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X-Ray Emission Spectra of Cubic $\text{TaC}_x\text{N}_{\sim 0.75-x}$ Carbonitrides

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X-ray emission spectroscopy (XES) was used to study the electronic structure of substoichiometric cubic tantalum carbonitrides TaC_xN_y , where $x+y \approx 0.75$. For the above system, the XES $\text{TaL}\beta_5$, $\text{NK}\alpha$ and $\text{CK}\alpha$ bands were obtained. It has been established that, substitution of carbon atoms by nitrogen atoms in the $\text{TaC}_x\text{N}_{\sim 0.75-x}$ system under study results in decreasing the intensity of the main maximum of the $\text{TaL}\beta_5$ band and increasing its half-width. For all the studied substoichiometric tantalum carbonitrides, half-widths of the $\text{NK}\alpha$ and $\text{CK}\alpha$ bands remain constant within the experimental error. Results of the present experimental studies of the $\text{TaC}_x\text{N}_{\sim 0.75-x}$ system indicate that, substitution of carbon atoms by nitrogen atoms leads to increasing the metallic component and decreasing covalent component of the chemical bonding. A strong hybridization of the $\text{Ta}5d$ -like and $\text{C(N)}2p$ -like states is characteristic for all the compounds of the $\text{TaC}_x\text{N}_{\sim 0.75-x}$ system studied.

Keywords: X-Ray emission spectroscopy; Tantalum carbide; Tantalum nitride; Electronic structure; Chemical bonding.

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Introduction

Transition metal carbides and nitrides attract a great deal of interest both in technology and in science because of their unique physical and chemical properties. The compounds possess high hardness and high melting temperature, good corrosion resistance, metallic conductivity, they show plasticity at intermediate and high temperatures etc. [1-3]. Many transition metal carbides and nitrides are capable to form unlimited solid solutions with one other [2]. Some physical and chemical properties of such carbonitrides as a function of the MC/MN ratio, where M denotes a transition metal atom, are non-monotonous and depend strongly on the composition [1,4]. The alloying of the sub-lattices of transition metal interstitial alloys with atoms of a different type is one of the most promising methods for modification of their service characteristics. Changes of physical and chemical properties of the compounds can be predicted and understood by considering their electronic structure. Therefore, studies of the electronic structure of transition metal carbides and nitrides are of great importance in theoretical and experimental science [4,5].

It is well known that, synthesis of a continuous solid solution of cubic TaC (NaCl structure) and hexagonal TaN (CoSn structure) compounds is not possible using conventional powder metallurgy methods: specimens of the TaC-TaN system containing less than 40 at.% cubic TaC are two-phase materials [2,6,7]. As it was

established in Refs. [7,8], a continuous TaC-TaN solid solution can be obtained either by "the method of self-spreading high temperature synthesis" or under high temperature-high pressure conditions. The latter method was used in Ref. [9] for synthesis of the stoichiometric cubic $\text{TaC}_x\text{N}_{1-x}$ system. In this work, the electronic structure of the $\text{TaC}_x\text{N}_{1-x}$ system was investigated using spectroscopy methods.

However, transition metal carbides and nitrides are well known for their ability to form rather wide homogeneity regions, where the compounds contain a great number of vacancies in some of their sublattices (mainly, in the non-metal sublattice) preserving their crystal structures unchanged. Physical and chemical properties of the compounds (e.g., electrical and thermal conductivities, hardness, melting points etc.) change dramatically with an increasing number of the non-metal vacancies [1,2,4]. Some of the properties can be explained by considering the electronic structure of transition metal carbides and nitrides. Therefore, it is interesting to investigate the influence of formation of vacancies on the non-metal sublattice upon the electronic structure of cubic tantalum carbonitrides.

In the present work, the X-ray emission spectroscopy (XES) method was employed to investigate the electronic structure of a cubic $\text{TaC}_x\text{N}_{\sim 0.75-x}$ system synthesized due to high pressure-high temperature treatment. The content of the non-metal atoms in the above system is close to the lowest borders of the homogeneity region of both cubic tantalum monocarbide and cubic tantalum mononitride [1,2,10]. The aim of the work was to study

the influence of non-metal vacancies upon the electronic structure of cubic tantalum carbonitrides. Therefore, the present results are compared with the previous results of similar studies of stoichiometric cubic $\text{TaC}_x\text{N}_{1-x}$ system [9].

