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Bonding mechanism in the nitrides Ti$_2$AlN and TiN: An experimental and theoretical investigation

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The electronic structure of nanolaminate Ti$_2$AlN and TiN thin films has been investigated by bulk-sensitive soft x-ray emission spectroscopy. The measured Ti $L_{2,3}$, N K, Al $L_2,3$, and Al $L_{2,3}$ emission spectra are compared with calculated spectra using ab initio density-functional theory including dipole transition-matrix elements. Three different types of bond regions are identified; a relatively weak Ti 3$d$-Al 3$p$ bonding between −1 and −2 eV below the Fermi level, and Ti 3$d$-N 2$p$ and Ti 3$d$-N 2$s$ bondings which are deeper in energy observed at −4.8 eV and −15 eV below the Fermi level, respectively. A strongly modified spectral shape of 3$s$ states of Al $L_{2,3}$ emission from Ti$_2$AlN in comparison with pure Al metal is found, which reflects the Ti 3$d$-Al 3$p$ hybridization observed in the Al $L_2,3$ emission. The differences between the electronic and crystal structures of Ti$_2$AlN and TiN are discussed in relation to the intercalated Al layers of the former compound and the change of the materials properties in comparison with the isostructural carbides.

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I. INTRODUCTION

Ternary carbides and nitrides $M_{n+1}AX_n$ (MAX phases), where $n=1$, 2, and 3 refers to 211, 312, and 413 crystal structures, respectively, have recently been the subject of much research. 1–3 $M$ denotes an early transition metal, A is a $p$ element, usually belonging to the groups IIIA and IVA, and X is either carbon and nitrogen. 4 These nanolaminated materials exhibit a technologically important combination of metallic and ceramic properties, with high strength and stiffness at high temperatures, resistance to oxidation and thermal shock, in addition to high electrical and thermal conductivities. 5 The macroscopic properties are closely related to the underlying electronic and crystal structures of the constituent elements and their stacking sequence. The family of MAX-phase compounds, with more than 50 energetically stable variants, has a hexagonal crystal structure with near close-packed layers of the $M$ elements interleaved with square-planar slabs of pure A elements, where the X atoms (C or N) fill the octahedral sites between the $M$ atoms. The A elements are located at the center of trigonal prisms that are larger than the octahedral X sites.

The 211-crystal structure was derived in the early 1930s when these materials were referred to as Hägg phases with certain stability criteria depending on the ratio of the radii of the constituent atoms. 6 The recent improvements in synthesis processes has led to a renaissance of these compounds with the discovery of the unique mechanical and physical properties and the refined single-crystal thin film processing techniques. 5,7

The Ti-Al-N ternary systems include Ti$_2$AlN (211) and Ti$_4$AlN$_3$ (413). These materials have been known in their bulk form since the 1960s. Recently, single-crystal thin films were synthesized, 8 which provide better opportunities to determine their electronic structure properties. Intercalation of Al monolayers into the TiN matrix implies that the strong Ti-N bonds are broken up and replaced by weaker Ti-Al bonds with a cost of energy. Thus, in Ti$_2$AlN, every second single monolayer of N atoms in TiN have been replaced by an Al layer, in effect resulting in understoichiometric TiN.

The Ti$_2$N slabs surrounding the Al monolayers are then twinned with the Al layers as mirror planes. Figure 1 shows the crystal structure of Ti$_2$AlN with thermodynamically stable nanolaminates of binary Ti-N-Ti layers separated by softer Ti-Al-Ti layers with weaker bonds. 9 As shown in Fig. 1, the 211-crystal structure contains Ti$_{10}$ atoms with chemical bonds both to the N and the A atoms while stoichiometric TiN contains Ti$_{16}$ atoms which only bond to N. The chemical bonding contains a mixed contribution of covalent, metallic, and ionic characters where the strength of the covalent contribution is slightly different for TiN and TiC.

The material’s elastic properties depend on X (C or N) and crystal structure. Young’s modulus ($E$) of single-crystal films of Ti$_2$AlN [270 GPa (Ref. 8)] is higher than for Ti$_2$AlC [260 GPa (Ref. 10)] which are both significantly lower than for the corresponding binary compounds TiN [449 GPa (Ref.

FIG. 1. (Color online) The hexagonal crystal structure of 211 (Ti$_2$AlN). There is one A (Al) layer for every second layer of $M$ (Ti) in Ti$_2$AlN. The $M_{10}$ (Ti$_{10}$) atoms have chemical bonds to both X (N) and A (Al), while $M_4$ (Ti$_4$) atoms only bond to N in the case of TiN. The lengths of the measured (calculated) $a$ and $c$ axes of the unit cell of Ti$_2$AlN are 2.98 (3.01) Å and 13.68 (13.70) Å, respectively.
and TiC\textsubscript{0.8} (388 GPa).\textsuperscript{12} On the contrary, the hardness of Ti\textsubscript{2}AlN [16 GPa (Ref. 8)] is lower than for Ti\textsubscript{2}AlC [20 GPa (Ref. 10)] and comparable to the case of TiN [21 GPa (Ref. 11)] and TiC\textsubscript{0.8} [30 GPa (Ref. 12)]. The change of elastic properties with X is mainly related to the additional valence electron in N and the larger electronegativity compared to C. The weak Ti-Al bonds also affect the tribological properties, such as wear performance and friction.\textsuperscript{5} The physical properties of crystallographically oriented thin films of MAX phases provide opportunities for particular industrial applications such as wear protective coatings on cutting tools and diffusion barriers in contact materials in micro- and nanoelectronics.

