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Oxygen incorporation in Ti$_2$AlC: Tuning of anisotropic conductivity

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The substitution of oxygen for carbon in Ti$_2$AlC $M_{(n+1)}AX_n$ (MAX) phase, forming Ti$_2$AlC$_{1-x}$O$_x$, has recently been reported. In this paper we simulate the effect of oxygen incorporation on mechanical and electronic properties using *ab initio* calculations. While the mechanical properties are not sensitive to the change in composition, the electronic properties can be tuned by varying the oxygen concentration. As the concentration increases, the conduction changes from in plane, typical of MAX phases, to conduction also in the c-direction. The conduction along c passes from insulating to n-type and then finally to p-type. These findings reveal an anisotropic semiconducting material. © *2010 American Institute of Physics.* [doi:10.1063/1.3472280]

The $M_{(n+1)}AX_n$ (MAX) phases form a family of nanolaminate ternary nitrides or carbides (X), involving early transition metal (M) and an A-group elements (A).[1] These compounds are attracting an increasing attention due to their unique combination of ceramic and metallic properties,[2] such as high stiffness, oxidation resistance, machinability, and high damage tolerance. Hence, MAX phases are promising candidates for, in selection, high temperature structural applications, protective coatings, electrical contacts, and low friction surfaces.

Based on *ab initio* electronic structure calculations, the static conductivity in MAX phases is predicted to be dependent on crystal orientation.[3] The band structure shows metallic behavior in the basal plane, with numerous bands crossing the Fermi level, while no bands cross the Fermi level in c-direction (Γ-A), as shown in Fig. 1. This conduction anisotropy has not yet been measured experimentally. Bulk MAX phase samples are typically polycrystalline materials with small randomly oriented grains. The single crystals that would be needed for anisotropic measurements have been prepared as thin films, with a film growth direction parallel to the c-direction. However, resistivity measurements have so far been performed in the basal plane only. Measurements of the dielectric function in the photon energy range 2 to 100 eV have been performed for Ti$_2$AlC and Ti$_2$AlN, which confirm the presence of conductivity anisotropy at high frequencies.[4]

Over the past few years, pulsed cathodic arc has been demonstrated as a method for MAX phase synthesis.[5] Evidence has been presented for substantial oxygen incorporation in the arc deposited Ti$_2$AlC MAX phase, while retaining the MAX phase crystal structure.[6] The results indicated that the O impurities occupy the C lattice sites, bound to Ti, and hence, a MAX phase with X=C+O was identified. The existence of this phase has now been confirmed experimentally[7] and its stability verified theoretically.[8,9] Due to the recent finding of this phase, there are currently no reports on its physical properties. Using *ab initio* calculations, we have investigated the effect of oxygen incorporation on the elastic and electronic properties.

Ab initio calculations based on density functional theory (DFT) were performed using the Perdew and Wang (PW91) generalized gradient approximation,[10] using a plane wave cutoff of 500 eV and a Γ-centered grid of $7 \times 7 \times 5$ k-points, as implemented in the VASP software.[11] $M_{(n+1)}AX_n$ phases crystallize in a hexagonal structure ($P6_3/mmc$ space group), which can be described as a nanolaminate with layers of binary nitride or carbide (MX) interleaved with a single layer of A elements. For the present study, a $2 \times 2 \times 1$ supercell of Ti$_2$AlC was created, and one, two, and four O atoms were inserted in the C atomic positions, in all possible nonequivalent configurations. This corresponds to 3.125, 6.25, and 12.5 at. % O. It was concluded that for both 6.25 and 12.5 at. % O, the lowest energy configurations are those with O distributed between the two C layers. Pure Ti$_2$AlC and supercell configurations of O in positions [(0,0,0)], [(0,0,0), (0.5,0.5,0.5)], and [(0,0,0), (0.5,0.5,0), (0,0,0.5), (0.5,0.5,0.5)] were chosen for further analysis, however, test calculations on other configurations showed no significantly different results. The five elastic constants characterizing a hexagonal material were calculated using the stress method[12] based on approximations proposed by Fast *et al.*[13] These constants, in turn, were used to calculate the bulk-, shear- and Young's modulus (B, G, and E, respectively), for further details, see Ref. 12. Analysis of electronic properties was performed through calculations of band structure, partial- and total density of states (DOS), and band character. Charge density was evaluated using Bader analysis.[14]
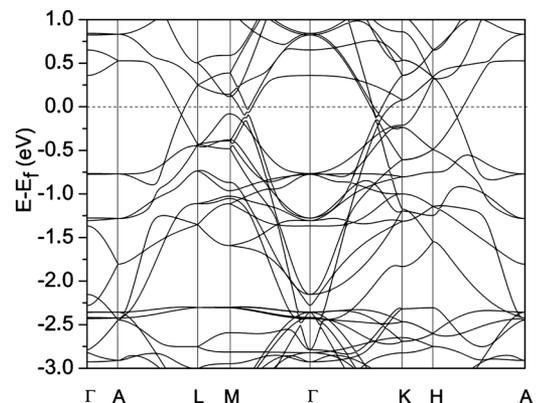

