in the MAX phase synthesis with transition metal hydrides as a starting material [32–34].

The reason why the Fe content of Mo_2AC can significantly exceed the Au content in the A layers may be found in the Au-Fe phase diagram. Presumably, the Fe atoms in the Au-Fe mixture may hinder the diffusion of Au atoms away from the mixture in order to keep the thermodynamic equilibrium concentration at a given condition, that is, $(\text{Au} : \text{Fe}) \sim (87 : 13)$ at.% in the FCC structure, as shown in the Au-Fe phase diagram [19]. This means that when Ga out-diffuses from the Mo_2GaC crystal, Fe from the Au-Fe mixture can diffuse into the vacancy in Mo_2GaC more easily as the Fe content in the mixture can be supplied and maintained by the excess Fe layer on the surface. In this way, it is realistic to have a higher relative atomic concentration of $(\text{Fe} : \text{Au})$ in the Mo_2AC crystal with $A = (\text{Ga}, \text{Fe}, \text{Au})$ than in the Au-Fe mixture directly on top. A more detailed explanation on the concentration of $(\text{Ga} : \text{Fe} : \text{Au}) \sim (2 : 3 : 1)$ in the A layers of the Mo_2AC crystal requires the Fe-Ga-Au ternary phase diagram, which has not yet been assessed and proposed in the literature.

Finally, we note that Fe incorporation in a MAX phase has been a quest in the field of magnetic MAX phases in the past decade. Our discovery of a Mo_2AC phase with ~ 50 at.% Fe on the A site cannot be overemphasized, and it opens a venue for exploration of resulting magnetic characteristics. However, further materials optimization is required before assessing the magnetic properties, for example, removal of Fe-containing oxides and intermetallic phases.

In conclusion, we have discovered an Fe-containing MAX phase, Mo_2AC with ~ 50 at.% Fe on the A site, synthesized by a thermally induced substitutional reaction in an Au/Fe-covered Mo_2GaC thin film. In the A layers

of the retained nanolaminated structure, chemical analysis shows a relative atomic composition of (Ga:Fe:Au) $\sim$ (2:3:1), while no clear structural change can be observed as compared with the original Mo_2GaC phase. In contrast, the substitution reaction does not occur in another annealed Mo_2GaC thin film covered with only Fe, implying an essential role of Au in the substitution reaction of Ga for Fe + Au.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

J.R. and P.E. acknowledge support from the Swedish Foundation for Strategic Research (Stiftelsen för Strategisk Forskning, SSF) through the Synergy Grant FUNCASE. J.R., P.E., and L.H. also acknowledge support from the Knut and Alice Wallenberg (KAW) Foundation for a Scholar Grant, a Fellowship Grant, Project funding [KAW 2015.0043], and for support to the Linköping Ultra Electron Microscopy Laboratory. The Swedish Research Council (Vetenskapsrådet, VR) is gratefully acknowledged through projects 621-2012-4425, 642-2013-8020, and 2013-4018, and we also thank the Swedish Government Strategic Research Area (SFO) [Grant No. 2009-00971] in Materials Science on Advanced Functional Material (MatLiU AFM).

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