Previous experimental investigations of the occupied and unoccupied electronic structure of Ti\textsubscript{2}AlN and TiN include valence-band photoemission\textsuperscript{14} and soft x-ray absorption spectroscopy. However, these methods are rather sensitive to surface contamination. In addition, SXA is hampered by significant core-hole effects in the final state for both C and N. Due to the lack of dipole selection rules in Auger spectroscopy, the N K\textit{L}\textsubscript{2,3} and Ti L\textsubscript{1,2,3} lines directly overlap in TiN.\textsuperscript{16,17} Theoretically, it has been shown by band-structure calculations that there should be significant differences between the valence-band partial density of states (pDOS) of Ti, N, C, and Al of Ti\textsubscript{2}AlN, Ti\textsubscript{2}AlC, TiN, and TiC.\textsuperscript{15,18–20} In recent studies of carbides, applying soft x-ray emission (SXE) spectroscopy, we investigated the three 312 phases Ti\textsubscript{3}SiC\textsubscript{2}, Ti\textsubscript{3}GeC\textsubscript{2}, and Ti\textsubscript{4}SiC\textsubscript{3},\textsuperscript{21} the 413 phase Ti\textsubscript{4}SiC\textsubscript{5},\textsuperscript{22} and the 211 phase Ti\textsubscript{2}AlC compared to TiC.\textsuperscript{23} In contrast to Ti\textsubscript{3}SiC\textsubscript{2}, Ti\textsubscript{3}GeC\textsubscript{2}, and Ti\textsubscript{4}SiC\textsubscript{3}, a pronounced peak at −1 eV below the Fermi level was identified in the Ti 2\textit{p} electron transition-matrix elements. The objective of the present investigation is to study the nanolaminated internal electronic structures and the influence of hybridization among the constituent atomic planes in the Ti\textsubscript{2}AlN and TiN nitride compounds, in comparison with the isostructural Ti\textsubscript{2}AlC and TiC carbide systems with the aim to obtain an increased understanding of the physical and mechanical properties.

II. EXPERIMENT

A. Deposition of the Ti\textsubscript{2}AlN and TiN films

The films were deposited by reactive dc magnetron sputtering from two 3 in. elemental Ti and Al targets in an ultra-high vacuum chamber with a base pressure of $\sim 10^{-8}$ Torr. Polished MgO[111] substrates, $10 \times 5 \times 0.5$ mm\textsuperscript{3} in size, were used as substrates, cleaned by subsequent ultrasonic baths in trichloroethylene, acetone, and 2-propanol, and degassed by holding 900 °C for 1 h prior to deposition. The thickness of the Ti\textsubscript{2}AlN, respectively, TiN was 600 nm, with an initial 120 nm thick TiN[111] seed layer for the Ti\textsubscript{2}AlN, to prevent Al interdiffusion to the substrate. The depositions were carried out in an Ar/N\textsubscript{2} gas mixture of 3.5 mTorr total pressure, with a nitrogen partial pressure of 0.26 mTorr, and Ti and Al magnetron powers set to 360 and 100 W, respectively.

The structural properties of the as-deposited films were characterized by x-ray diffraction with a Philips powder diffractometer using Cu Ka radiation. The scans in 2\texttheta-2\texttheta geometry of Ti\textsubscript{2}AlN (top) and TiN (bottom) are depicted in Fig. 2. Both scans reveal MgO 111 and 222 substrate peaks as denoted. Due to the lattice-matched cube-cube epitaxial growth for TiN, i.e., TiN[111] $\|\$ MgO[111] and TiN[\bar{1}1\bar{0}] $\|\$ MgO[\bar{1}1\bar{0}]$, the TiN peaks for the seed and TiN layer cannot be resolved from the MgO substrate peaks. For Ti\textsubscript{2}AlN, we find two competing epitaxial orientations. The main contribution originates from Ti\textsubscript{2}AlN 000\ell peaks, indicating a parallel basal plane texture with Ti\textsubscript{2}AlN(0001) $\parallel\$ MgO[111] and Ti\textsubscript{2}AlN[\bar{2}1\bar{1}0] $\parallel\$ MgO[\bar{1}1\bar{0}]$. Another contribution stems from a tilted basal plane orientation, leading to the Ti\textsubscript{2}AlN 202$\bar{3}$ peak at a scattering angle of 75.5°. The corresponding epitaxial relationship is given by Ti\textsubscript{2}AlN(202$\bar{3}$) $\parallel\$ MgO[111] and Ti\textsubscript{2}AlN[\bar{2}1\bar{0}] $\parallel\$ MgO[1\bar{1}0]$. This tilted basal plane growth is induced above a critical thickness, which is subject of ongoing investigations, but does not influence the SXE measurements. The lattice parameters for the films, as determined from reciprocal space maps are $a=4.24$ Å for TiN and $a=2.98$ Å and $c=13.68$ Å for the Ti\textsubscript{2}AlN, respectively. The latter are in good agree-
ment with tabulated values of $a=2.989$ Å and $c=13.614$ Å.\textsuperscript{24} Chemical analyses by Rutherford backscattering spectroscopy and elastic recoil detection showed constant elemental distribution over the whole film thickness with compositions according to the formulas given above.

