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Abstract

We used *ab initio* calculations to systematically investigate the adsorption of atomic oxygen on non-stoichiometric polar TiC(111) and Ti_xC_y(111) with Ti/C vacancies surface simulating its potential tructions with laser radiation. Local atomic structures of O/Ti_xC_y(111) polar surfaces were studied in the selected models as well as their thermodynamic and electronic properties based on the density functional theory. The bond length and adsorption energy for various reconstructions of the O/Ti_xC_y(111) surface atomic structure were established. We also have examined the effects of oxygen adsorption upon the band and electron spectra of TiC(111) surface in its various reconstructions. We have established a correlation between the energy level of flat bands (-5.1 eV and -5.7 eV) responsible for the doublet of singular peaks corresponding to partial densities of oxygen $2p$ electrons and the

energy of oxygen adsorption in non-stoichiometric O/TiC$_y$(111) systems. Effective charges of the oxygen atom and the titanium and carbon atoms nearest to it were identified in the examined adsorption models. We have established charge transfer from titanium atom to oxygen and carbon atoms determined by the reconstruction of local atomic and electronic structures. Charge transfer correlates with the electronegativity values of titanium, carbon, and oxygen atoms, and chemisorption processes. Calculated values of structural parameters in the studied models of ultrathin O/TiC(111) and O/Ti$_x$C$_y$(111) films correlate well with experimental findings and other theoretical results.

Key words: Titanium carbide; Density functional theory; Electronic properties; Adsorption; Vacancy.

1   Introduction

Titanium carbide remains a widely popular object of scientific research as a candidate for high tech, structural and functional applications including such areas as metallurgy, automobile and aircraft construction, space, electronics, medicine, coatings in nuclear reactors, due to its outstanding properties, such as extremely high melting temperature and hardness, durability, electric and thermal conductivity [1–5]. Study of the atomic structure of titanium carbide surface represents an essential aspect in the understanding of its material properties [6]. Potential opportunities existing for tuning of material surface properties in the process of crystal growth appear to be important, for example, during surface nanostructuring with laser radiation [7]. The process involves melting, high-gradient cooling, and crystallization of the surface layer, which can be regulated using variation of energy density and laser pulse duration [8, 9]. Chemical activity of (111) surface towards

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gas adsorption is considerably higher in comparison with (001) surface [10]. Therefore we consider the (111) titanium carbide surface here as a model surface during analysis of the gas-surface interaction in the process of surface nanostructuring with laser radiation. Experimental and theoretical study of TiC(111) atomic structure shows that the polar surface is terminated by titanium atoms [10–12].

Structure analysis using He+ ion scattering spectroscopy shows [13] that oxygen-adsorbed TiC(111) polar surface can have atomic structure of two types: 1×1 and $\sqrt{3}\times\sqrt{3}$ $R30$. At room temperature, adsorption of atomic oxygen forms a 1×1 structure on TiC(111) surface [14]. Heating the TiC(111)-1×1-O structure to 1000 ^{0}C results in its reconstruction into the TiC(111)-$\sqrt{3}\times\sqrt{3}$ $R30$-type [14, 15]. Examination of TiC(111) surface with adsorbed oxygen using scanning tunneling microscopy at atomic resolution has demonstrated [15] that oxygen atoms may occupy hollow sites without carbon atoms below (in the second layer), i.e. fit the so-called face-centered cubic (FCC) arrangement.

Study of chemical adsorption represents an essential step in order to understand the nature of interaction between the material surface and the environment [12, 16]. DFT-based systematic study of chemisorption of atoms from the first three periods of the periodic system of elements on TiC(111) polar surface have been considered [12]. The research facilitated better understanding of the nature of interaction between adsorbate and the substrate. Among the processes of TiC(111) surface nanostructuring with laser in air, oxygen adsorption should be studied first of all. Within the framework of DFT calculation was shown that maximum value of the energy of oxygen adsorption on polar TiC(111) surface in FCC arrangement is 8.75 eV/atom [12]. Oxygen position on hexagonal close-packed TiC(111) surface is estimated as metastable while bridge and Ti-top sites appear to be intermediate during the diffusion of atomic oxygen from HCP to FCC formation [12].

Reconstructions of TiC(111) atomic surface are manifested in the electron

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spectrum of titanium and carbon subsystems of the top layer similarly to the O/TiC(001) system [17]. Electronic structure (1×1) of oxygen-adsorbed layer on TiC(111) surface was studied using angle-resolved X-ray photoemission electron microscopy [14]. It was demonstrated that oxygen $2p_{x,y}$ orbitals are most essential for chemisorption processes on TiC(111) surface compared with the $2p_z$ orbital. They stabilize the surface with adsorbed atoms through hybridization with titanium $3d$ orbitals [14]. DFT study of the atomic, electronic structure, and thermodynamics of TiC (111) surface with adsorbed atoms from the first three periods of the periodic system of elements [12]. In particular, a chemisorption model was suggested on the basis of calculated electronic structures.

