Thin film synthesis and characterization of a chemically ordered magnetic nanolaminate (V,Mn)₃GaC₂

Q. Tao, R. Salikhov, A. Mockute, J. Lu, M. Farle, U. Wiedwald, and J. Rosen

Citation: APL Mater. 4, 086109 (2016); doi: 10.1063/1.4961502
View online: http://dx.doi.org/10.1063/1.4961502
View Table of Contents: http://scitation.aip.org/content/aip/journal/aplmater/4/8?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
A magnetic atomic laminate from thin film synthesis: (Mo0.5Mn0.5)2GaC
APL Mater. 3, 076102 (2015); 10.1063/1.4926611

Above room-temperature ferromagnetism of Mn delta-doped GaN nanorods

Effect of carbon tailoring on magnetic properties of Mn3GaC

MnP films and MnP nanocrystals embedded in GaP epilayers grown on GaP(001): Magnetic properties and local bonding structure
J. Appl. Phys. 109, 113910 (2011); 10.1063/1.3580270

Microstructural and magnetic properties of (La0.7Sr0.3MnO3)0.7:(Mn3O4)0.3 nanocomposite thin films
J. Appl. Phys. 109, 054302 (2011); 10.1063/1.3552594
Thin film synthesis and characterization of a chemically ordered magnetic nanolaminate (V,Mn)$_3$GaC$_2$

Q. Tao, R. Salikhov, A. Mockute, J. Lu, M. Farle, U. Wiedwald, and J. Rosen

1Thin Film Physics, Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden
2Faculty of Physics and Center for Nanointegration (CENIDE), University Duisburg-Essen, 47057 Duisburg, Germany
3Center for Functionalized Magnetic Materials (FunMagMa), Immanuel Kant Baltic Federal University (IKBFU), Kaliningrad, Russia

(Received 16 June 2016; accepted 10 August 2016; published online 19 August 2016)

We report on synthesis and characterization of a new magnetic nanolaminate (V,Mn)$_3$GaC$_2$, which is the first magnetic MAX phase of a 312 stoichiometry. Atomically resolved energy dispersive X-ray mapping of epitaxial thin films reveals a tendency of alternate chemical ordering between V and Mn, with atomic layers composed of primarily one element only. Magnetometry measurements reveal a ferromagnetic response between 50 K and 300 K, with indication of a magnetic ordering temperature well above room temperature.© 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

$\text{M}_n\text{A}_1\text{X}_n$ (MAX) phases, for which $M$ is an early transition metal, $A$ is an A-group element, and $X$ is C or N ($n = 1$-$3$), are a family of inherently nanolaminated compounds combining both ceramic and metallic characteristics with extreme damage tolerance. Like ceramics, these materials have a high decomposition temperature while being resistant to oxidation and thermal shock, and similar to metals they are good electric and thermal conductors. Besides ternary $\text{M}_n\text{A}_1\text{X}_n$ compounds, stable quaternary alloy phases have been reported with isostructural solid solutions obtained in M, A, and/or X sites.

Since 2013 systematic theoretical and experimental investigations have resulted in the discovery of the new class of magnetic MAX phases, including the quaternary (Cr,Mn)$_2$AC ($A = \text{Al, Ge, Ga}$) and the ternary Mn$_2$GaC compounds, the latter containing Mn as the exclusive M-element. Along that effort, other combinations of transition metals in quaternary systems, such as (Mo,Mn)$_2$GaC, are being explored. Observations include structural changes linked to the magnetic anisotropy and spin-orbit effects, and a rich magnetic phase diagram which can be manipulated through temperature and magnetic field. For Mn$_2$GaC, first-principles calculations show that all theoretically identified lowest energy collinear spin configurations have ferromagnetic (FM) ordering within a Mn–C–Mn (M–X–M) trilayer. However, the calculated energies of antiferromagnetic (AFM) and FM spin alignments in Mn–Ga–Mn chains are close to degenerate, suggesting a strong dependence of the magnetic configuration on the temperature and external magnetic field. The FM long-range order in a basal (M–X–M) plane has been proven experimentally for the (Cr$_{0.3}$Mn$_{0.7}$)$_2$GaC system. Furthermore, an AFM configuration, consistent with suggested FM ordering within the Mn–C–Mn trilayer, has been confirmed recently for Mn$_2$GaC using neutron diffraction.

Until recently, all studied quaternary magnetic MAX phases were confined to the 211 stoichiometry ($n = 1$), with a random mixing of the M elements on the M site in the MAX phase.
structure. Facilitating chemically ordered configurations of the M elements can, however, promote specific magnetic characteristics and could potentially allow insight into magnetism of low dimensional systems. Unlike random mixing in 211 stoichiometry, the tendency for self-ordering of the M elements into distinct atomic layers in MAX phase alloys with 312 (n = 2) and 413 (n = 3) stoichiometry has been systematically investigated from first principles calculations and experimentally discovered in \((\text{Cr}_{2/3}\text{Ti}_{1/3})\text{AlC}_2\), \((\text{Mo}_{2/3}\text{Ti}_{1/3})\text{AlC}_2\), \((\text{Cr}_{0.5}\text{V}_{0.5})\text{AlC}_2\) systems.