B. X-ray emission and absorption measurements

The SXE and SXA measurements were performed at the undulator beamline IS11-3 at MAX II (MAX-lab National Laboratory, Lund University, Sweden), comprising a 49-pole undulator and a modified SX-700 plane grating monochromator.\textsuperscript{25} The SXE spectra were measured with a high-resolution Rowland-mount grazing-incident grating spectrometer\textsuperscript{26} with a two-dimensional multichannel detector with a resistive anode readout. The Ti $L$ and $N K$ SXE spectra were recorded using a spherical grating with 1200 lines/mm of 5 m radius in the first order of diffraction. The Al $L_1$ and $L_{2,3}$ SXE spectra were recorded using a grating with 300 lines/mm of 3 m radius in the first order of diffraction in the spectrometer. The SXA spectra at the Ti $2p$ and N $1s$ edges were measured with 0.1 eV monochromator resolution using total electron yield and total fluorescence yield, respectively. During the Ti $2p$ measurements, the resolutions of the beamline monochromator were 0.5, 0.3, 0.2, and 0.01 eV, respectively. The SXE measurements, the resolutions of the beamline monochromator were 0.5, 0.3, 0.2, and 0.01 eV, respectively. All SXA measurements were performed with a base pressure lower than $5 \times 10^{-9}$ Torr. In order to minimize self-absorption effects,\textsuperscript{27} the angle of incidence was 20° from the surface plane during the emission measurements. The x-ray photons were detected parallel to the polarization vector of the incoming beam in order to minimize elastic scattering.

III. COMPUTATIONAL DETAILS

A. Calculation of the x-ray emission spectra

The x-ray emission spectra were calculated within the single-particle transition model by using the augmented plane wave plus local orbitals (APW+lo) band-structure method.\textsuperscript{28} Exchange and correlation effects were described by means of the generalized gradient approximation as parametrized by Perdew \textit{et al.}\textsuperscript{29} A plane wave cutoff, corresponding to $R_{MTK_{\text{max}}}=8$, was used in the present investigation. For Ti, $s$, $p$, and $d$ local orbitals were added to the APW basis set to improve the convergence of the wave function, while for Al and N, only $s$ and $p$ local orbitals were used in their basis set. In order to calculate the Al $L_1$ and Al $L_{2,3}$ edges, the $1s$, $2s$, and $2p$ orbitals of Al were treated as core states, with the $3s$ and $3p$ electrons inside the valence shell. The charge density and potentials were expanded up to $\ell =12$ inside the atomic spheres, and the total energy was converged with respect to the Brillouin zone integration.

The x-ray emission spectra were evaluated at the converged ground-state density by multiplying the angular momentum projected density of states by the transition-matrix elements.\textsuperscript{30} The electric-dipole approximation was employed so that only the transitions between the core states with orbital angular momentum $\ell$ to the $\ell \pm 1$ components of the electronic bands were considered. The core-hole lifetimes used in the calculations were 0.73 eV, 0.12 eV, 1.3 eV, and 0.3 eV for the Ti $2p$, N $1s$, and Al $2s$, $2p$ edges, respectively. A direct comparison of the calculated spectra with the measured data was finally achieved by including the instrumental broadening in the form of Gaussian functions corresponding to the experimental resolutions (see Sec. II B). The final state lifetime broadening was accounted for by a convolution with an energy-dependent Lorentzian function with a broadening increasing linearly with the distance from the Fermi level according to the function $a+b(E-E_F)$, where the constants $a$ and $b$ were set to 0.01 eV and 0.05 (dimensionless).\textsuperscript{31}

B. Balanced crystal orbital overlap population

In order to study the chemical bonding of the Ti$_2$AlN compound, we calculated the balanced crystal orbital overlap population (BCOOP) function by using the full-potential linear muffin-tin orbital method.\textsuperscript{32} In these calculations, the muffin-tin radii were kept as large as possible without overlapping each other (Ti=2.3 a.u., Al=2.35 a.u., and N =1.6 a.u.). To ensure a well-converged basis set, a double basis with a total of four different $k^2$ values were used. For Ti, we included the $4s$, $4p$, and $3d$ as valence states. To reduce the core leakage at the sphere boundary, we also treated the $3s$ and $3p$ core states as semicore states. For Al, $3s$, $3p$, and $3d$ were taken as valence states. The resulting basis formed a single, fully hybridizing basis set. This approach has previously proven to give a well-converged basis.\textsuperscript{33} For the sampling of the irreducible wedge of the Brillouin zone, we used a special-$k$-point method and the numbers of $k$ points were 1000 for Ti$_2$AlN and 1728 for TiN in the self-consistent total energy calculation. In order to speed up the convergence, a Gaussian broadening of 20 mRy widths was associated with each calculated eigenvalue.

