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Journal of Alloys and Compounds 262-263 (1997) 397-401

Journal of ALLOYS AND COMPOUNDS

Electronic structure of sub-stoichiometric titanium carbides, nitrides and carbonitrides: comparison of TB-LMTO calculations and valence XPS spectra

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Abstract

In this work, sub-stoichiometric titanium carbides $TiC_{0.49}$, nitrides $TiN_{0.45}$ and carbonitrides $TiC_{0.35}N_{0.35}$ have been synthesized by multiple energy ion implantation at the surface of pure titanium. Changes in the binary and ternary alloy electronic properties versus defect impurity and vacancy concentrations have been studied by valence X-ray Photoemission Spectra (v-XPS). Moreover, self consistent Tight Binding-Linear Muffin Tin Orbital (TB-LMTO) calculations with empty spheres in place of the missing nitrogen and/or carbon atoms gives, among other information, the total density of occupied states in comparison with observed v-XPS. © 1997 Elsevier Science S.A

Keywords: Electronic structure; TB-LMTO calculations; Valence XPS; Sub-stoichiometric compounds; TiC_xN_y

1. Introduction

It is well known that titanium carbides, nitrides and carbonitrides exhibit rather exceptional physical properties. Their electrical and thermal conductivities are close to pure metals. Their melting points allow them to be considered as refractory metals. The chemical stability at room temperature and the corrosion resistance of these compounds are very high and the corresponding hardness is among the highest after diamond [1,2]. However, it is virtually impossible to produce these refractory compounds as single phases with their nominal formulae. The electronic structure of the corresponding stoichiometric and near stoichiometric metal compounds has been studied by many authors for quite a long time (see e.g. [3,4]) because of the following two reasons. The first one is related to the synthesis methods which allow us to prepare these compounds quite easily near the stoichiometry. The second one is the fact that the properties of these materials were believed, so far, to be most interesting near stoichiometry. Hence, much more is known about the properties of these stoichiometric and near-stoichiometric binary materials rather than far from stoichiometry. In particular, the low carbon and nitrogen concentration limit of TiC_x and TiN_y compounds as well as carbonitrides TiC_xN_y have not yet been studied systematically as far as we know. In the present work, using multiple energy (180, 100, 50, 20 keV) ion implantation at a surface of titanium, sub-stoichiometric titanium carbides $TiC_{0.49}$, nitrides $TiN_{0.45}$ and carbonitrides $TiC_{0.35}N_{0.35}$ have been synthesized. For other concentrations we refer to a forthcoming paper [20]. Several techniques were used in order to characterize the layers thus synthesized [5-8]. All of the corresponding physical properties are related to their electronic structures. However, in this

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PII S0925-8388(97)00343-5

paper only our valence X-ray Photoemission spectra (v-XPS) of Ti carbides, nitrides and carbonitrides are compared to the corresponding total density of states (DOS). The calculations presented here for the electronic structure in the case of stoichiometric (and non-stoichiometric) TiC_x, TiN_y and TiC_xN_y compounds are performed within a self consistent Tight Binding-Linear Muffin Tin Orbital (TB-LMTO) method. For stoichiometric TiC, TiN and non-stoichiometric TiC_x and TiN_y compounds, there are many v-XPS results in the literature [9–13]. For stoichiometric TiC and TiN compounds, peak positions and widths agree fairly well with band-structure calculations [10,11], whereas for sub-stoichiometric TiC_x and TiN_y some discrepancies were found [12] between experimental and theoretical results [14a,b]. Let us emphasize that the v-XPS spectra of TiN_x has already been measured over the entire composition range of the rocksalt structure (with $0.5 \leq x \leq 1$) and analysed in terms of various theoretical results [9]. The great difficulty in theoretical calculations of the electronic structure of non-stoichiometric materials is mainly due to the problem of taking proper account of the lattice vacancies. To treat the vacancy problem some appropriate approximations have been made [14a,b–17]. Recently, using a TB-LMTO method [18,19] with ordered empty spheres for the vacancies, we were able to analyse the experimental v-XPS spectra for various concentrations of TiC_x obtained from ion implantation [8]. Here, we extend this work to TiN_y and TiC_xN_y compounds in comparison with our recent v-XPS data. Our calculations introduce empty spheres, if necessary, in the place of the missing nitrogen and/or carbon atoms. The paper is organised as follows. In Sec. 2 we present some experimental data for TiC_x, TiN_y and TiC_xN_y compounds with a special emphasis on v-XPS spectra. Next (Section 3) we give the results of our electronic structure calculations for a series of Ti carbides, nitrides and carbonitrides. Section 4 is devoted to discussion and conclusion.