I. Experimental

The method of synthesis of substoichiometric cubic tantalum carbonitrides TaC_xN_y , where $x+y \approx 0.75$, was analogous to that used earlier for obtaining stoichiometric $\text{TaC}_x\text{N}_{1-x}$ system [9]. The synthesis was made at the Institute of Solid State Physics and Semiconductors (National Academy of Sciences of Belarus, Minsk) using high pressure-high temperature treatment ($p \approx 7\text{--}10$ GPa, $t \approx 2100\text{--}2400^\circ\text{C}$). The synthesis of the cubic $\text{TaC}_x\text{N}_{0.75-x}$ system under study was made using the following powder precursors: hexagonal mononitride $\text{TaN}_{0.99}$ (CoSn structure), cubic monocarbide $\text{TaC}_{0.98}$ (NaCl structure), and metallic tantalum. Into preliminary mixtures of the above powder substances, the following nitrogen-containing heterocyclic compounds were also introduced in order to achieve additional nitriding of the final products: melamine ($\text{C}_3\text{H}_6\text{N}_6$), 5,6-dimethylbenzimidazole ($\text{C}_9\text{H}_{10}\text{N}_2$), γ,γ' -dipyridyl ($\text{C}_{10}\text{N}_2\text{H}_8$). The method of synthesis of cubic tantalum carbonitrides was discussed in detail in Refs. [7,11]. Oxygen content in the studying $\text{TaC}_x\text{N}_{0.75-x}$ carbonitrides was found to be less than 0.3 wt.%, but nonbonded carbon was either absent or its content was less than 0.1 wt.%. The $\text{TaC}_x\text{N}_{0.75-x}$ specimens under study were prepared in the form of cylinders, $d = 4\text{--}5$ mm diameter and $h = 2\text{--}3$ mm height. X-Ray diffraction analysis employing $\text{CuK}\alpha$ radiation (a DRON-3 diffractometer) revealed that all the $\text{TaC}_x\text{N}_{0.75-x}$ specimens investigated in the present work were single-phase materials (Table 1). As data of X-ray diffraction analysis indicate, the lattice parameter a increases from 0.4345 ± 0.0008 nm for $\text{TaN}_{0.78}$ to 0.4416 ± 0.0004 nm for $\text{TaC}_{0.75}$, with some deviation from Vegard's law. It should be mentioned that the sample $\text{TaN}_{0.78}$ was found to contain a small admixture of carbon and the $\text{TaC}_{0.05}\text{N}_{0.78}$ formula can be ascribed to the compound.

Table 1

Lattice parameters of the substoichiometric cubic $\text{TaC}_x\text{N}_{0.75-x}$ carbonitrides studied

Compound	a , nm
$\text{TaC}_{0.75}$	0.4416
$\text{TaC}_{0.57}\text{N}_{0.22}$	0.4410
$\text{TaC}_{0.42}\text{N}_{0.34}$	0.4398
$\text{TaN}_{0.78}^*$	0.4345

*The sample contained some admixture of carbon as mentioned in the Experimental section