FIG. 1. Band structure of Ti$_2$AlC.

TABLE I. Values of the five principal elastic constants, bulk modulus (B), shear modulus (G), and Young's modulus (E), in GPa, upon oxygen incorporation (0–12.5 at. %).

O_{conc}	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	B	G	E
0	305	60	60	275	110	139	116	271
3.125	287	62	67	270	114	137	111	263
6.25	280	51	83	263	119	140	111	263
12.5	286	63	88	270	122	147	111	266

The five principal elastic constants are presented in Table I. It is evident that introduction of oxygen in pure Ti_2AlC results in a clear trend and a significant change for C_{13} and C_{44} only, both increasing with increasing oxygen concentration. For calculated B, G, and E, maximum deviation from the reference value (at 0 at. % O) is 5.7, 4.2, and 3.3 %, respectively, and we therefore suggest only a minor change in mechanical properties of the MAX phase upon O incorporation.

Results from our calculations of the electronic properties of pure Ti_2AlC are consistent with the literature, see Ref. 4. Figure 1 shows in-plane conduction and insulating behavior in the c-direction, the latter is evident because the Fermi level is situated in a band gap of 1.73 eV. It is well known that DFT in the generalized gradient approximation underestimates band gaps in semiconductors and insulators.[15] We therefore do not expect that our calculated band gaps are accurate, rather we limit our study to exploring trends with oxygenation. The difficulty arises because DFT is least rigorous for the unoccupied states of a system. However, accumulated experience shows that DFT produces the correct relative sizes of energy gaps across modifications of a structure obtained by doping.[16] When oxygen is introduced, in plane electronic properties remain metallic, based on a Fermi level that continues to cross several bands. Figure 2 shows that conduction in the c-direction (Γ-A direction in reciprocal space) is more sensitive to the incorporation of oxygen. From the Γ-A band structure, it is evident that *the material goes from insulating (a), to n-type (c) and then p-type (d) conduction with increasing oxygen content*. Also, even
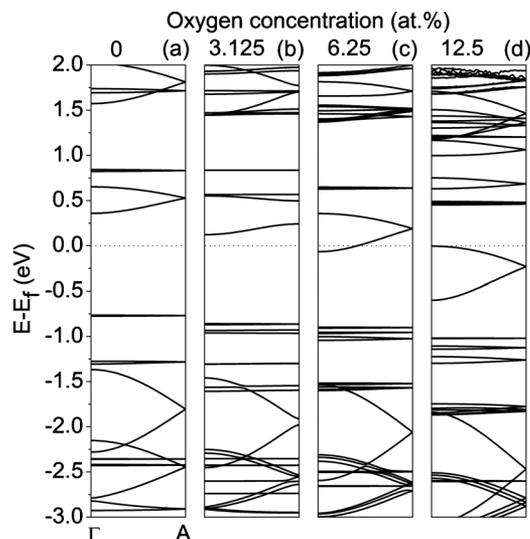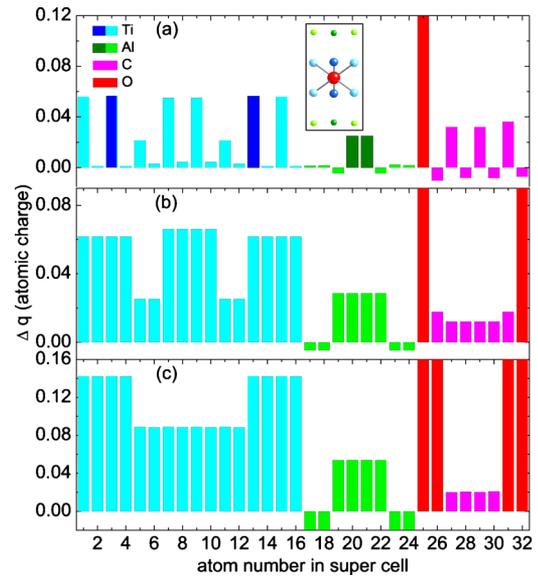