2. Experimental study of TiC_x, TiN_y and TiC_xN_y: XPS results.

The XPS analysis was performed with a VG II apparatus equipped with two chambers: a preparation chamber where the 5-keV argon ion etches were performed with a cold cathode ion gun and an analyser chamber where the photoelectrons excited by the Al*Kα* radiation were analysed with a hemispherical analyser. The analyser pass-energy was fixed at 20 eV which corresponds to approx. 0.6 eV resolution. Taking into account the Al$K\alpha_{1,2}$ line width, the whole apparatus resolution was approx. 1.2 eV. The energy calibration was carried out by setting the Au 4f7/2, the Cu L_3VV and Cu 2p3/2 peaks at energies equal to 84.0, 568.0 and 932.7 eV, respectively. The vacuum was maintained at 10^{-10} torr, during the measurements with a cryo-pumping system. The XPS spectra showed that the surfaces of several samples were mainly covered with titanium oxide (probably TiO_2) which disappears quickly under argon bombardment. In order to reduce selective sputtering effects by argon bombardment on the surface composition, this cleaning procedure was carried out under small incident angle. Thus, we believe that argon bombardment did not extensively affect the recorded spectra. In order to compare our experimental results to the theory (see Sec. 3), the carbide, nitride and carbonitride valence band spectra are shown in Figs. 1–3 for $TiC_{0.49}$, $TiN_{0.45}$ and $TiC_{0.35}N_{0.35}$ together with the theoretical results. The carbonitrides display four characteristic structures which can also be seen partially in carbides and nitrides: (i) a peak at approx. −16.5 eV, corresponding to the N2s electron band; (ii) another peak around −12 eV corresponding to the C2s electron band; (iii) a strong peak at −5.5 eV due to the Ti3d-C2p-N2p hybridization; (iv) a shoulder

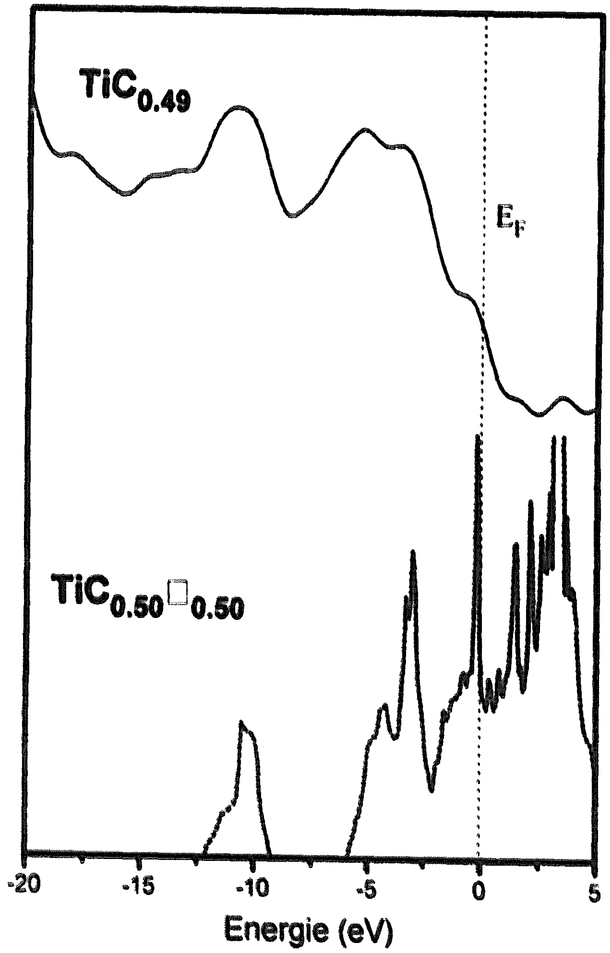

Fig. 1. Experimental valence-XPS spectrum of $TiC_{0.49}$ (full line) compared to the calculated $TiC_{0.50}\square_{0.50}$ total DOS (dashed line).