The technique of the present XES studies of the

electronic structure of cubic $\text{TaC}_x\text{N}_{0.75-x}$ carbonitrides was analogous to that described in detail when studying the stoichiometric $\text{TaC}_x\text{N}_{1-x}$ system [9]. Briefly, the fluorescent XES $\text{TaL}\beta_5$ bands ($L_{\text{III}} \rightarrow O_{\text{IV,V}}$ transition) reflecting primarily the energy distribution of the $\text{Ta}5d$ -like states were collected using a DRS-2M X-ray spectrograph. A BKhV-7 X-ray tube with gold anode operating at accelerating voltage of $U_a = 45$ kV and anode current of $I_a = 75$ mA was used as a source of primary excitation. The bands were derived with the spectrograph energy resolution of $\Delta E_{\text{min}} \approx 0.3$ eV in the second order of reflection from the (0001) plane of a quartz crystal prepared according to Johann. Accumulation time for receiving spectra of sufficient intensities was 140–190 h depending on surface sizes of the sample under investigation. The $\text{CK}\alpha$ and $\text{NK}\alpha$ emission bands ($K \rightarrow L_{\text{II,III}}$ transition) reflecting the energy distribution of the $\text{C}2p$ - and $\text{N}2p$ -like states, respectively, were obtained with the same energy resolution using an RSM-500 X-ray spectrometer-monochromator. The dispersing element was a diffraction grating with 600 lines/mm and a radius of curvature of $R \approx 6$ m. The detector was a secondary electron multiplier VEU-6 with a CsI photocathode. The spectra were recorded under conditions of oil-free evacuation eliminating impact of hydrocarbon vapours on the target. The X-ray chamber was evacuated to ca. 1×10^{-6} Pa. The operating conditions of the X-ray tube during the present experimental studies of the cubic $\text{TaC}_x\text{N}_{0.75-x}$ system were the following: $U_a = 5$ kV, $I_a = 5\text{--}7$ mA. Surfaces of the tantalum carbonitrides under study were prepared by argon-ion bombardment in the spectrometer chamber as described in Ref. [9].

The XES $\text{TaL}\beta_5$ bands were normalized on the same integral intensities of the X-ray $\text{TaL}\beta_9$ lines of the corresponding compound. The relative intensities of the $\text{CK}\alpha$ and $\text{NK}\alpha$ emission spectra could not be measured because there were not standard X-ray lines in the range of energies corresponding to the energy of the bands [12].

II. Results and discussion

Figure 1 shows the XES $\text{TaL}\beta_5$ bands of $\text{TaC}_x\text{N}_{0.75-x}$ normalized, as mentioned in the Experimental section, on the same integral intensities of the corresponding X-ray $\text{TaL}\beta_9$ lines not subjected to the effect of the chemical bonding. As can be seen from the figure, in addition to the main peak “B”, the existence of one low-energy peculiarity “A” and one high-energy feature “C” is characteristic for every X-ray emission $\text{TaL}\beta_5$ band in the cubic $\text{TaC}_x\text{N}_{0.75-x}$ carbonitrides studied. The deconvolution of the Md -like states in cubic tantalum carbides and nitrides indicates [13,14] that the main maximum “B” of the band is created by the $\text{Ta}5d$ -like states taking part in the formation of covalent $d_{\text{Ta}}\text{--}p_{\text{X}}$ bonds owing to the $\text{Ta}5d\text{--}X2p$ -like hybridization ($X = \text{C}, \text{N}$), while the high-energy feature “C” of the band is formed due to contributions of the $\text{Ta}5d$ -like states responsible for the forming Ta–Ta bonds in cubic

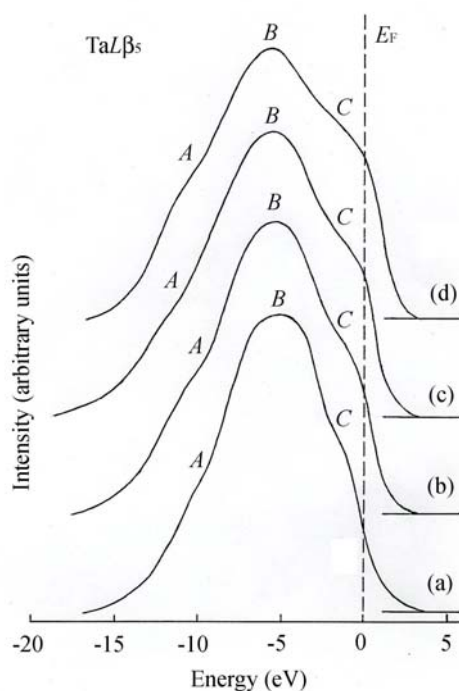


Fig. 1. X-Ray emission $\text{TaL}\beta_5$ bands of $\text{TaC}_{0.75}$ (a), $\text{TaC}_{0.57}\text{N}_{0.22}$ (b), $\text{TaC}_{0.42}\text{N}_{0.34}$ (c) and $\text{TaN}_{0.78}$ (d). The dashed line indicates the position of the Fermi energy, E_F , of the ES-2401 spectrometer energy analyzer.