In recent years, many authors have been used the standard DFT to study adsorption with defects [18–20]. However, the character of oxygen adsorption on low defect TiC(111) surface with distributed Ti and C vacancies and substitutional and interstitial defects remains unexplored yet. The above allows to assume that the effects of oxygen adsorption on non-stoichiometric substrates, which control thermodynamic and electronic properties of a O/Ti$_x$C$_y$(111) type system are insufficiently studied so far. Therefore, in present study, we used the density functional theory (DFT) to study the adsorption of atomic oxygen, structural, and electronic electronic and thermodynamic properties of stoichiometric O/TiC(111) and non-stoichiometric O/Ti$_x$C$_y$(111) systems with the focus on their influence on the nanostructuring of ultrathin film surface with laser radiation. Our calculations are in good agreement with other theoretical and experimental results for stoichiometric O/TiC(111) system. We also considered the surface as an ideal infinite slab without terraces and steps. The generation of the terraces, the effects of number and distribution of defects on electronic structure and thermodynamic properties were not studied in this work. This study is in progress and will be the subject of our next communication.
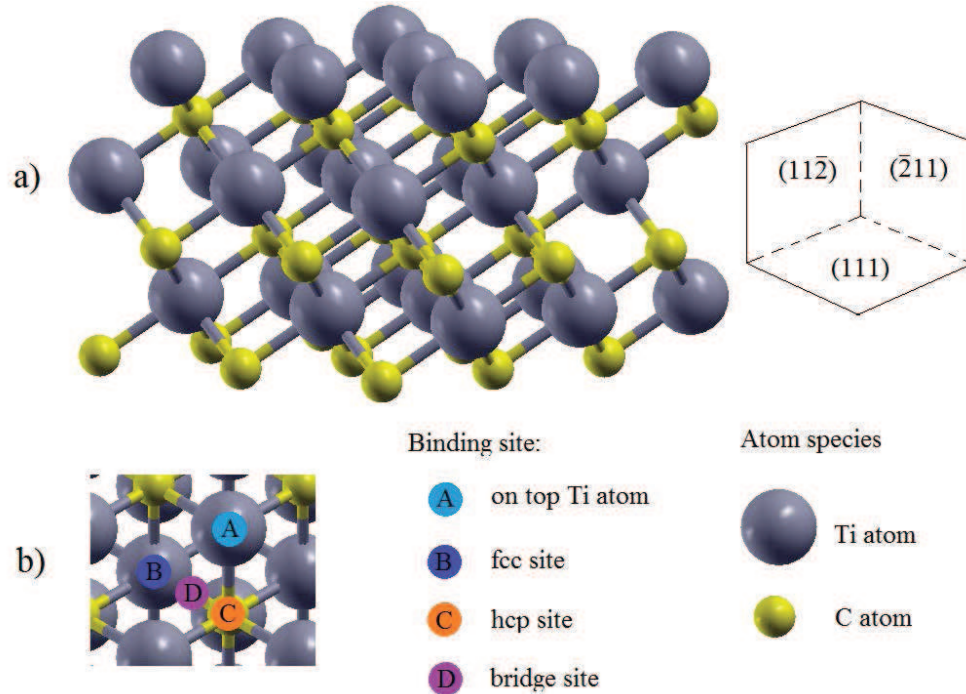
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2   Model and method

Fig. 1. Calculated TiC(111) surface (a) and binding sites of oxygen atom (b) on TiC(111) surface (top view)

In this work, we performed self-consistent DFT calculations to determine the total energy using pseudopotential approximation (Quantum Espresso software) [21]. The exchange-correlation energy is described by the generalized gradient approximation of (PBE-GGA) [22, 23]. Brillouin zone sampling is performed using $8 \times 8 \times 1$ Monkhorst-Pack k-points meshes for (111) surface calculations. The plane-wave cutoff energy in our calculations is 400 eV, which assures a total-energy convergence of 10^{-6} eV/atom. To describe the interaction of valence electrons with the core, we used Vanderbilt ultrasoft pseudopotentials. The pseudopotentials were generated based on the most reliable Troullier-Martins scheme [24]. The following electronic configurations were used for the atoms: Ti $-$ [Ar]$3d^2 4s^2$, O $-$ [He]$2s^2 2p^4$, C $-$ [He]$2s^2 2p^2$. [Ar] and [Ne] states attributed to the core.

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Theoretical model of the O/TiC(111) system under study is based on three-dimensional periodic slab scheme. Fig. 1a demonstrates a fragment of the TiC(111) slab, Fig. 1b indicates potential positions of the adsorbate atom. We have examined six various configurations of oxygen atom placement on a TiC(111) slab: (A) - O atom was placed above the Ti atom of layer 1 (layer 1 is the top layer) (on top Ti atom); (B) - O atom placed above the Ti atom of layer 3 (FCC hollow); (C) - O atom placed on C atom of layer 2 (HCP hollow); (D) - O atom placed in the bridge site; (A$_{vac}$) - above the surface vacancy of the Ti atom of layer 1; (C$_{vac}$) - above the vacancy of the C atom of layer 2.

The energy of oxygen atom adsorption in the O/TiC(111) system was determined as: $E_{ads} = E_{tot} - E_{ref} - E_0$, where E_{tot} stands for the total energy of the O/TiC(111) system, E_{ref} is total energy of the relaxed surface without oxygen, and E_0 is the energy of an isolated oxygen atom. Lowdin population analysis [25] allowed to determine the effective charges of the oxygen atom as well as the surface titanium and carbon atoms nearest to it in six O-adsorbed O/Ti$_x$C$_y$(111) models. In present work, we performed convergence tests to determine the sufficient number of layers. The results have shown that model with three double layers in the slab gives an error in determining the interplanar distance of less than one percent.

3 Results and discussion

3.1 Atomic structure and adsorption of oxygen on Ti$_x$C$_y$(111) surfaces

To study the adsorption of oxygen atom on non-stoichiometric atomic configurations of 2D O/Ti$_x$C$_y$(111) surfaces, we calculated relaxation for a top double atomic layer (Ti, C) of a titanium carbide slab with adsorbate. Initially, oxygen atom was placed 2 Å away from the TiC(111) surface. Two lower layers of the

Table 1

The established bond length between the oxygen atom and atoms of stoichiometric and non-stoichiometric TiC(111) surface

Bond length d, Å	O atom position on TiC(111) and Ti_xC_y(111)surfaces					
	A	B	C	D	A, Ti_{vac}	C, C_{vac}
d_{Ti-O}	1.711	1.972	2.009	1.972	3.129	1.943
d_{Ti-C}	2.090	2.056	2.009	2.056	1.986	2.119

2D O/Ti_xC_y(111) system were "frozen". Relaxation was carried out until the sum total of all forces in the system was reduced below 0.001 eV/Å. Atomic structure of a three-layer slab with oxygen for six various configurations of the O/Ti_xC_y(111) system after relaxation is shown in Fig. 2. We established equilibrium parameter values for the lattices, atomic sites of the oxygen, carbon atoms of the top TiC(111) layer. Established bond length values between the oxygen atom and atoms of stoichiometric and non-stoichiometric TiC(111) slab are summarized in Table 1.