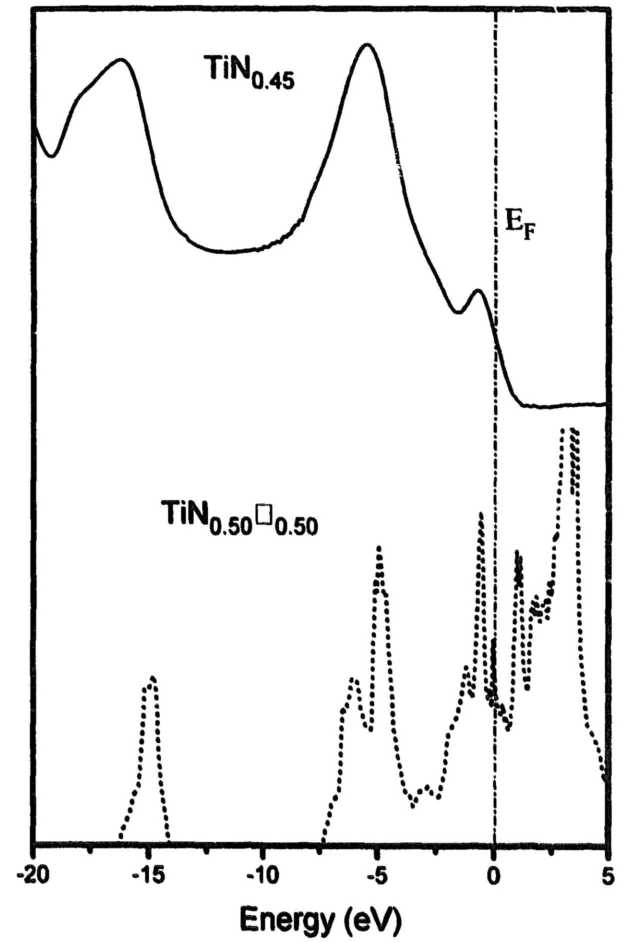

Fig. 2. Experimental valence-XPS spectrum of $\mathrm{TiN_{0.45}}$ (full line) compared to the calculated $\mathrm{TiN_{0.50}\square_{0.50}}$ total DOS (dashed line).

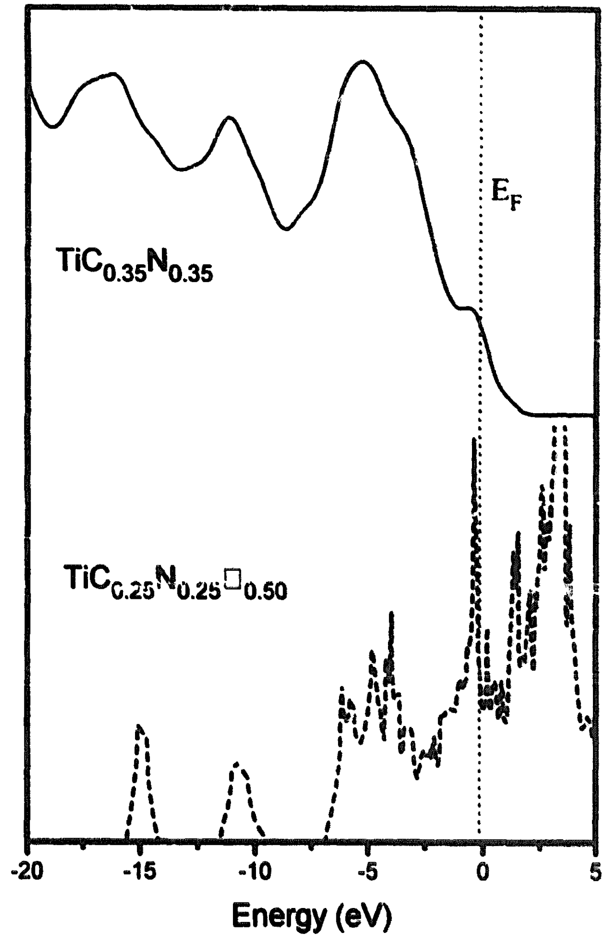

Fig. 3. Experimental valence-XPS spectrum of $\mathrm{TiC_{0.35}N_{0.35}}$ (full line) compared to the calculated $\mathrm{TiC_{0.25}N_{0.25}\square_{0.50}}$ total DOS (dashed line).

near the Fermi level which is also observed in the valence XPS of the sub-stoichiometric titanium carbides and nitrides and which will be interpreted in terms of 'vacancy states' as explained below.