IV. RESULTS

A. Ti $L_{2,3}$ x-ray emission

Figure 3 shows Ti $L_{2,3}$ SXE spectra following the $3d4s \rightarrow 2p_{3,2,1/2}$ dipole transitions of Ti$_2$AlN (full curves) and TiN (dotted curves) excited at 457.0, 462.5, and 490 eV photon energies. For comparison, a Ti $L_{2,3}$ spectrum of pure Ti metal excited at 490 eV is shown by the dashed line. SXA measurements (top, right curves) following the $2p_{3/2,1/2} \rightarrow 3d4s$ dipole transitions were used to locate the energies of the absorption peak maxima at the Ti $2p_{3/2}$ and $2p_{1/2}$ thresholds (vertical ticks). The SXA spectra were normalized to the step edge (below and far above the Ti $2p$ thresholds). The spectra were plotted on a photon energy scale (top) and a relative energy scale (bottom) with respect to the Fermi level ($E_F$). The SXE spectra appear rather delocalized (wide bands) which usually makes electronic structure calculations suitable for the interpretation, particularly for nonresonant spectra. Calculated Ti $L_{2,3}$ spectra of Ti$_2$AlN, TiN, and Ti are shown at the bottom of Fig. 3. For comparison of the peak intensities and energy positions, the integrated areas of the experimental and calculated spectra of the three systems.
FIG. 3. (Color online) (Top) Ti $L_{2,3}$ x-ray emission spectra of Ti$_2$AlN and TiN excited at 457.0, 462.5 (resonant) and 490 eV (nonresonant). The pure Ti spectrum was nonresonantly excited at 490 eV. The excitation energies for the resonantly excited emission spectra are indicated by vertical ticks in the x-ray absorption spectra (top, right curves). (Bottom) Fitted spectra with the experimental $L_{2,3}$ peak splitting of 6.2 eV and the $L_3/L_2$ ratio of 4.2:1.

were normalized to the calculated Ti 3$d$+4$s$ charge occupations of Ti$_2$AlN: (3$d$, 1.467e; 4$s$, 2.026e), TiN (3$d$, 1.429e; 4$s$, 2.025e), Ti (3$d$, 1.458e; 4$s$, 2.049e). The area for the $L_2$ component was scaled down by the branching ratio and added to the $L_3$ component. For each excitation energy, the spectra were normalized to the time and incoming photon flux by the measured current from a gold mesh in the photon beam.

The calculated spectra consist of the Ti 3$d$ and 4$s$ pDOS obtained from full-potential ab initio density-functional theory projected by the 3$d$4$s$→2$p$ dipole matrix elements and broadening corresponding to the experimental values. The core-hole lifetime broadening was set to 0.73 eV both for the $2p_{3/2}$ and $2p_{1/2}$ thresholds. To account for the $L_2$→$L_3M$ Coster-Kronig decay preceding the SXE process, the $L_3/L_2$ branching ratio from the statistical ratio (2:1), the calculated spectra were fitted to the experimental nonresonant $L_3/L_2$ ratio of 4.2:1 for Ti$_2$AlN and Ti while it is 2.2:1 for TiN. The observed $L_3/L_2$ ratio (4.2:1) for Ti$_2$AlN and Ti is smaller for the nitrides than for the isostuctural carbides (6.0:1), which are both larger than for the more ionic TiN compound (2.2:1). The calculated ab initio values of spin-orbit splittings in band-structure calculations are generally underestimated for the early transition metals (in this case 5.7 eV for Ti $2p$) and overestimated for the late transition metals. The reason for this is not presently known, but must represent effects beyond effective, one-electron theory, e.g., many-body effects. In Fig. 3, the fitted $2p_{3/2,1/2}^3$ spin-orbit splitting was set to the experimental value of 6.2 eV.

The energy positions and intensities of the peaks in the fitted spectra of Ti$_2$AlN and TiN are generally in good agreement with the experimental results. Since our calculations do not include a treatment of polarization effects, we attribute some of the intensity difference to the involvement of the non-spherically symmetric Ti $2p$ core levels.