DFT calculations of interplanar spacing for clean (111) surface agreement well with known date in Ref. [12]. In particular, we calculated total DOS for TiC using standard DFT and DFT+U method. It is shown that the results of our DFT-calculations are in good agreement with experimental data [26]. The distance that appears between carbon and titanium atom layers in the (111) direction has the average value of d_1 = 1.041 Å. The estimate agreement well with other theoretical and experimental results [12, 27]. The distance between the second carbon layer and the third titanium layer reached d_2 = 1.354 Å, which also agreement with DFT calculation in Ref. [12]. Variations of these distances in different reconstructions of the TiC(111) atomic surface structure in the presence of adsorbate represented by an oxygen atom pose certain interest. Distance values d_1 and d_2 for various atomic configurations of the O/TiC(111) surface are offered in the Table 2 in comparison

with clean TiC(111) surface and partially describe the local atomic structure. In the presence of adsorbate, for example, above the titanium atom (in site A), the distance decreases to $d_1 = 1.037$ Å. However, in other binding sites we observe increase of the d_1 distances by 2.5% simultaneously with decrease of d_2 distances by 1.1%.

a) A site

b) A site with Ti vacancy

c) B site

Ti atom
C atom
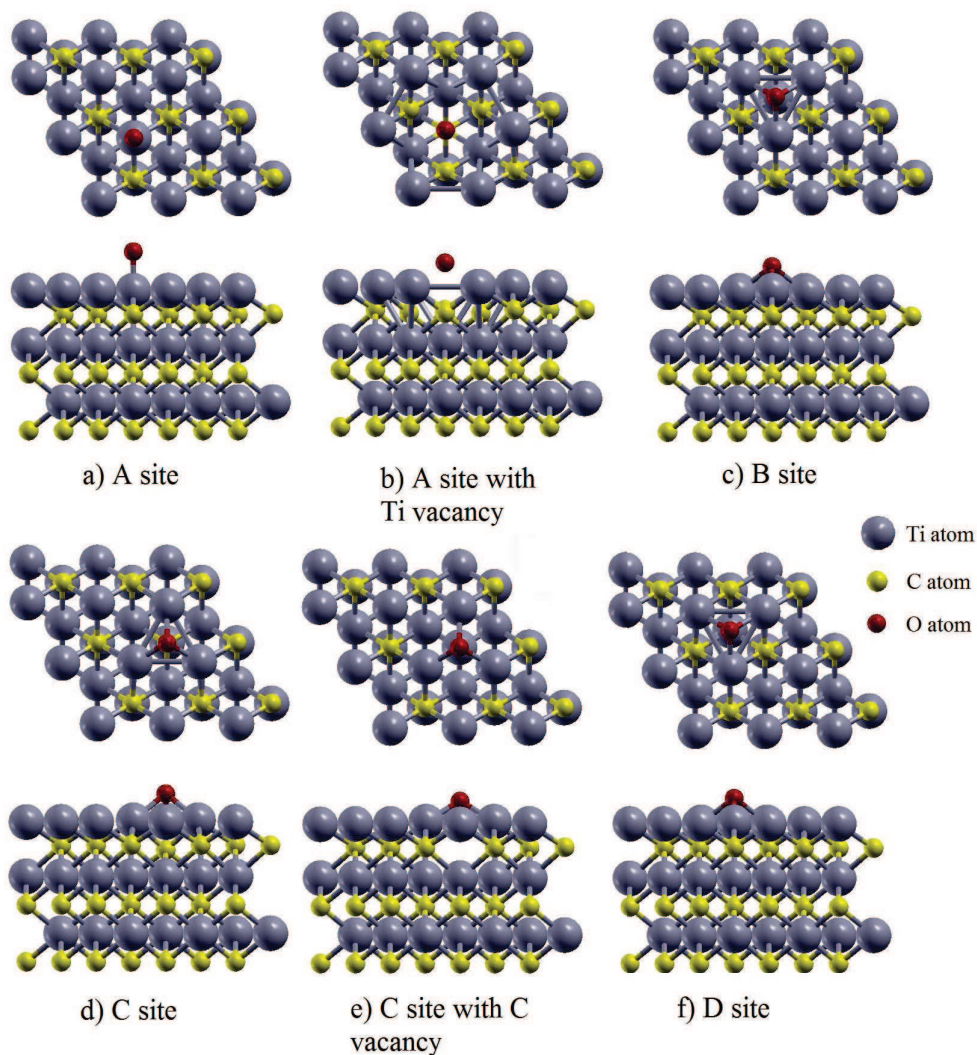O atom

d) C site

e) C site with C vacancy

f) D site

Fig. 2. Supercells of the adsorption model (a, c, d, f) for the O/TiC(111) system and (b, e) O/Ti$_x$C$_y$(111) system after relaxation (side and top view)

Summarizing the data of Table 1, we can point out considerable rearrangement of the local atomic structure determined by the binding site of adsorbate on

Table 2

Vertical distance between the adsorbate and the first Ti layer d_0 (Å), first Ti layer and C layer d_1 (Å), C layer and the third Ti layer d_2 (Å), O atom adsorption energy for binding sites on TiC(111) and Ti_xC_y(111) surfaces E_{ads} (eV/atom), total energy of the substrate with oxygen E_{tot} (Ry), total energy of the original substrate surface E_{ref} (Ry), and work function Φ (eV)