$\text{TaC}(\text{N})$ compounds.

As one can see from Fig. 2, in the sequence $\text{TaC}_{0.75} \rightarrow \text{TaN}_{0.78}$ the intensity of the main maximum “B” of the $\text{TaL}\beta_5$ band decreases (for clarity, in the figure the peak intensity of the band in cubic $\text{TaC}_{0.98}$ carbide is normalized to 1.00), while the intensity of the high-energy feature “C” of the band increases (see Fig. 1). The above facts indicate that the covalent component of the chemical bonding decreases, but the metallic component increases with increasing nitrogen content in the cubic $\text{TaC}_x\text{N}_{1-x}$ carbonitrides studied. From Fig. 2 it is apparent that the same effect was also characteristic for the stoichiometric cubic $\text{TaC}_x\text{N}_{1-x}$ system studied previously in Ref. [9]. However, the smallest peak intensity of the $\text{TaL}\beta_5$ band was observed for the intermediate composition of the stoichiometric $\text{TaC}_x\text{N}_{1-x}$ system (mainly, for the $\text{TaC}_{0.52}\text{N}_{0.49}$ compound), while decreasing the peak intensity of the band is almost monotonous when going from $\text{TaC}_{0.75}$ to $\text{TaN}_{0.78}$.

It should be mentioned that, as Fig. 2 reveals, the intensities of the maximum “B” of the $\text{TaL}\beta_5$ bands in the cubic $\text{TaC}_x\text{N}_{1-x}$ carbonitrides are smaller somewhat as compared to those in compounds with close nitrogen to carbon ratios in the $\text{TaC}_x\text{N}_{1-x}$ system. The above fact indicates that the formation of vacancies on the non-metal sublattice of the cubic tantalum carbonitride leads to breaking some covalent $d_{\text{Ta}}-p_{\text{X}}$ bonds. As a result, part of the $\text{Ta}5d$ -like states, which do not take part in forming covalent $d_{\text{Ta}}-p_{\text{X}}$ bonds due to $\text{Ta}5d-\text{X}2p$ -like hybridization, according to the calculation [15] should fill the high-energy $\text{Ta}d_{2g}$ -like orbitals. The mentioned filling of the $\text{Ta}d_{2g}$ orbitals leads to significant increasing the $\text{TaL}\beta_5$ band half-width in the sequence

$\text{TaC}_{0.75} \rightarrow \text{TaN}_{0.78}$ (Table 2). As it was established in Ref. [9], in the stoichiometric $\text{TaC}_x\text{N}_{1-x}$ system the half-width of the $\text{TaL}\beta_5$ band is maximum for the $\text{TaC}_{0.52}\text{N}_{0.49}$ compound, while in the substoichiometric $\text{TaC}_x\text{N}_{1-x}$ carbonitrides under study the $\text{TaL}\beta_5$ band half-width increases monotonously in the sequence $\text{TaC}_{0.75} \rightarrow \text{TaN}_{0.78}$ (see Table 2).

The XES $\text{CK}\alpha$ and $\text{NK}\alpha$ bands in the studying cubic $\text{TaC}_x\text{N}_{1-x}$ carbonitrides are presented in Figs. 3 and 4, respectively (it should be mentioned that, the intensity of the $\text{NK}\alpha$ band in $\text{TaC}_{0.57}\text{N}_{0.22}$ was too small to be able to