3. Electronic structure calculation of Ti carbides, nitrides and carbonitrides

For simplicity our calculations are restricted to the NaCl crystallographic structure which is adapted to $\mathrm{TiC_{0.49}}$ whereas $\mathrm{TiN_{0.45}}$ is a mixture of hexagonal and NaCl structures. Nevertheless, a NaCl band structure calculation of TiN_x for the whole range of concentrations already gives important information to be compared to the v-XPS data [20]. The same remark holds for $\mathrm{TiC}_x\mathrm{N}_y$. The NaCl lattice is composed of two face centred cubic (FCC) sub-lattices, one containing the titanium atoms and the other the metalloid atoms (C and/or N). Let us just recall that when the z-axis of an FCC structure is perpendicular to its (111) face, the structure becomes hexagonal with $a = b = a_0/(2)^{1/2}$ and $c = a_0(3)^{1/2}$, where a_0 is the FCC-lattice constant. If c is different than $a_0(3)^{1/2}$, the structure can not be treated as FCC. At the moment this value of $c \neq a_0(3)^{1/2}$, of hexagonal $\mathrm{TiN_{0.45}}$ for example, is not available. Thus we limit our theoretical study to FCC and NaCl structures only. For the electronic structure calculation we use the TB-LMTO method: the exchange correlation effect is included through Local Density Approximation (LDA). For Ti, we consider s, p, d orbitals corresponding to four valence electrons ($3d^2 4s^2 4p^0$); for C we have $2s^2 2p^2$ electrons and for N, $2s^2 2p^3$ electrons. The departure from stoichiometry in $\mathrm{TiC}_x\square_{1-x}$, $\mathrm{TiN}_x\square_{1-x}$ $(0 < x < 1)$ and $\mathrm{TiC}_x\mathrm{N}_y\square_{1-x-y}$ $(0 < x + y < 1)$ is described by ordered vacancies (□) with empty Wigner–Seitz spheres in the metalloid lattice. Configurations $\mathrm{Ti_4Z_4}$, $\mathrm{Ti_4Z_3\square_1}$, $\mathrm{Ti_4\ Z_2\square_2}$, $\mathrm{Ti_4Z_1\square_3}$ correspond to $x = 1$, 0.75, 0.5, 0.25, respectively, and an increasing concentration $(1 - x)$ of vacancies with Z = C or N [8,20]. The stoichiometric carbonitrides, $\mathrm{Ti_4C_1N_3}$, $\mathrm{Ti_4C_2N_2}$ and $\mathrm{Ti_4C_3N_1}$, correspond to $\mathrm{TiC}_x\mathrm{N}_y$ with $(x,y) =$ (0.25, 0.75); (0.50, 0.50); and (0.75, 0.25), respectively. It is obvious that the lattice parameter of titanium carbonitrides is a function of their composition. Thus, for stoichiometric TiC_xN_{1-x} carbonitrides it varies linearly from a = 0.4241 nm for TiN to a = 0.4327 nm for TiC [20]. Finally, for sub-stoichiometric carbonitrides, $Ti_4C_2N_1\square_1$, $Ti_4C_1N_2\square_1$ and $Ti_4C_1N_1\square_2$ correspond to $TiC_xN_y\square_z$ with $(x, y, z) = (0.50, 0.25, 0.25)$; $(0.25, 0.50, 0.25)$; and $(0.25, 0.25, 0.50)$, respectively, and a linear interpolation for the lattice parameter in the case of one or two vacancies per unit cell [20]. For the k-space integration by the tetrahedron method, 405 k-points are used in the irreducible Brillouin zone. This number of k-points is found to be sufficient to obtain a completely converged result. Also, all the electronic energies are given with reference to the Fermi energy, E_F.