Phase	d_0	d_1	d_2	E_{ads}	E_{tot}	E_{ref}	Φ
TiC(111)	-	1.041	1.354	-	-	-3456.5663	4.84
O/TiC (A)	1.709	1.037	1.356	-8.376	-3488.7557	-3456.5663	5.02
O/TiC (B)	1.105	1.069	1.349	-10.676	-3488.9249	-3456.5663	4.69
O/TiC (C)	1.214	1.065	1.347	-9.851	-3488.8641	-3456.5663	4.72
O/TiC (D)	1.105	1.069	1.349	-10.676	-3488.9249	-3456.5663	4.69
O/TiC (A-Ti_{vac})	1.057	1.053	1.346	-5.140	-3371.6716	-3339.7200	4.61
O/TiC (C-C_{vac})	0.971	1.064	1.344	-11.055	-3477.3891	-3445.0028	4.69

the surface of 2D TiC(111) surface. For example, deformation of the Ti-C bond length in the A and C sites, and also in the B and D sites reached 3.5% and 5.0%, respectively relative to the similar bond length 2.165 Å [28] in a 3D TiC crystal . Identical length of Ti-O and Ti-C bonds in the B and D binding sites of O atom on TiC(111) surface is explained by relaxation, which results in relocation of the O atom from D to B. Deformation of the Ti-C bond length in the A and C sites in low defect of non-stoichiometric Ti_xC_y(111) films was 8.3% and 2.1% respectively relative to a 3D TiC crystal. O atom adsorption in binding sites on 2D TiC(111) films results in considerable change of interplanar spacing between the top layers of titanium and carbon atoms (see Table 2). The character of rearrangement observed in the atomic structure of ultrathin TiC surface and related to the adsorption of atomic oxygen on their surface may be understood upon close study of thermodynamics and electronic structure in each of the examined oxygen adsorption models.

For six examined configurations of oxygen atom placement on ultrathin TiC(111) and Ti_xC_y(111) slabs, we obtained the total energy values E_{tot} for the oxygen atom and the surface, total energy of clean surface E_{ref} , adsorption energy, and work

function Φ also offered in the Table 2. Low defect surfaces of ultrathin Ti$_x$C(111) and TiC$_y$(111) slabs are metastable. However, their metastability decreases considerably with adsorption of atomic oxygen placed above the vacancies of titanium and carbon atoms in the binding sites A and C. Binding sites and D are equivalent for the oxygen atom in respect of the total energy E_{tot}. Total energy preference for the so-called FCC arrangement (here, site B) correlates well with theoretical [12] and experimental results [13, 27] for oxygen adsorption on TiC(111). Maximum adsorption energy is observed when the oxygen atom is located above the carbon vacancy (site) reaching -11.055 eV/atom. In non-stoichiometric ultrathin 2D TiC$_y$(111) films high adsorption energy indicates high chemical reactivity of carbon vacancies of this type towards oxygen. When the oxygen atom occupies site C (Fig. 2e), the distance between the layers of titanium and carbon atoms in the top binary layer increases by 1.2% compared with clean TiC(111) surface. In this configuration local atomic structure of the surface undergoes considerable reconstruction (see Table 1). During relaxation the oxygen atom initially placed at the distance of 2 Å from TiC$_y$(111) surface shifts in the direction of the carbon atom vacancy to the distance of 0.97 Å. Bond length between oxygen and titanium atoms resulting from relaxation is d_{O-Ti} = 1.94 Å thus defining the chemical bond character. In that site the effective charge accumulated by the oxygen atom is -0.79e, titanium atom +0.92e, carbon atoms -1.12e. High energy of oxygen atom adsorption is determined in our opinion by the change in the local atomic structure and the number of titanium atoms participating in the interaction with the oxygen atom. Such carbon vacancy may appear upon laser action affecting the surface of ultrathin titanium carbide films, which may "lose" carbon atoms in conformity with the physics views in Ref. [29]. As DFT calculation has demonstrated, the process is accompanied with a decrease of the Ti-C bond length to d_{Ti-C} = 2.12 Åfor surface atoms.

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Low defect surface of ultrathin $Ti_xC(111)$ slabs demonstrates considerably lower chemical reactivity of titanium vacancies of this type towards oxygen. Obtained estimate of the adsorption energy E_{ads} = -5.140 eV/atom in this adsorbate position appears to be 1.6 times lower compared with stoichiometric TiC(111) slabs in the same position (see Table 2). In this position total energy of the $O/Ti_xC(111)$ system is 117.08 Ry higher than the same of the O/TiC(111) system thus indicating its metastability. However, surface nanostructuring with laser makes such position of the oxygen atom quite feasible. In non-stoichiometric $Ti_xC(111)$ with the oxygen atom located above the titanium atom vacancy (in the position A, Fig. 2b) the distance between the layers of Ti and C atoms in the top layer increased considerably in comparison with the stoichiometric system (see Table 2). In this configuration local atomic structure of the top layer undergoes considerable reconstruction. During relaxation the oxygen atom originally placed at 2 Å from the surface shifts towards the Ti atom vacancy (Fig 2b, top view). Vertical distance between atomic oxygen and the plane containing Ti atoms was d_{O-Ti}= 1.057 Å. The length of bonds between the O atoms and Ti (C) atoms was d_{O-Ti} = 3.129 Å and d_{O-C} = 1.99 Å . In that binding site the effective charge accumulated by the oxygen atom is -0.85e, titanium atom +1.0e, carbon atoms -0.95e. We should note that titanium and carbon atoms form a strong covalent bond with significant ionic contribution. There is a strong electrostatic attractive interaction between titanium and carbon atoms that causes shifting of the oxygen atom towards the titanium atom's vacancy (see Fig. 2b, top view). As our DFT calculations have demonstrated, this position of the oxygen atom on $Ti_xC(111)$ surface corresponds to an adsorption energy value 1.8 times higher than on $Ti_xC(001)$ surface [17]. Decrease in the energy of oxygen adsorption on $Ti_xC(111)$ surface compared with TiC(111) surface is determined by the change in geometry and the number of atoms participating in surface interaction with the oxygen atom in this binding site.

The energy of oxygen atom adsorption on stoichiometric TiC(111) surface in position according to our estimates is E_{ads}= -8.376 eV/atom, which is 1.6 times higher than on low defect $Ti_xC(111)$ surface. We have to note also that the length of the bond between oxygen and titanium atoms in that position was d_{Ti-O}= 1.71 Å, which is 1.8 times smaller compared with $Ti_xC(111)$ surface. Such bond length allows chemisorption processes accompanied by formation of a TiO_x compound. The assumption is confirmed by the results of [30] demonstrating that at temperatures above 300 dissociation of oxygen molecules and formation of a TiO_x oxide is observed. The mentioned change in the local atomic structure should manifest itself in the electron energy spectrum of surface titanium and oxygen atoms in the first configuration of the O/TiC(111) system. The adsorption energy of this atomic surface configuration appears to be 1.3 times higher than earlier findings of -6.5 eV/atom [12]. Increase of the adsorption energy is determined by the change of the local atomic structure in this oxygen adsorption model.