FIG. 3. (Color online) Change in atomic charge, Δq, of various atoms in Ti_2AlC upon O incorporation of (a) 3.125, (b) 6.25, and (c) 12.5 at. %. Please note the different scale of the y axes in (a), (b), and (c).

though anisotropy is not concluded based on DOS, the total DOS at the Fermi level for $Ti_2AlC_yO_x$ increases with increasing x, which may be indicative of increased conductivity. Our band structure analysis shows that oxygen incorporation can be used to tune the electronic properties of the Ti_2AlC MAX phase along the c-direction to produce an anisotropic semiconductor.

As C is exchanged for O, the changes in the chemical environment induce charge redistribution. Bader analysis shows the change in the charge on each atom in the cell. Figure 3(a) shows the change in atomic charge, Δq, for the 32 atoms, as one C atom (no. 25) is exchanged for O. The addition of two electrons as O replaces C results in Δq for the site of only about 1.5e (beyond the range of the y-axis in the figure). The charge discrepancy of about 0.5e is explained by charge transfer to other atoms. The six closest Ti atoms, as shown in the insert (three above and three below) have a charge increase of about 0.06e each. Above/below these Ti atoms are 3/3 Al atoms (rotated 60° with respect to the three Ti), and of these, two are in symmetrically equivalent positions (light green). The third Al atom receives an additional charge of about 0.03e. Evident from Fig. 3(a) is also a charge increase for the three C atoms in the same layer as the O. Figures 3(b) and 3(c) show the charge transfer for further oxygen content. For the structure with 6.25 at. % O, as shown in Fig. 3(b), the charge is transferred primarily in the c-direction, to Ti as well as Al, which is a trend even more pronounced in Fig. 3(c). These results are further supported by analysis of band character, showing that states in bands of primarily Ti character are being filled upon O incorporation. Due to the charge contribution from more than one O, specific Ti atoms gain up to more than 0.14e, and neighboring Al atoms about 0.06e. The Al atoms not situated above/below an oxygen atom experience a reduction in charge of about 0.02e. These results, together with the Γ-A band structure in Fig. 2, suggest that there is charge available for conduction in plane (due to metallic layers), as well as in

FIG. 2. Band structure of Ti_2AlC as a function of O concentration.

the c-direction where oxygen has promoted a vertical charge redistribution.

These results are of importance as they present a means for tuning the MAX phase properties into semiconducting behavior along c. This is potentially attractive in various technological applications, such as low friction contacts. The orientation of lowest friction requires conduction along the c direction to form a useful contact.

In conclusion, we have presented qualitative information regarding the elastic properties and the static conduction characteristics of Ti_2AlC upon oxygen incorporation. The material exhibits anisotropy with crystal orientation, with conduction in-plane. By varying the O concentration, we predict the formation of an anisotropic semiconductor, where the conduction behavior along c can be tuned from insulating to n-type as well as p-type. At the same time, the elastic properties are retained. We recommend that experimental studies be undertaken to test these predictions.

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