Figs. 1–3 also report the calculated DOS of $TiC_{0.50}$, $TiN_{0.50}$ and $TiC_{0.25}N_{0.25}$ in comparison with the corresponding v-XPS spectra. As is well known, TiN is qualitatively similar to TiC (Figs. 4 and 5), except that for TiN, E_F now falls above the pseudogap minimum because of the additional 2p nitrogen electron. Therefore $n(E_F)$ is increased when going from TiC to TiN. This effect is hindered when going from $TiC_{0.50}$ to $TiN_{0.50}$ (Figs. 1 and 2), since, in the carbides, vacancy states appear then as a superstructure closer to E_F than in the case of the nitrides (see also Figs. 4 and 5). The total DOS of stoichiometric carbonitrides TiC_xN_y is shown in Fig. 6 for $(x, y) = (0.50, 0.50)$. The first two peaks on the left originate from N2s and C2s and their intensities are proportional to y and x, respectively [20]. Finally, Figs. 3 and 6 both report our calculated DOS for sub-stoichiometric carbonitrides $TiC_xN_y\square_z$ with $(x, y, z) = (0.25, 0.25, 0.50)$. Again, we distinguish the N2s and C2s peaks on the left side of the energy scale. Also vacancy states are visible as a superstructure like a peak of density of states near the Fermi level in agreement with the experimental v-XPS spectrum of Fig. 3. Of course it is well known that for any stoichiometric carbides, nitrides or carbonitrides there is no shoulder present at or near E_F in the XPS spectra. To find out the origin of the vacancy states near the Fermi level, we have studied the individual contributions of different symmetries coming from different atomic origins. This check makes it evident that the vacancy state is mainly due to Ti-3d. The overall weight of this orbital in the vacancy state, for example just below the Fermi level, is approx. 80% for $TiC_{0.50}$, $TiN_{0.50}$ or $TiC_{0.25}N_{0.25}$.

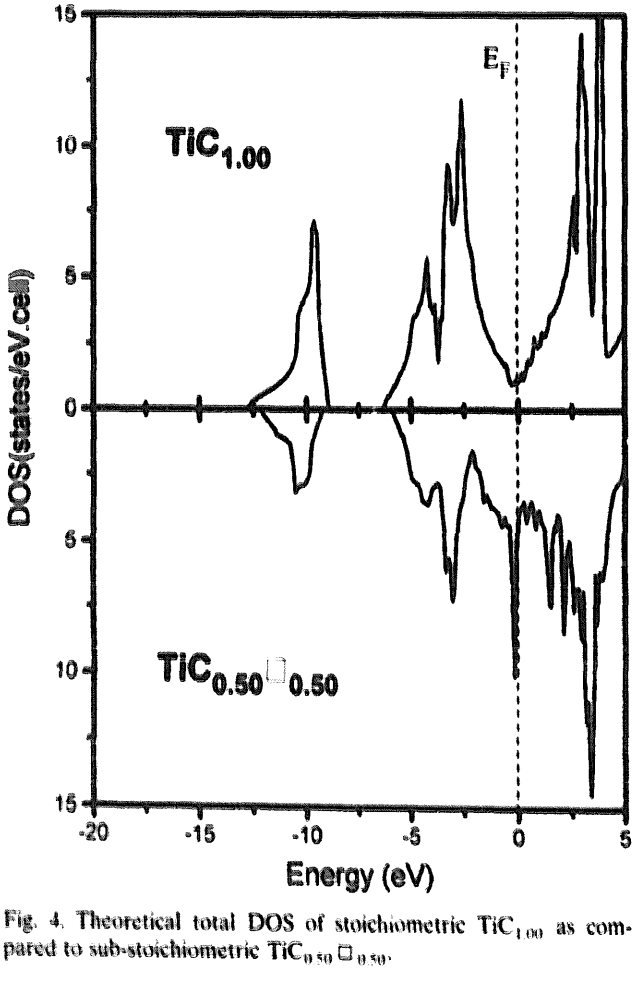

Fig. 4. Theoretical total DOS of stoichiometric $TiC_{1.00}$ as compared to sub-stoichiometric $TiC_{0.50}\square_{0.50}$.