When the oxygen atom is in position C (on top of the carbon atom of layer 2) on stoichiometric TiC(111) surface, adsorption energy reaches considerable value of E_{ads} = -9.851 eV/atom. In ultrathin 2D TiC(111) films, high adsorption energy value indicates high chemical reactivity towards oxygen in this configuration type. As shown above, the distances between the layers of titanium and carbon atoms of three upper layers change by 1.7 % on the average compared with clean TiC(111) surface; the fact determines considerable reconstruction of the local atomic surface structure. Relaxation results in oxygen atom placement at 1.21 Å from the surface. Bond length between oxygen and titanium atoms is d_{O-Ti} = 2.01 Å, thus defining the character of chemisorption processes. In that site the effective charge accumulated by the oxygen atom is -0.80e, titanium atom +1.01e, carbon atoms -1.02e. High energy of oxygen atom adsorption is determined in our opinion by the change in the local atomic structure and the number of titanium atoms participating

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in the interaction with the oxygen atom. In this model of atomic oxygen adsorption, surface reconstruction is accompanied with a decrease of the Ti-C bond length to d_{Ti-C} = 2.09 Åfor surface atoms.

In case of oxygen atom placement above the titanium atom of layer 3 (FCC hollow, position B, Fig. 2c), the distance between the layers of titanium and carbon atoms increased insignificantly to d_1= 1.07 Å, while the d_2 distance decreased to 1.35 Å. During relaxation the oxygen atom shifts in the direction of the TiC(111) surface forming the distance of d_0 = 1.11 Å. In that site the effective charge accumulated by the oxygen atom is -0.78e, titanium atom +1.05e, carbon atoms -1.09e. According to our DFT calculations, the adsorption energy of oxygen atom in binding sites B and D reached E_{ads}= -10.676 eV/atom, which is 1.3 times higher than the data in Ref. [12]. As DFT calculation has demonstrated, this model of oxygen adsorption is accompanied with a decrease of the Ti-C bond length to d_{Ti-C} = 2.06 Å for surface atoms.

Examination of O/Ti$_x$C(111) and O/TiC$_y$(111) atomic surface configurations in comparison with O/TiC(111) has demonstrated that, first, oxygen atom adsorption on ultrathin 2D TiC(111) films results in considerable rearrangement of their atomic structure; second, that the energy of oxygen atom adsorption on polar (111) surface is 1.5 times higher than on nonpolar (001) surface [12, 17]. The results of DFT-calculated effective charges of the oxygen atom and its nearest surface titanium and carbon atoms in the examined configurations of O/Ti$_x$C$_y$(111) and O/TiC(111) systems are provided in the Table 3. Their analysis allows to note the charge transfer from the titanium atom to the oxygen and carbon atoms adding ionic contribution to the covalent bond. Charge transfer is in our opinion determined by considerable difference existing between Pauling electronegativity values of titanium (1.5X), oxygen (2.55X), and carbon (3.44X) atoms [31]. The mentioned deformation in the local atomic structure should manifest itself in the electron energy

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Table 3

Effective charges of the interface atoms for various binding sites of the oxygen atom on TiC(111) and Ti_xC_y(111) surfaces

Phase	Effective charge, e		
	Ti	C	O
TiC(111)	0.887	-1.111	-
TiC-O (A)	1.059	-1.139	-0.703
TiC-O (B)	1.045	-1.093	-0.782
TiC-O (C)	1.013	-1.023	-0.802
TiC-O (D)	1.045	-1.093	-0.782
TiC-O (A, Ti_{vac})	0.999	-0.952	-0.851
TiC-O (C, C_{vac})	0.917	-1.124	-0.792

spectrum of surface titanium, carbon, and oxygen atoms in the configurations of the O/Ti_xC_y(111) system examined above.

3.2 Electronic structure of the O/Ti_xC_y(111) system

To understand the character of binding of oxygen atom chemisorbed in the O/Ti_xC_y(111) system, we calculated the band structure for six various configurations of the O/Ti_xC_y(111) and O/TiC(111) systems after relaxation. Band structure of these systems demonstrated in Fig. 3 reveals dependence upon the local atomic structure specific to each configuration, and corresponds to the metallic type. Total and partial electron density states also shown in Fig. 3 characterize the peculiarities of chemical bond with adsorbed oxymetallicgen atom on TiC(111) surface.

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We should note hybridization between C$2p$, O$2p$ orbitals and Ti$3d$ orbitals. It is indicated by matching energy of the peaks of occupied states in O, C, and Ti atoms (Fig. 3). In particular, the energy level of primary peak on the total DOS curve is within a narrow (1.7 ÷ 2.3) eV interval of energies. The peak is mostly formed by Ti$3d$ states of the surface layer with a small contribution of C$2p$ and O$2p$ states.

Several regularities should be noted in the band structure of non-stoichiometric O/Ti$_x$C(111) configuration in position A shown in Fig. 3b. In particular, the mentioned hybridization of O$2p$ orbitals with Ti$3d$ orbitals evidently plays a significant role in the formation of a broad (1.9 ÷ 2.3) eV peak of unoccupied electronic states in O/Ti$_x$C(111). The +0.07 eV peak of the total DOS curve in the electron energy spectrum is formed by unsaturated bonds of oxygen, carbon and titanium atoms on the surface of the O/Ti$_x$C$_y$(111) system. The peak at the Fermi level is mostly formed by contributions from Ti$3d$ states in the surface layer with a small added contribution of C$2p$ and O$2p$ states. This maximum of total DOS is present in the energy spectrum of all TiC(111) configurations with or without adsorbate, which we have examined. Bonding states are associated with a tight covalent bond characterized by hybridization of Ti$3d$-C$2p$ orbitals in the -2.5 ÷ -3.8 eV interval of energies and defining the main properties of adsorbing TiC(111) surface. Rearrangement of local atomic structure caused by nonstoichiometry and adsorption of atomic oxygen results in a change of the electron energy spectrum. In particular, the electronic structure is characterized by Ti$3d$-C$2p$-O$2p$ hybridization in the energy intervals of 0 ÷ -0.7 eV and -1.5 ÷ -2.3 eV, as illustrated by the band structure and partial DOS in Fig. 3b. Statistical weight of partial states should be specifically noted for the electrons participating in hybridization of Ti$3d$-C$2p$-O$2p$ orbitals. Analysis of Fig. 3b allows to conclude that the regions overlapping between O$2p$, Ti$3d$ and C$2p$ orbitals are insignificant, in correlation with low value of the O-adsorption energy (-5.14 eV/atom). The latter is practically related to the ab-