In the spectra excited at 462.5 and 490 eV, three peaks are observed at −1 eV, −7 eV, and −11 eV, on the relative energy scale at the bottom of Fig. 3. Note that there is a 1.2 eV chemical shift to higher energy for the −1 and −7 eV peak positions in TiN due to the smaller charge occupation and different coordination of the Ti atoms compared to Ti$_2$AlN and Ti. For the −11 eV peak, the chemical shift is only 0.3 eV due to its different origin. The −1 eV peak which is not observed in the $L_1$ spectrum excited at 457.0 eV is attributed to Ti $L_2$ emission which is most intense at 462.5 eV excitation energy. The spectral shape of the $L_2$ component is broader and less pronounced than the $L_3$ component due to the larger $2p_{1/2}$ core-hole lifetime broadening.

The −11 eV peak which is absent in the pure metal Ti $L_{2,3}$ spectrum has earlier been interpreted as an intense anomalous satellite peak on the low-energy side of the main $L_3$ band in various oxides and nitride compounds. The −11 eV peak is attributed to strong hybridization between the Ti 3$d$4$s$ orbitals and the N $2p$ orbitals giving rise to a filled $p$–$d$ band at −4.8 eV below $E_F$. The intensity of the −11 eV peak is ~26% lower in Ti$_2$AlN than in TiN. This is consistent with the observed decrease in stoichiometry when going from TiN to Ti$_2$AlN.

From our band structure calculations, we interpret the origin of the −11 eV peak as due to the $L_3$ component of the Ti 3$d$ pDOS peak at −4.8 eV below $E_F$ which is shifted −6.2 eV by the $2p$ spin-orbit splitting. The weak $L_2$ component of the 3$d$ pDOS contribution (~4.8 eV below $E_F$) overlaps with the much stronger $L_3$ contribution at −7 eV. The weak and broad structure observed in the region −19 to −25 eV with a small peak at −21 eV on the relative energy scale in both Ti$_2$AlN and TiN is due to Ti 3$d$−N $2s$ hybridization at the bottom of the valence band, −12 to −19 eV below $E_F$. Note that this feature is absent in the spectrum of pure Ti.

The origin of the −7 eV peak is related to the $L_3$ component of a series of flat bands of Ti 3$d$ character resulting in high pDOS close to the $E_F$, shifted −6.2 eV by the 2$p$ spin-orbit splitting. Comparing the Ti$_2$AlN and TiN systems to the corresponding carbide systems, the Ti $L_{2,3}$ peak at −7 eV is absent both in ternary carbide systems when Al has been replaced by Si and Ge (Ref. 21) and in TiC. On the contrary, the −7 eV peak is strong in both Ti$_2$AlC and Ti$_3$AlC$_2$. This is a signature of relatively strong hybridization between the Ti 3$d$ states and the Al states at the top of the valence band. The disappearance of the −7 eV peak in TiC can be explained by the fact that the Ti 3$d$ pDOS close to the $E_F$ is very low in TiC, while there is a sharp Ti 3$d$ pDOS peak at
The SXA spectra were normalized to the step sorption maxima and the resonant excitation energy for the calculated N 1s core levels than for TiN. The Ti₃AlN spectra have an additional peak structure at −2 eV below the E_F attributed to N-Al interaction. Note that the N K intensity and N 2p occupation close to the E_F is lower for Ti₃AlN than for TiN due to the additional interaction with Al, concentrating the bond regions deeper into the valence band. As the excitation energy is changed from resonant (397.7 eV) to nonresonant (430.0 eV), the spectral changes are rather small. For resonant excitation, the −6 eV shoulder is slightly more pronounced in Ti₃AlN. The TiN spectra indicate what the N electronic structure of Ti₃AlN would look like if all Al atoms would be exchanged by N atoms. Due to the additional valence electron in N compared to C, the positions of the spectral features related to N are at a lower energy in the nitrides than C in the carbides. This is evident when comparing the N K SXE spectra to the C K SXE of the isostructural carbides, as the C K emission of Ti₂AlC has its main peak at −2.9 eV, a shift of +1.9 eV compared to the N K emission of Ti₃AlN (−4.8 eV). The peak shift to lower energy from the E_F in Ti₃AlN indicates stronger interaction and bonding.

**C. Al L₁ and L₂,₃ x-ray emission**

Figure 5 shows Al L₁ (top panel) and Al L₂,₃ (bottom panel) SXE spectra of Ti₃AlN and an Al(001) single crystal, following the 3p −→ 2s and 3s,3d −→ 2pₓᵧ₂,₁/₂ dipole transitions, respectively. The measurements were carried out nonresonantly at 140 and 110 eV photon energies. Calculated spectra with the dipole projected pDOS and appropriate broadening are shown by the dotted and dashed curves. A common energy scale with respect to the E_F is indicated in the middle of Fig. 5. For comparison of the peak intensities and energy positions, the integrated areas of the experimental and calculated spectra of the two systems were normalized to the calculated Al 3p and 3d+3s charge occupations in Ti₃AlN: (3p, 0.574e; 3d, 0.063e, 3s, 0.592e) and pure Al metal (3p, 0.526e; 3d, 0.090e; 3s, 0.592e). The area for the L₂ component was scaled down by the experimental branching ratio and added to the L₃ component.