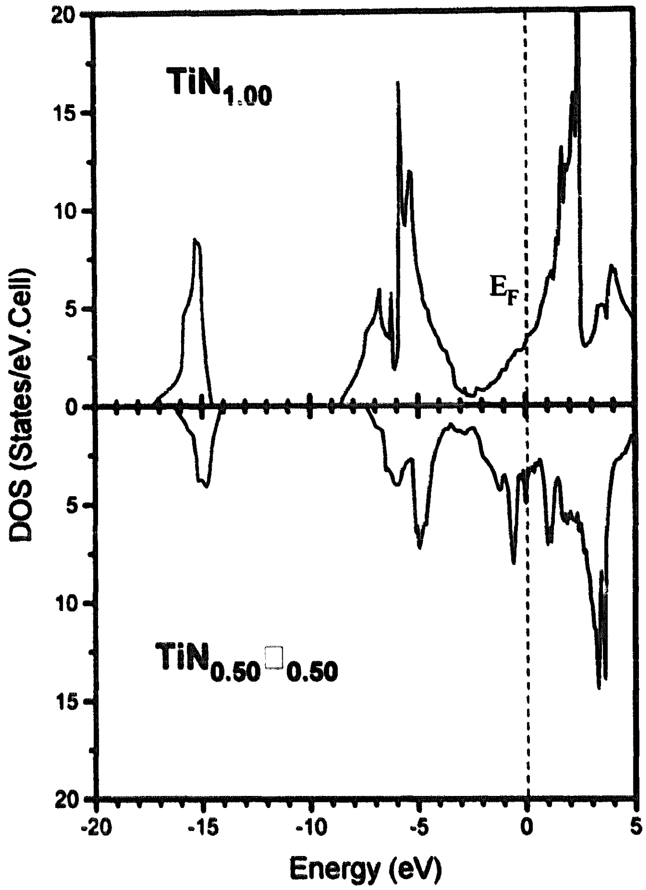

Fig. 5. Theoretical total DOS of stoichiometric $TiN_{1.00}$ as compared to sub-stoichiometric $TiN_{0.50}\square_{0.50}$.

4. Concluding remarks

In order to facilitate the comparison between the-

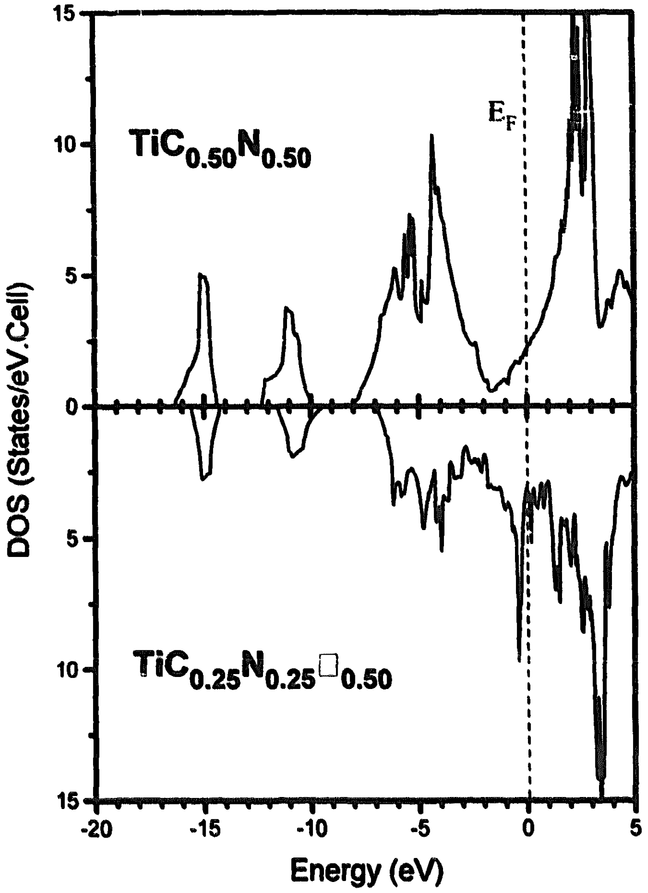

Fig. 6. Theoretical total DOS of stoichiometric $TiC_{0.50}N_{0.50}$ as compared to sub-stoichiometric $TiC_{0.25}N_{0.25}\square_{0.50}$.

ory and experimental spectra we have shown our calculated DOS of $TiC_{0.50}$ and $TiN_{0.50}$ (Figs. 1 and 2) just below the measured v-XPS of $TiC_{0.49}$ and $TiN_{0.45}$. Although stoichiometry does not exactly coincide between theory and experiment, the small peak within 1 eV below E_F exists both experimentally and theoretically as well as the other structures below E_F. There are slight differences of energy positions, however, the overall agreement is quite satisfactory. The same agreement can be observed in Fig. 3 where we compare our theoretical DOS of $TiC_{0.25}N_{0.25}$ to the v-XPS spectrum of $TiC_{0.35}N_{0.35}$, although, here also, the stoichiometries are slightly different. In conclusion, we can say that we have been quite successful in studying the interesting effect of atoms (C, N) and vacancy concentrations on the electronic structure of (sub)stoichiometric TiC_x, TiN_y and TiC_xN_y compounds. The existence of vacancy (superstructure) states in the TiC, TiN and TiCN pseudogaps is confirmed both by our v-XPS measurements and our ab-initio calculations.

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