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sence of partial DOS of oxygen in the -2.5 ÷ -3.8 eV energy region representing the main part of occupied partial DOS of titanium and carbon atoms. Comparison of the electronic structure of this atomic configuration to a stoichiometric O/TiC(111) in position (Fig. 3) reveals the opposite case. Fig. 3a shows that the main part of partial DOS of oxygen, carbon and titanium atoms is in the -2.2 ÷ -4.0 eV interval of energies. The energy region exhibits primary peaks of partial densities of states of titanium, carbon, and oxygen.

We should note that the regions overlapping between $O2p$, $Ti3d$ and $C2p$ orbitals are significant, in correlation with high value of the oxygen atom adsorption energy in the binding site A on TiC(111) surface. Hybridization of $Ti3d$-$C2p$-$O2p$ orbitals demonstrated in Fig. 3a is specific to the entire -2.2 ÷ -4.0 eV energy interval. Statistical weight of partial states of the electrons in O, C, and Ti atoms participating in the hybridization of $Ti3d$-$C2p$-$O2p$ orbitals is higher in case of stoichiometric TiC(111) surface. We attribute specifically to the aforementioned circumstance the high value of oxygen adsorption energy in position A (Ti-top) compared with the position above the titanium vacancy (Ti_{vac}-top) .

Electronic structure has some peculiarities in case of non-stoichiometric O/TiC$_y$(111), where oxygen atom occupies the position above the carbon atom vacancy in the second layer of the lattice (Fig. 3d). Bond length in that configuration is d_{O-Ti} = 1.94 Å; the fact determines a tight chemical bond between the atoms of oxygen and their nearest titanium neighbors. In particular, the chemical bond energy of oxygen atom on TiC$_y$(111) surface is E_{coh} = 5.7 eV. We associate the value of bond energy E_{coh} with the positions of two main peaks reflecting the states of oxygen $2p$ electrons in the -5.1 eV and -5.7 eV interval of energies (Fig. 3d). The main part of partial DOS of carbon and titanium atoms is in the -1.9 ÷ -3.7 eV interval of energies. It determines the basic properties of the O/TiC$_y$(111) system. The energy region demonstrates a wide band of partial DOS of titanium and carbon. The -4.5 ÷ -5.7
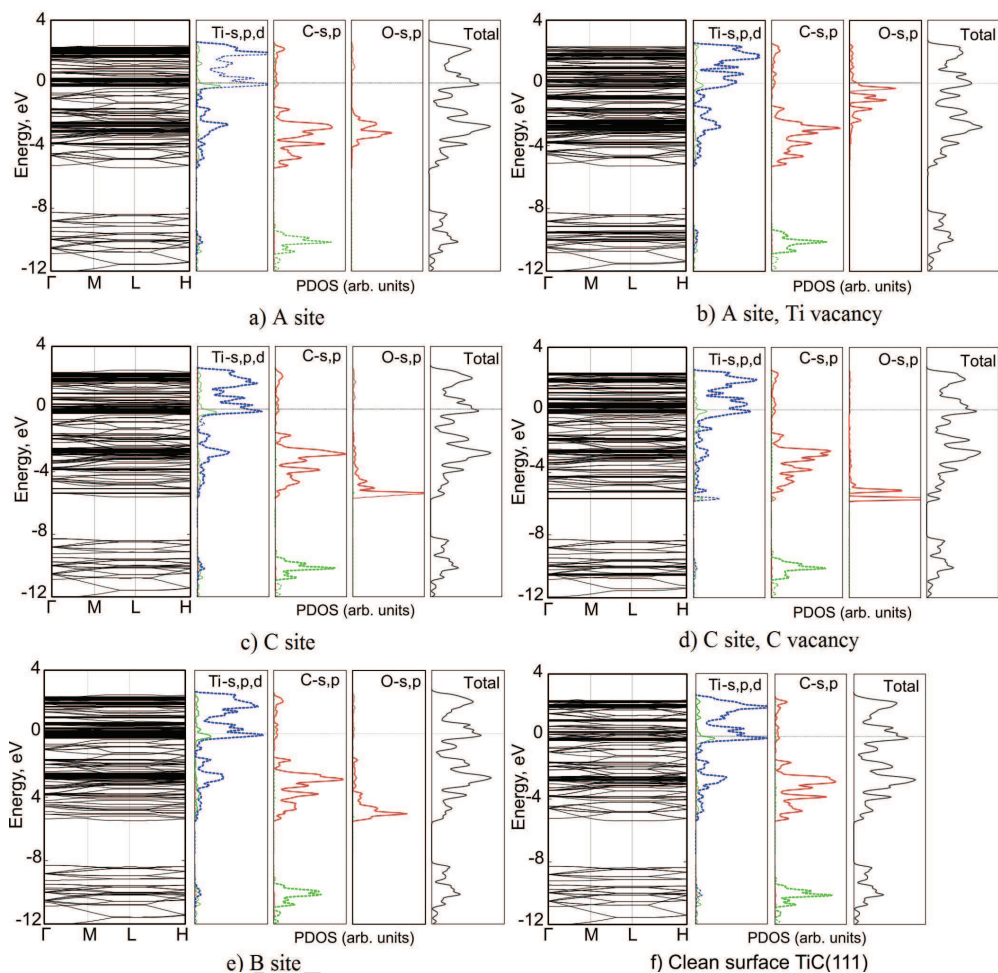
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Fig. 3. DFT calculation of the band structure, partial DOS for titanium, carbon and oxygen atoms, and total DOS in the binding sites on titanium carbide (111) surface: (a, c, e) - stoichiometric and (b, d) non-stoichiometric O/TiC and O/Ti$_x$C$_y$ respectively, (f) - clean TiC surface. Partial DOS: s - green, p - red, d - blue, and total DOS - black, respectively)

eV interval of energies shows mixing of partial states of electrons in O, C, and Ti atoms, which plays a decisive role forming the corresponding chemical bond and adsorption energy. The energy of oxygen atom adsorption on non-stoichiometric TiC$_y$(111) surface (Fig. 2e) has maximum value of E_{ads} = -11.06 eV/atom. The increase of the E_{ads} value in this configuration correlates with two flat bands (-5.1 eV and -5.7 eV) emerging in the band spectrum and responsible for the doublet of