The general agreement between experiment and theory is better for the L₁ emission involving spherically symmetric 2s core levels than for the L₂,₃ emission involving 2p core levels. Compared to the spectra of pure Al metal, the spectral structures of Ti₃AlN are more focused to specific energy regions, a few eVs below the E_F as a consequence of bonding to Ti and N. Comparing Ti₃AlN to Ti₃AlC, the shift of the N 2p orbitals to lower energy in comparison with C 2p orbitals (from −2.3 to −4.8 eV) implies a shift of the Ti 3d pDOS toward lower energy which also affects the spectral
In particular, this is evident in the Al $L_2$ spectrum of pure Al metal where a very sharp peak has its maximum at $-0.22$ eV. The small shoulder at $+0.24$ eV above $E_F$ is due to Al $L_2$ emission. We find the Al $L_2/L_3$ branching ratio of pure Al metal (4.15:1) to be smaller than in the case of Ti metal (6.3:1). The $2p$ spin-orbit splitting is 0.46 eV, slightly larger than our calculated ab initio spin-orbit splitting of 0.44 eV. In contrast to the $L_{2,3}$ SXE spectrum of pure Al metal, the Al $L_{2,3}$ spectrum of Ti$_2$AlN has a strongly modified spectral weight toward lower emission energy. The main peak has a maximum between $-4.8$ and $-5$ eV below $E_F$ and a shoulder at $-6$ eV, indicating hybridization with the N $2p$ orbitals. The Al 2p spin-orbit splitting is not resolved in Ti$_2$AlN. The partly populated 3$d$ states are withdrawn from the $E_F$ and form the broad peak structure around $-2$ eV. For the Al $L_{2,3}$ SXE spectra, the calculated 3$s$, 3$d$ $\rightarrow$ 2$p_{3/2,1/2}$ matrix elements are found to play an important role for the spectral shape by reducing the intensity at the bottom of the valence band although this effect is not enough for pure Al metal.

D. Chemical bonding

For Ti$_2$AlN, the equilibrium $a$- and $c$-axis values were calculated to be 3.00 Å and 13.70 Å presented in Sec. II A. In order to analyze the chemical bonding in more details, we show in Fig. 6 the calculated BCOOP of Ti$_2$AlN compared to TiN and the corresponding isostructural carbides Ti$_2$AIC and TiC. The BCOOP makes it possible to compare the strength of two similar chemical bonds where a positive function below $E_F$ means bonding states and a negative function above $E_F$ means antibonding states. The strength of the covalent bonding is determined by comparing the integrated areas under the BCOOP curves. Also, an increased energy distance of bonding peak positions from the $E_F$ implies a larger strength of the covalent bonding. The integrated bonding area below $E_F$ in Fig. 6 is $\sim 50\%$ larger for TiC than for TiN. However, the distance of the main peak from the $E_F$ is approximately two times larger in TiN ($\sim 5.4$ eV) in comparison with TiC ($\sim 2.6$ eV). From this, it can be understood that the covalent Ti$_{ii}$ 3$d$-N $2p$ bonding in TiN is stronger than the Ti$_{ii}$ 3$d$-C $2p$ bonding in TiC. This is also consistent with the shorter Ti$_{ii}$-N bond length in Table I. The 3$d$ states in the BCOOP curves in Ti$_2$AlN are generally located further away from the $E_F$ than in Ti$_2$AIC which indicates that the Ti$_{ii}$-N bond is stronger in Ti$_2$AlN than the Ti$_{ii}$-C bond in Ti$_2$AIC. As the Ti atoms bond stronger to N and C in one direction than to Al in the other direction, the Ti$_{ii}$-N and Ti$_{ii}$-C bonds are even stronger in Ti$_2$AlN and Ti$_2$AIC than the Ti$_{ii}$-N and Ti$_{ii}$-C bonds in TiN and TiC, as shown by the shorter bond lengths in Table I.

The Ti$_{ii}$-Al BCOOP peak at $-1.1$ eV in Ti$_2$AlN has $\sim 15\%$ larger integrated intensity than the corresponding Ti$_{ii}$-Al peak at $-0.64$ eV in Ti$_2$AIC. This shows that the Ti$_{ii}$-Al chemical bond in Ti$_2$AlN is stronger than in Ti$_2$AIC as also indicated by the shorter bond length in Table I. This is also verified experimentally by the fact that the spectral weight of the Al $L_{2,3}$ SXE spectrum is stronger and slightly

![Graph showing Al $L_1$ and $L_{2,3}$ x-ray emission spectra](image_url)
shifted away from the $E_F$ in Ti$_2$AlN in comparison with Ti$_2$AlC which plays a key role for the physical properties.