In this letter, we report the experimental realization of \((\text{V,Mn})_3\text{GaC}_2\), which is the first magnetic MAX phase alloy of a 312 stoichiometry as well as with chemical ordering of the M elements, in the form of alternating V and Mn atomic layers.

Thin films synthesis was performed by ultrahigh vacuum DC magnetron sputtering from three targets in confocal configuration: elemental 2 in. Ga (99.9999% purity) and 3 in. C (99.99% purity) as well as compound 3 in. V/Mn (50/50 at. %). The depositions were carried out for 10 min in power controlled mode with 10, 185, and 55 W on Ga, C, and V/Mn targets, respectively, at a base pressure of \(7.4 \times 10^{-8}\) mbar and at a growth temperature of 600 °C. Process optimization was performed in line with Ref. 16. Ar was introduced as the sputtering gas at a partial pressure of 4.0 \(\times 10^{-3}\) mbar. MgO(111) substrates were used, cleaned in acetone, methanol, and isopropanol ultrasonic baths for 10 min each, and held for 25 min at the growth temperature in order to remove surface contaminants and ensure a homogeneous temperature distribution.

X-ray diffraction (XRD) was performed using a Panalytical Empyrian MRD equipped with a line focus Cu Kα source (\(\lambda = 1.54\) Å) and a hybrid mirror optics on the incident beam side for 0–20 measurements. Figure 1 shows the XRD pattern of a 25 nm film on a MgO(111) substrate. Apart from two MgO peaks, the major peaks can be assigned to 004, 008, and 0016 of a 312 MAX phase. In order to probe non-basal atomic planes, scans with a tilted sample stage were performed. For example, the 101 peak could be accessed by tilting the sample stage to \(\chi = 82.69°\), which is the angle between (101) and (002) atomic planes, calculated assuming a 312 MAX phase structure and using a \(c\) lattice parameter extracted from a regular 0–20 measurement. Insets in Fig. 1 show scans of 101 and 104 peaks obtained by setting \(\chi\) to 82.69° and 60.09°, respectively. The 312 MAX phase structure was further confirmed by scans of additional non-basal peaks (102, 105, and 107) detected

![FIG. 1. XRD 0–20 scan of a 25 nm (V,Mn)_3GaC_2 film on a MgO(111) substrate. The insets show the scans of the non-basal 101 and 104 peaks obtained by tilting the sample stage.](image_url)
at corresponding expected \( \chi \) values (not shown here). The lattice parameters determined from XRD scans are \( a = 2.925 \) Å and \( c = 17.452 \) Å. The small bump around 50° marked as (*) is likely related to another stacking sequence, e.g., 523, which can also be found locally in transmission electron microscopy (TEM) micrographs.

A cross-sectional sample for TEM analysis was prepared by conventional mechanical methods followed by low-angle ion milling (5 kV at 5°) with a final fine polishing step at low acceleration voltage (1 kV at 5°). The doubly Cs corrected Linköping Titan\(^{6}\) 60-300 was used for high resolution STEM imaging and HRSTEM-EDX (energy-dispersive X-ray spectroscopy) mapping. The STEM images were recorded by the high-angle annular dark-field (HAADF) detector with a resolution of 70 pm. The same electron probe was used for the STEM-EDX mapping, employing all four Super-X detectors.

Figure 2(a) shows a STEM image from a cross section of the thin film. Most of the stacking sequences in the regions investigated are consistent with a 312 structure, i.e., transition metal carbide \( M_3C_2 \) layers separated by a single Ga layer. In some regions, however, stacking faults are also present, as shown in the figure, which likely account for the broadening of the XRD peaks. Fig. 2(b) shows the distribution of V and Mn from EDX mapping, for which the relative composition of V:Mn is approximately 2:1. Fig. 2(c) shows a higher magnification STEM image, clearly displaying the 312 structure. The overall V:Mn:Ga atomic ratio from TEM-EDX is 46:24:30, with an estimated error bar of ±5%, i.e., the composition is consistent with a 312 MAX phase alloy. It can be seen clearly from Fig. 2(b) that Mn and V tend to separate from each other to form ordered alternating layers of V and Mn. It should be noted that this ordering is not equivalent to the out-of-plane chemical ordering found in previous 312 MAX phases like \( (Cr_{2/3}Ti_{1/3})_3AlC_2 \).\(^{13}\) In \( (Cr_{2/3}Ti_{1/3})_3AlC_2 \), Cr and Ti share the same \( M_3C_2 \) layers, while our material can be viewed as alternating V-rich \( M_3C_2 \) layers and Mn-rich \( M_3C_2 \) layers. It should be stressed that the chemical order is not random phase separation, instead it is controlled alternation with change in M-element upon crossing a Ga layer. Furthermore, pure \( Mn_2GaC \) and \( V_2GaC \) have similar \( a \) lattice parameters, \( a = 2.90 \) Å and 2.93 Å, respectively,\(^{5,17}\) which supports a stabilized chemically ordered alloy.