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primary peaks reflecting the O2p states. We have to note that the configurations examined earlier exhibited no flat bands of the oxygen atom in the mentioned energy interval.

However, a similar correlation is observed for stoichiometric O/TiC(111) configuration with the oxygen atom in positions B and C (Fig. 2c, d). In particular, Fig. 3e shows in the band spectrum within the -4.6 ÷ -5.0 eV interval of energies two flat bands responsible for the doublet structure of partial densities of O2p electrons. In the electron energy spectrum of this atomic configuration (Fig. 2c), these two flat bands are located practically in the same interval of energies as in the previous configuration (Fig. 2e). Therefore the energy of atomic oxygen adsorption in that configuration is high (-10.68 eV/atom). The principal regularity for the electronic structure of stoichiometric O/TiC(111) configuration in position C (Fig. 2d) is in the existence of a correlation similar to the one described above. Fig. 3c shows in the band spectrum three flat bands with the bond energy of -4.9 eV, -5.1 eV, and -5.3 eV corresponding to singular peaks of partial densities of O2p and C2p states. These peaks characterize hybridization of C2p-O2p orbitals, with fractional mixing of Ti3d orbitals. e attribute the existing hybridization between C2p, O2p orbitals and Ti3d orbitals in titanium on (111) surface to the matching peaks of occupied states of O, C, and Ti atoms at -0.4 eV. The main part of partial DOS of carbon and titanium atoms is in the -2.1 ÷ -4.9 eV interval of energies. It determines the basic properties of the O/TiC(111) system. The energy interval exhibits hybridization between C2p-Ti3d orbitals. The -2.1 ÷ -4.9 eV interval of energies shows a slight mixing of partial states of electrons in O, C, and Ti atoms, which is caused by adsorption. Average value of the bond energy for oxygen atom in position C is E_{coh} = 5.2 eV.

Hence we can conclude that the revealed correlation between position of the noted flat bands and adsorption energy is important for understanding of the char-

acter of oxygen atom adsorption on a non-stoichiometric TiC(111) surface. We should note that the atomic and electronic structures of stoichiometric O/TiC(111) configuration in the bridge position (Fig. 2f) are identical to the configuration of that system in position (Fig. 2c).

Electronic properties of stoichiometric and low defect O/TiC(111) and O/Ti$_x$C$_y$(111) systems in different surface reconstructions can be understood based on the analysis of work function provided in Table 2. Work function was calculated as the difference between the average vacuum electrostatic potential and Fermi energy similarly to [16]. Calculated work function values for clean polar TiC(111) surface are Φ = 4.84 eV, and thus agreement with known data of Φ = 4.7 [10]. Evidently, work function in low defect ultrathin O/Ti$_x$C$_y$(111) films becomes lower by $\Delta\Phi$ = -0.19 eV on the average relatively to clean TiC(111) surface. In stoichiometric O/TiC(111) the work function decrease for positions B, C, and D was $\Delta\Phi$ = -0.14 eV, for position A (Ti-top) the work function increased by $\Delta\Phi$ = 0.18 eV. Better understanding of the change in electronic properties requires an estimate of electron transfer between oxygen atom and its nearest neighbors (Ti and C atoms). Electron transfer is determined by the local atomic structure and high electronegativity of oxygen compared with titanium and carbon. Table 3 contains the effective charges of the oxygen atoms and their nearest titanium and carbon atoms. Analysis of the data in Table 3 allows to estimate electron transfer in the surface layer of the O/Ti$_x$C$_y$(111) and O/TiC(111) systems.

4   Conclusion

Thus, we used *ab initio* calculations based on the DFT method to study the adsorption energy of atomic oxygen, local atomic structure, thermodynamic, and electronic properties of non-stoichiometric O/Ti$_x$C$_y$(111) systems in various sur-

face reconstructions in comparison with stoichiometric O/TiC(111) systems. We have examined six reconstructions of TiC(111) surface determined by the scheme of atomic oxygen placement on it. We have performed DFT calculations of the adsorption energy for atomic oxygen on non-stoichiometric O/Ti$_x$C$_y$(111) surface in various configurations simulating potential reconstructions of the surface with laser radiation. Adsorptions of atomic oxygen on low defect Ti$_x$C$_y$(111) surfaces in various binding sites results in considerable rearrangement of the local atomic structure and the band spectrum, and the rearrangement determines the total energy of atomic configurations are considered. A correlation between the energy level of flat bands in the -5.1 eV and -5.7 eV energy regions responsible for the doublet of singular peaks corresponding to partial densities of O2p states, and the energy of oxygen adsorption in low defect O/TiC$_y$(111) systems are established. It should be mentioned that a similar correlation is also observed in stoichiometric O/TiC(111) configuration with the oxygen atom placed above the carbon atom of the second layer and in position B. The band spectrum within the -4.6 ÷ -5.3 eV interval of energies contains two (three) flat bands responsible for the doublet (triplet) structure of partial densities of O2p states. The revealed correlation plays an important role in the understanding of the character of oxygen atom adsorption onto non-stoichiometric TiC(111) surface.