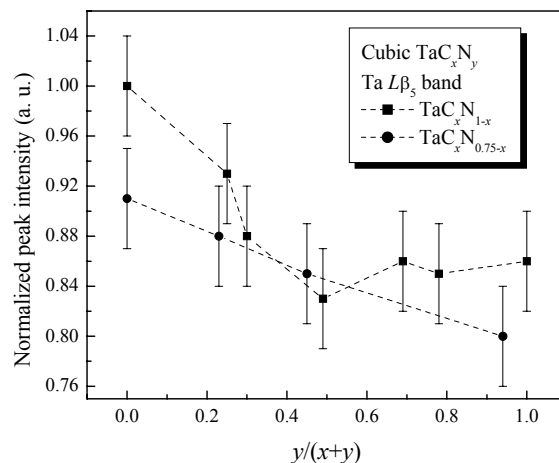


Fig. 2. Dependence of the peak intensity of the normalized $\text{TaL}\beta_5$ bands upon content of carbon and nitrogen atoms in the cubic $\text{TaC}_x\text{N}_{1-x}$ carbonitrides studied (●). For comparison, the similar results from Ref. [9] for stoichiometric $\text{TaC}_x\text{N}_{1-x}$ system (◆) are also presented.

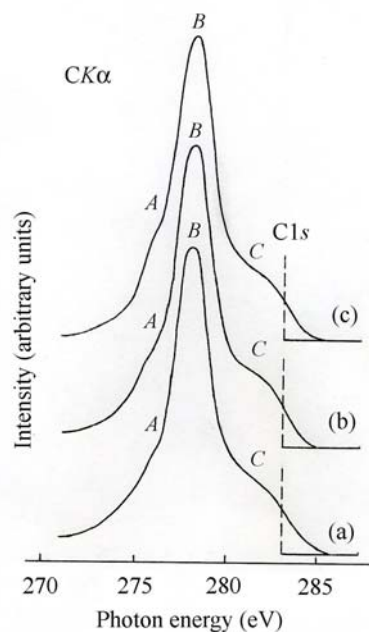


Fig. 3. X-Ray emission $\text{CK}\alpha$ bands of $\text{TaC}_{0.75}$ (a), $\text{TaC}_{0.57}\text{N}_{0.22}$ (b) and $\text{TaC}_{0.42}\text{N}_{0.34}$ (c). The dashed lines indicate positions of the X-ray photoelectron $\text{C}1s$ core-level lines in the specimens under study.

Table 2

Half-widths (in eV) of the emission bands in the cubic $\text{TaC}_x\text{N}_{1-x}$ carbonitrides studied

Compound	Ta $L\beta_5$ band	C $K\alpha$ band	N $K\alpha$ band
$\text{TaC}_{0.75}$	8.8	2.80	-
$\text{TaC}_{0.57}\text{N}_{0.22}$	9.6	2.85	-
$\text{TaC}_{0.42}\text{N}_{0.34}$	10.3	2.75	2.5
$\text{TaN}_{0.78}$	11.4	-	2.4
Uncertainty	± 0.2	± 0.05	± 0.1

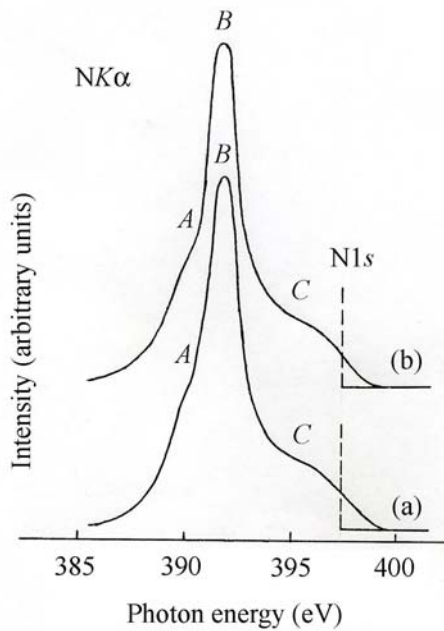


Fig. 4. X-Ray emission $\text{NK}\alpha$ bands of $\text{TaC}_{0.42}\text{N}_{0.34}$ (a) and $\text{TaN}_{0.78}$ (b). The dashed lines indicate positions of the X-ray photoelectron $\text{N}1s$ core-level lines in the specimens under study.

