Graphene-like titanium carbides and nitrides $Ti_{n+1}C_n$, $Ti_{n+1}N_n$ (n = 1, 2, and 3) from de-intercalated MAX phases: First-principles probing of their structural, electronic properties and relative stability

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ABSTRACT

Very recently [32], an elegant exfoliation approach was proposed to prepare a new family of 2D-like transition metal carbides, when selective etching of aluminum layers from some MAX phases yielded 2D materials Ti_2C, Ti_3C_2. Moreover, according to the newest data [47,48], more complex 2D carbides (TiNbC) or carbonitrides (Ti_3CN_x) can be prepared.

Here, employing first-principle band structure calculations, we have examined systematically the trends in structural, electronic properties and relative stability of a representative group of 2D (graphene-like, GL) materials: titanium carbides and nitrides $Ti_{n+1}C_n$, $Ti_{n+1}N_n$ (n = 1, 2, and 3). The peculiarities of atomic relaxation effects for GL $Ti_{n+1}C_n$ and GL $Ti_{n+1}N_n$ were established and discussed in terms of so-called distortion indexes of basic polyhedrons. Our analysis of stability of GL $Ti_{n+1}C_n$ and GL $Ti_{n+1}N_n$ (in terms of cohesive energies and formation energies) has shown relative stabilization of these GL systems with the growth of their thickness (i.e. with the growth of index n). The most interesting feature of the electronic structure for GL $Ti_{n+1}C_n$ and GL $Ti_{n+1}N_n$ is a considerable growth of the density of near-Fermi states which becomes 2.5 to 4.5 times higher than for the parent MAX phases. The origin of this effect was explained by redistribution of Ti $3d$ states from broken Ti–Al bonds into delocalized Ti–Ti metallic-like bonding states placed in the window around the Fermi level. We also found that for "ideal" atomic-clean free-standing GL $Ti_{n+1}X_n$ magnetization is likely to take place, when the ground state is AFM, with ferromagnetic ordering of the spin moments on Ti1 atoms within each external Ti sheet, and these opposite external titanium sheets of GL are coupled antiferromagnetically, whereas the internal Ti sheets remain non-magnetic. The possibility to design in future experiments a rich variety of new GL materials with variable electronic and magnetic properties (semiconductors, non-magnetic and magnetic metals) by modulating the type and degree of GL termination by various adatoms or molecules was proposed.

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1. Introduction

Graphene, a two-dimensional (2D) mono-atomic-thick sheet of sp^2 hybridized carbon, exhibits a unique combination of structural, mechanical, electronic, thermal, and possibly magnetic properties [1–7] and is viewed today as a very promising material for various applications in a vast range of nanotechnologies, reviews [8–14]. But "graphene is not the end of the road" [15]; and a lot of related 2D crystals of other elements or compounds are now in focus of current researches.

Generally speaking, two main groups of such 2D systems can be noted: so-called graphene-based (GB) and graphene-like (GL)

materials. The first group includes such new materials as graphane, fluorographene, graphene oxides, and many other related 2D systems which can be produced by functionalization of graphene.

The most famous examples of graphene-like materials (free-standing carbon-free 2D crystals) are single-atom-thick BN (so-called "white graphene") or more complex single-layer-thick MoS_2 or WS_2 [16–18].

Undoubtedly, the most obvious candidates for search of GL materials are layered compounds (like graphite) which possess a sharply anisotropic system of inter-atomic bonding including strong bonds inside each layer versus very weak van der Waals-type bonding between the adjacent layers. Therefore, for such systems the same techniques (mechanical exfoliation (micro-mechanical cleavage), various chemical approaches), which were developed for production of graphene [8–14], can be successfully used to obtain their 2D graphene-like forms [16–18].

On the other hand, the existence of GL forms of isotropic crystals with a 3D-like system of directional inter-atomic bonds seems much more problematic.

Transition metal (M) monocarbides (MC) and mononitrides (MN) with a cubic structure ($B1$ type) belong to such materials with a 3D system of strong directional bonds. These metallic-like phases with outstanding physical properties (enhanced hardness, high melting points, chemical stability, high corrosion resistance, etc.) are widely used in the industry as cutting tools and have potential applications as materials for coating of magnetic sheets, high power energy industry, for optoelectronics, etc. [19–22]. Although a set of nano-sized carbides and nitrides (such as nanocrystallites [23], hollow polyhedrons [24], monolithic nanorods [25,26], so-called metallocarbohedrenes [27], etc.) have been synthesized (review [28]) and some other nanoforms (for example, nanotubes [29–31]) have been predicted theoretically, no data on graphene-like forms of transition metal carbides and nitrides were available until recently as far as we know.

In 2011, a fascinating idea [32] was proposed to prepare graphene-like carbides not from their 3D parent phases ($B1$-MC), but from so-called ternary MAX phases (known also as nanolaminates [33]), which include various 2D-like layers of transition metal carbides (or nitrides) as building blocks.

A set of MAX phases (with the general formula $M_{n+1}AX_n$, where $n = 1, 2,$ or 3) with different stoichiometry is known: 211 ($n = 1$), 312 ($n = 2$), and 413 ($n = 3$) systems. Here, M are transition d metals from groups III–VI; X are C or N, and A are Cd, Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, As or S [33–39]. Some experimental and theoretical evidences are also given for the existence of higher MAX phases: 514 ($n = 4$) [40], 615 ($n = 5$) [41], and 716 ($n = 6$) [42]. Note that in recent years the MAX phases have attracted tremendous attention as materials with remarkable mechanical properties, fully reversible plasticity, exceptional shock resistance, damage tolerance, negligible thermopower, high thermal conductivity, and some others, which are very attractive for various industrial applications [33–39].