For the Ti $L_{2,3}$ SXE spectra of Ti$_2$AlN, discussed in Sec. IV A, the BCOOP calculations confirm that the Ti 3d-N 2p hybridization and strong covalent bonding is the origin of the intense Ti pDOS peak at $-4.8$ eV below the $E_F$ in Fig. 3 when the spin-orbit splitting is taken into account. Although a single peak is observed experimentally at $-11$ eV on the relative energy scale, the BCOOP analysis shows that there are several energy levels in the region between $-4$ and $-7$ eV below $E_F$.

Figure 7 shows a calculated electron density difference plot between Ti$_2$AlN and Ti$_2$N$_2$, where in the latter case Al has been replaced by N in the same 211-crystal structure representing a highly twisted TiN cubic structure, i.e., Ti$_2$N$_2$. The plot was obtained by taking the difference between the charge densities in the $(1\bar{1}20)$ diagonal plane of the hexagonal unit cell. The lower valence band energy was fixed to $-4.0$ Ry ($-54.4$ eV) and all the Ti 3$s^2$, 3$p^6$, 3$d^2$, 4$s^2$, Al 3$s^2$, 3$p^1$, and N 2$s^2$ 2$p^3$ valence states were taken into account.

charge densities of the two systems in the $(1\bar{1}20)$ planes of the hexagonal unit cell. Positive values (green/light) mean gain of density and negative values (red/dark) loss of density.

When introducing the Al atoms into the Ti$_2$N$_2$ matrix, we first observe an electron density loss (red/dark colors) at the Al atomic sites since Al atoms have three valence electrons, while N have five. Around the Ti atoms, an anisotropic charge density variation is observed with a considerable loss of density (red/dark color). On the other hand, gain of electron density (yellow-green/light color) in the direction toward the N and Al atoms is observed indicating the formation of the Ti-N and Ti-Al bonds. The consequence of the electronic movement is the creation of a certain polarization with a loss of electron density on the neighboring Ti-Ti bonding and therefore reducing its strength. The locally introduced anisotropic electron density distribution around the Ti atoms results in a charge modulation along the Ti-Al-Ti zigzag bonding direction that propagates throughout the unit cell. The yellow-green/light areas around the N atoms mean a gain of electron density mainly from Ti but also from Al.

**TABLE I.** Calculated bond lengths (Å) for TiN, TiC, Ti$_2$AlN, and Ti$_2$AlC, where X is either N or C. Ti$_1$ is bonded to X while Ti$_{II}$ is bonded to both X and A, as illustrated in Fig. 1.

<table>
<thead>
<tr>
<th>Bond type</th>
<th>Ti$_1$–X</th>
<th>Ti$_{II}$–X</th>
<th>Ti$_{II}$–Al</th>
<th>Al–X</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN</td>
<td>2.129</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiC</td>
<td>2.164</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti$_2$AlN</td>
<td>2.088</td>
<td>2.834</td>
<td>3.826</td>
<td></td>
</tr>
<tr>
<td>Ti$_2$AlC</td>
<td>2.117</td>
<td>2.901</td>
<td>3.875</td>
<td></td>
</tr>
</tbody>
</table>
This shows that the nitrogen atoms respond markedly to the introduction of the Al planes and implies that Al substitution of N results in local modifications to the charge density. Note that in comparison with C in Ti2AlC, N in Ti2AlN is more electronegative and withdraws a larger part of the electronic density from Al, leading to a stronger Al-N interaction as also indicated by the shorter Al-N bond length in Table I. The charge transfer from Ti and Al toward N is in agreement with the BCOOP presented in Fig. 6.

V. DISCUSSION

Comparing the crystal structure of Ti2AlN in Fig. 1 with TiN, it is clear that the physical properties and the underlying electronic structure of the Ti-Al-N system is strongly affected by the intercalated Al layers. The Ti L2,3 XSE spectra in Fig. 3 show that the intensity at the $E_F$ is higher in TiN in comparison with Ti2AlN. This is completely opposite to the case for the isosstructural carbides Ti2AlC and TiC.25 The electrical conductivity/resistivity properties therefore differ significantly between the nitrides and the carbides. Both TiN and Ti2AlN generally have more dominating Ti 3d pDOS at the $E_F$ indicating more metallic-like properties than for the isosstructural carbides where the $E_F$ is close to a pronounced pseudogap (a region with low density of states).25 The intercalation of Al monolayers into the TiN matrix mainly changes the character of the Ti pDOS close to the $E_F$. Intuitively, the conductivity would increase since Al metal is a good conductor. However, the conductivity is largely governed by the Ti metal bonding and is roughly proportional to the number of states at the Fermi level (TiN, 0.43 states/eV atom; Ti2AlN, 0.41 states/eV atom; TiC, 0.12 states/eV atom; Ti2AlC, 0.34 states/eV atom). Experimentally, Ti2AlN films thus have lower resistivity [0.39 $\mu\Omega$ m (Ref. 8)] compared to Ti2AlC [0.44 $\mu\Omega$ m (Ref. 41)] while the resistivity of TiN is even lower [0.13 $\mu\Omega$ m (Ref. 42)] and for TiC more than an order of magnitude higher [2.50 $\mu\Omega$ m (Ref. 43)]. From our previous 312 study of ternary carbides,23 it was clear that the Ti$_{111}$ layers contribute more to the conductivity than the Ti$_1$ layers. Therefore, one would also expect that Ti2AlN has higher conductivity than other ternary nitrides since it only contains Ti$_{111}$. Indeed, the resistivity of the other stable nitride system, Ti$_2$AlN$_3$, is almost an order of magnitude higher than for the Ti2AlN film. Apart from the covalent contribution, the chemical bonding in binary and ternary carbides and nitrides also has an ionic component. The ionic contribution is expected to be stronger in the nitride systems than in the carbides because of the higher electronegativity of N with respect to C. The latter effect is also observed in the charge density plot (Fig. 7).