Magnetic hysteresis loops were measured by SQUID magnetometry in external fields \( \mu_0H = \pm 4.5 \) T and variable temperatures in a Quantum Design MPMS XL system. The measured signal is strongly governed by the large diamagnetic contribution of the MgO substrate having a strictly linear response with the field. At an external field of \( \mu_0H = 1 \) T, for example, the diamagnetic signal from the substrate is up to two orders of magnitude larger as compared to the ferromagnetic response of the film. This leads to a small signal-to-noise ratio after the diamagnetic slope has

![FIG. 2. (a) STEM image of a region including various atomic stacking sequences of metal carbide separated by Ga layer(s). (b) Corresponding lattice resolved EDX mapping including V and Mn, showing a clear V and Mn separation. (c) A higher magnification STEM image. Bright lines correspond to Ga layers.](image-url)
The results of the magnetic characterization are shown in Fig. 3. At all studied temperatures (Fig. 3(a)), open hysteresis loops with coercive fields ($H_C$) around 35 mT and almost independent of temperature in the range 100-300 K are observed. The saturation magnetization is reached at about 1 T and only slightly decreases with increasing temperature. The magnetization shows an “S-shape” behavior with a reduced remanence similar to other magnetic MAX phases reported earlier.\textsuperscript{3,6} This indicates a non-collinear spin configuration in small external fields which most probably is the result of competing ferromagnetic (FM) and antiferromagnetic (AFM) interactions between ferromagnetic M-X-M networks separated by the A element and the Zeeman energy in the applied magnetic field favoring FM alignment.\textsuperscript{3,6,8} The nonzero remanent magnetization $M_R$ is evident and the ratio of $M_R/M_S$, where $M_S$ denotes the saturation magnetization, is about 0.23 at $T = 100$ K. Both the non-vanishing $M_R$ and the coercive field $H_C$ confirm the existence of ferromagnetic long range order. The fact that both, $M_R$ and $H_C$, do not show a noticeable temperature dependence (inset of Fig. 3(a)) suggests a high magnetic ordering temperature, far above ambient. The temperature dependent magnetization only decreases by 26% in the interval 100-350 K, suggesting an ordering temperature above 400 K (not shown). The saturation magnetic moment per $M$ atom is determined to be $0.036 \pm 0.004 \mu_B$ at $T = 100$ K. Fig. 3(b) shows the comparison of hysteresis loops measured in in-plane and out-of-plane geometry at $T = 300$ K. The higher $M_R$ and $H_C$ indicate the easy axis of magnetization parallel to the film plane.

The importance of the current study is not only the synthesis of a new atomically laminated magnetic material, but also as proof-of concept for ordering of magnetic/non-magnetic elements in these layered materials. It has previously been suggested that magnetic MAX phases, (Cr$_{0.5}$Mn$_{0.5}$)$_2$GaC in particular, can be considered as naturally formed quasi-2D ferromagnets.\textsuperscript{9} This

---

**FIG. 3.** (a) Hysteresis loops of a 25 nm thick sample at different temperatures. Inset shows the enlarged view at low magnetic field. (b) In-plane and out-of-plane hysteresis loops at 300 K. Inset shows the enlarged view at low magnetic field.
is most likely here accentuated through the substantial increase of spacing between magnetic Mn layers in our (V,Mn)$_3$GaC$_2$ and may result in a further enhancement of the 2D nature.

In conclusion, we have synthesized a new nano-laminated material, (V,Mn)$_3$GaC$_2$, which is the first evidence of a magnetic MAX phase of a 312 stoichiometry, and with lattice parameters of $a = 2.925$ Å and $c = 17.452$ Å. The structure is confirmed by high resolution STEM, also revealing a chemically layer-wise ordered distribution of V/Mn by atomic scale EDX mapping. Viewed as a quasi-2D ferromagnet, this material shows a ferromagnetic response between 50 K and 300 K, with indications of a record high ordering temperature well above room temperature.

J.R. acknowledges funding from the Swedish Research Council (VR) under Grant Nos. 621-2012-4425 and 642-2013-8020, from the Knut and Alice Wallenberg (KAW) Foundation, and from the Swedish Foundation for Strategic Research (SSF) through the synergy grant FUNCASE. R.S. acknowledges DFG for Grant No. SA 3095/2-1.