discuss its fine-structure peculiarities). The $\text{CK}\alpha$ and $\text{NK}\alpha$ spectra in the above figures have been normalized so that the intensities of their main peaks “B” are equal. From the above figures it is obvious that, similar to the $\text{TaL}\beta_5$ spectra, for the X-ray emission $\text{CK}\alpha$ and $\text{NK}\alpha$ bands of cubic $\text{TaC}_x\text{N}_{1-x}$ carbonitrides the existence of one low-energy “A” and one high-energy “C” fine-structure peculiarities is also characteristic. We have not observed any changes of shapes (see Figs. 3 and 4) and half-widths (Table 2) of the $\text{CK}\alpha$ and $\text{NK}\alpha$ bands when carbon atoms were substituted for nitrogen atoms in the cubic $\text{TaC}_x\text{N}_{1-x}$ system. The relative intensities of the features “A” and “C” of the $\text{CK}\alpha$ and $\text{NK}\alpha$ bands remain constant within experimental errors for all the cubic $\text{TaC}_x\text{N}_{1-x}$ carbonitrides investigated.

Results of a comparison of the main maxima “B” of

the XES spectra of the cubic $\text{TaC}_x\text{N}_{1-x}$ carbonitrides in a single energy scale are presented in Fig. 5(a). Figure 5(b) represents the similar results from Ref. [9] for the stoichiometric cubic $\text{TaC}_x\text{N}_{1-x}$ carbonitrides. As can be seen from Fig. 5(a), the main peaks “B” of the $\text{TaL}\beta_5$ and $\text{CK}\alpha$ bands in $\text{TaC}_{0.75}$ and those of the $\text{TaL}\beta_5$ and $\text{NK}\alpha$ bands in $\text{TaN}_{0.78}$ coincide with each other. From the above figure it is apparent that, while the main peak “B” of the $\text{TaL}\beta_5$ band shifts by about 0.8 eV away from the Fermi level, E_F , when going from $\text{TaC}_{0.75}$ to $\text{TaN}_{0.78}$, the energy positions of the maxima “B” of the $\text{CK}\alpha$ and $\text{NK}\alpha$ bands do not change with respect to the position of E_F . If one compares Figures 5(a) and 5(b), one finds that the behaviour of the XES bands in $\text{TaC}_x\text{N}_{1-x}$ is very

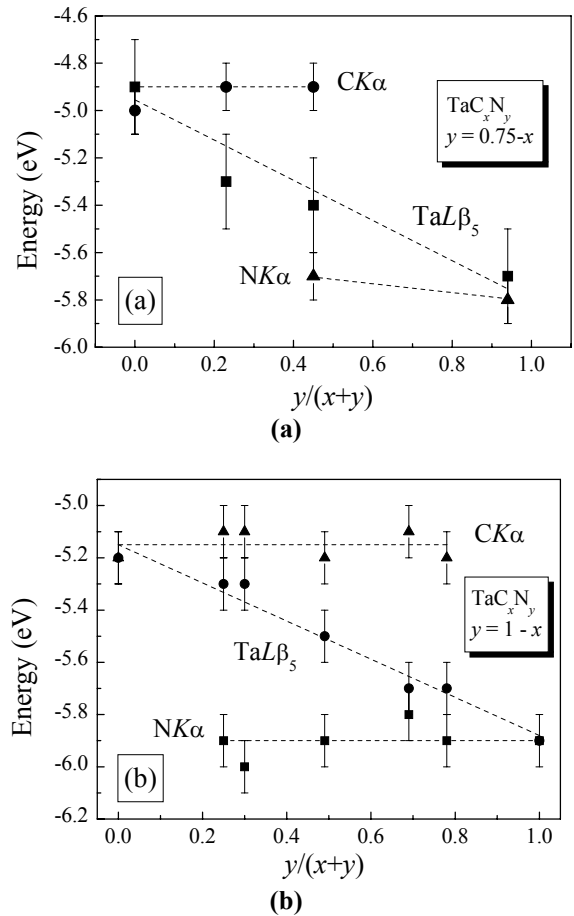


Fig. 5. Dependence of energy positions of the main maxima “B” of the emission bands upon content of carbon and nitrogen atoms in the cubic $\text{TaC}_x\text{N}_{1-x}$ (a) and $\text{TaC}_x\text{N}_{1-x}$ (b) [9] carbonitrides.

similar to that observed previously in Ref. [9] for the stoichiometric cubic $\text{TaC}_x\text{N}_{1-x}$ system. Therefore, like in the stoichiometric $\text{TaC}_x\text{N}_{1-x}$ carbonitrides, in the substoichiometric cubic $\text{TaC}_x\text{N}_{1-x}$ system under investigation, the existence of strong hybridization of the $\text{Ta}5d$ - and $\text{C(N)}2p$ -like states is characteristic. It is necessary to mention that, the $\text{Ta}5d$ - and $\text{C(N)}2p$ -like states are strongly hybridized in substoichiometric cubic tantalum carbides and nitrides too (see, e.g., Refs. [13, 14]).