From Figs. 3–6, we identified three types of covalent chemical bonds, the strong Ti 3d-N 2p bond, the weaker Ti 3d-Al 3p bond and the Ti 3d-N 2s bond. The Ti 3d-N 2p and Ti 3d-N 2s hybridizations are both much deeper in energy from the $E_F$ than the Ti 3d-Al 3p hybridization indicating stronger bonding. Strengthening the relatively weak Ti 3d-Al 3p bonding would effectively increase the stiffness of the material. Such a bond strengthening is indeed observed in Ti$_2$AlN in comparison with Ti$_2$AlC causing the $E$ modulus to increase from 260 GPa (Ref. 10) to 270 GPa (Ref. 8). However, the $E$ modulus of both Ti$_2$AlN and Ti$_2$AlC are both significantly lower than for TiN [449 GPa (Ref. 11)] and TiC [388 GPa (Ref. 12)]. Although we have shown that the Ti 3d-Al 3p bonding is slightly stronger in Ti$_2$AlN than in Ti$_2$AlC, the deformation and delamination mechanism is expected to be rather similar in both systems due to the fact that the Ti 3d-Al 3p bonds are still much weaker in comparison with the Ti$_3$ 3d-C 2p and Ti$_3$ 3d-N 2p bonds. By choosing C and/or N in the design of the ternary MAX phases, the physical and mechanical properties can thus be tailored for specific applications. A fractional substitution of C by N in quaternary (pseudo ternary) MAX phases allows further fine-tuning of the materials properties, following the evolution of the chemical bonds.

VI. CONCLUSIONS

In summary, we have investigated the electronic structures of Ti$_2$AlN and TiN and compared the results to those of the isosstructural Ti$_2$AlC, TiC, and pure Ti and Al metals. The combination of soft x-ray emission spectroscopy and electronic structure calculations show that the pronounced peak structures in Ti L2,3 x-ray emission have very different spectral intensity weights and energy positions in Ti$_2$AlN and Ti$_2$AlC. This clearly shows the difference in the bond scheme between these two compounds. The Ti L2,3/L1,2 branching ratio is significantly larger in Ti$_2$AlN and Ti than in TiN, indicating metallic properties in the former compounds and more ionic properties in TiN. A strong peak structure in the Ti L emission is observed −4.8 eV below the Fermi level in the Ti L2,3 emission and is attributed to intense Ti 3d-N 2p hybridization and strong covalent bonding while another peak observed −1 eV below the Fermi level is due to Ti 3d states hybridized with Al 3p states at −1.6 eV in the Al L1 emission in a weaker covalent bonding. In addition, Ti 3d-N 2p Ti 3d-N 2s hybridization is identified around −15 eV below the Fermi level as a weak spectral structure in the Ti L2,3 emission. Our data of the Al L2,3 emission in Ti$_2$AlN as compared to pure Al metal shows a significant shift toward lower energy. This signifies a transfer of charge from the Al 3d orbitals toward the Ti and N atoms. The Al L2,3 x-ray emission spectrum of Al in Ti$_2$AlN appear very different from the case of Ti$_2$AlC, exhibiting stronger hybridization and interaction between the Al atoms and Ti and N. The bond regions of Al 3p and 3s orbitals to Ti 3d and N 2p orbitals are identified when comparing the Al L1 and L2,3 spectra of Ti$_2$AlN to spectra of pure Al metal. The calculated orbital overlaps also show that the Ti 3d-N 2p Ti 3d-Al 3p bonding orbitals in Ti$_2$AlN are stronger than in Ti$_2$AlC which implies a change of the elastic properties (higher $E$ modulus) and a higher electrical and thermal conductivity. The analysis of the underlying electronic structure thus provides increased understanding of the chemical trend of materials properties when replacing C by N in Ti$_2$AlC and TiC to Ti$_2$AlN and TiN. Generally, the covalent bonding scheme is important for the understanding of the mechanical and physical properties of these thermodynamically stable
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nanolaminates. A tuning of the elastic properties and conductivity by alloying or partly exchanging C with N atoms in a material implies that these nanolaminated systems can effectively be tailored during the materials design.

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