The $M_{n+1}AX_n$ phases can be described as intergrowth structures consisting of hexagonal blocks [$M_{n+1}X_n$] and planar A atomic sheets with a characteristic "*zigzag*" stacking along z axis in the sequence ...$/[M_{n+1}X_n]/A/[M_{n+1}X_n]/A/...$ In turn, carbide (nitride) blocks [$M_{n+1}X_n$] have a $B1$-type structure similar to that of MX binary carbides (nitrides), wherein C(N) atoms are located in an octahedral M-atom coordination {M_6X}. The details of the interfacial structure and crystallographic relations between $B1$-type and MAX phases were discussed in Ref. [43]. For M_2AX phases, the carbide (nitride) blocks contain three atomic sheets M–X–M, whereas for M_3AX_2 and M_4AX_3 – five (M1–X–M2–X–M1) and seven (M1–X1–M2–X2–M2–X1–M1) atomic sheets, respectively, with two types of non-equivalent M and X atoms, Fig. 1. As a result, the system of inter-atomic interactions in MAX phases is very anisotropic with strong directional M–X bonds inside blocks [$M_{n+1}X_n$] and relatively weak bonds between A atoms and between A atomic sheets and blocks [$M_{n+1}X_n$] [33–38], thus A atoms in MAX phases are the most reactive [32].

For these reasons, using Ti_3AlC_2 as an example, efforts were undertaken to extract the most weakly bonded Al from this MAX phase [32]. As a result, a new 2D material with the nominal composition Ti_3C_2 (which the authors [32] termed as "MXene" – to denote the loss of the A element and to point out the similarity between this material and graphene) was successfully prepared by treatment of Ti_3AlC_2 powders for 2 h in HF and by further sonication of the product of reaction $Ti_3AlC_2 + 3HF = AlF_3 + 3/2H_2 + Ti_3C_2$ for exfoliation of nano-blocks Ti_3C_2.

These preliminary results [32] open very interesting prospects – at least, in four main directions. Firstly, as about 70 MAX phases have been experimentally synthesized by now [36,38] and also
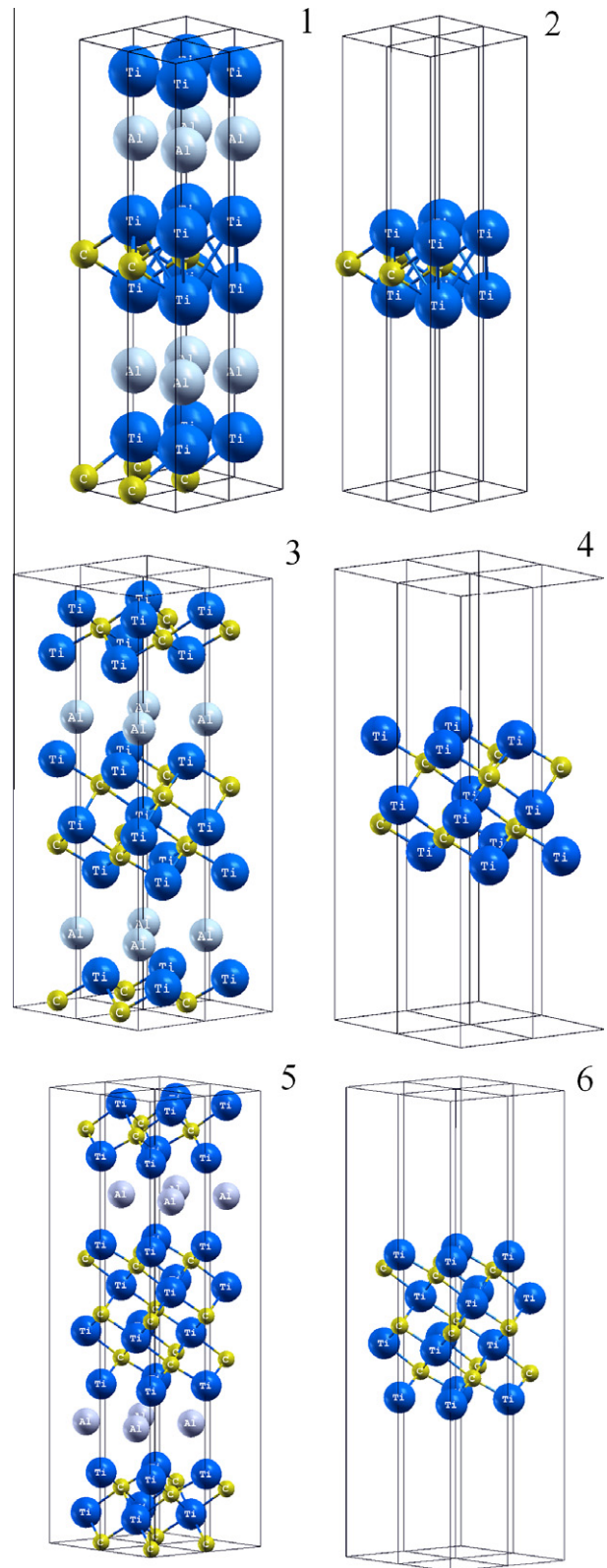

Fig. 1. Fragments of atomic structures of examined MAX phases $Ti_{n+1}AlC_n$ (1,3,5) and GL $Ti_{n+1}C_n$ (2,4,6).

some related phases were predicted theoretically (see for example Refs. [44–46]), we have a rich choice of potential "precursors" for search of new families of GL carbides and nitrides of Sc, Ti, V, Cr, Zr, Nb, Mo, Hf, and Ta with unexpected physical properties and novel functionalities. Secondly, the majority of $B1$-like carbides