Figure 5(a) reveals that, the energy positions of the main maxima “B” of the XES CK α and NK α bands remain constant (within experimental errors) when carbon atoms are substituted by nitrogen atoms in the cubic TaC_xN_{~0.75-x} system. In addition, as Figs. 3 and 4 show, no new peculiarities on the shapes of the CK α and NK α bands are formed in the sequence TaC_{0.75} \rightarrow TaN_{0.78}. Taking into account the above facts, one can conclude that the C2p–N2p-like hybridization is absent in the cubic TaC_xN_{~0.75-x} system studied.

Dashed lines in Figs. 3 and 4 representing positions of the binding energies (BEs) of the C1s and N1s core-level electrons, respectively, indicate that, in all the studied TaC_xN_{~0.75-x} compounds, values of the N1s core-level BEs are within (297.5–297.7)±0.2 eV, but those of the C1s spectra are within (283.0–283.1)±0.1 eV. We did not detect any tendency of changes of the N1s and C1s core-level BEs when going from TaC_{0.75} to TaN_{0.78} through the intermediate tantalum carbonitrides. Additionally, the Ta4f core-level BEs increase by about 0.3 eV in the sequence TaC_{0.75} \rightarrow TaN_{0.78} indicating an increase of the positive effective charge on tantalum atoms when carbon atoms are substituted by nitrogen atoms in the cubic TaC_xN_{~0.75-x} system. Therefore, in the above sequence of compounds the ionic component of the chemical bonding increases.

Conclusions

Half-widths of the TaL β 5 bands increase when carbon atoms are substituted for nitrogen atoms in the cubic TaC_xN_{~0.75-x} carbonitrides, while those of the CK α and NK α bands remain constant within accuracy of the experiments. The present XES studies reveal that the mentioned substitution leads to increasing the metallic and decreasing the covalent component of the chemical bonding in the cubic TaC_xN_{~0.75-x} system studied. For all the cubic tantalum carbonitrides studied, the energy positions of the main maxima of the NK α and CK α bands do not change with respect to the Fermi energy, while the main maximum of the TaL β 5 band shifts by about 0.8 eV towards EF when going from TaN_{0.78} to TaC_{0.75}. A strong Ta5d–C(N)2p-hybridization is characteristic for the cubic TaC_xN_{~0.75-x} carbonitrides.

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Рентгенівські емісійні спектри кубічних карбонітридів $TaC_xN_{\sim 0,75-x}$

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Із використанням рентгенівської емісійної спектроскопії (РЕС) досліджено електронну структуру нестехіометричних кубічних карбонітридів танталу TaC_xN_y , де $x+y \approx 0,75$. Для вказаної системи отримано РЕ $TaL\beta_5$ -, $NK\alpha$ - і $SK\alpha$ -смуги. Встановлено, що заміщення атомів вуглецю атомами азоту в системі $TaC_xN_{\sim 0,75-x}$ призводить до зменшення інтенсивності головного максимуму $TaL\beta_5$ -смуги та суттєвого зростання її півширини. Для всіх досліджених нестехіометричних карбонітридів танталу півширини $NK\alpha$ - і $SK\alpha$ -смуг залишаються сталими в межах точності експерименту. Результати експериментального дослідження системи $TaC_xN_{\sim 0,75-x}$ вказують на те, що заміщення атомів вуглецю азотом призводить до зростання металічної та зменшення ковалентної складових хімічного зв'язку. Для всіх сполук досліджуваної системи $TaC_xN_{\sim 0,75-x}$ характерна наявність сильної гібридизації $Ta5d$ - і $C(N)2p$ -станів.