We have established charge transfer from titanium atom to oxygen and carbon atoms. In our opinion, the charge transfer is caused by the reconstruction of local atomic and electronic structures; it correlates with the electronegativity values of the atoms under study. The study of chemisorption processes poses the greatest interest in case of non-stoichiometric TiC$_y$(111) with the oxygen atom located above the carbon atom vacancy. Relaxation results in oxygen atom substitution in the carbon vacancy forming the bond length of d_{O-Ti} = 1.94 Å. This configuration corresponds to the largest adsorption energy value of E_{ads} = -11.06 eV/atom,

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which in our opinion is determined by the change in the local atomic structure and the number of atoms participating in the interaction with the oxygen atom.

5 Acknowledgments

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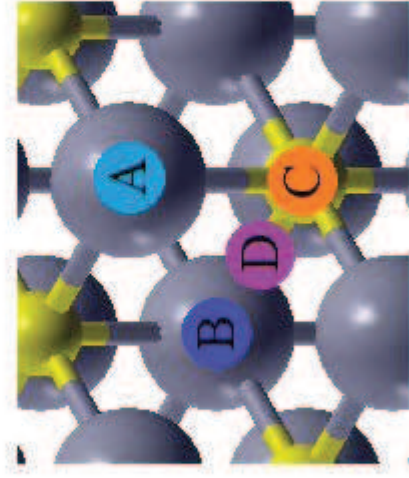
Graphical Abstract

a)

$(\bar{2}11)$

$(11\bar{2})$

(111)

Atom species

Ti atom

C atom

b)
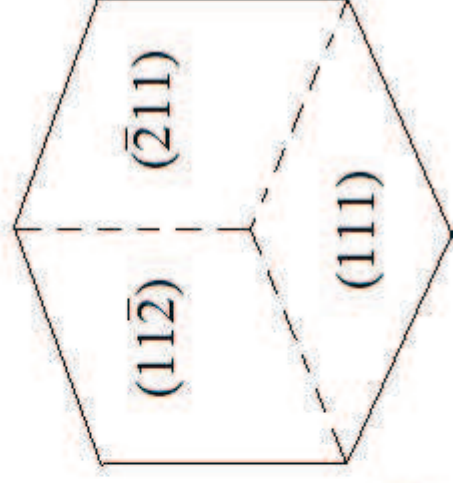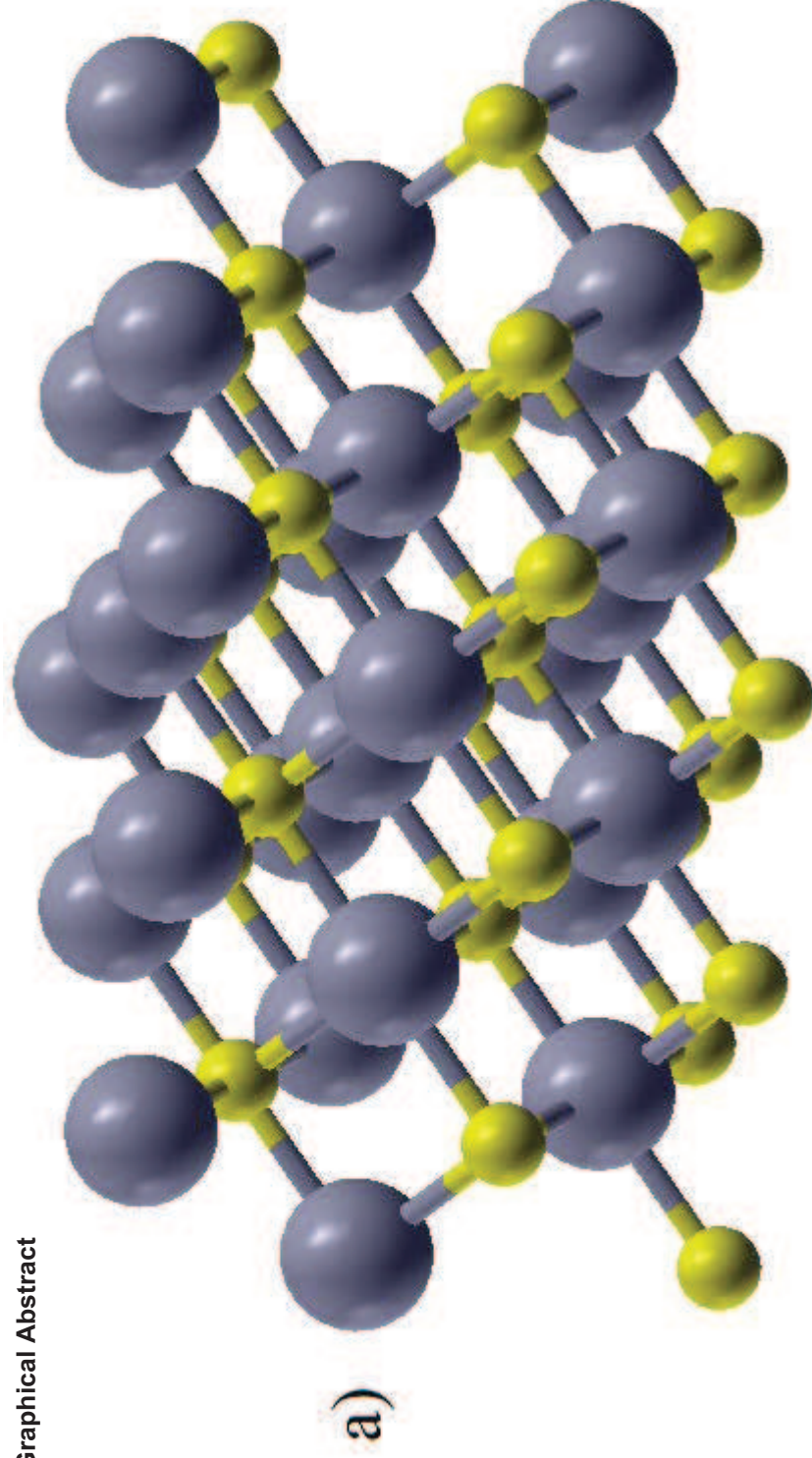
Binding site:

A — on top Ti atom

B — fcc site

C — hcp site

D — bridge site

HIGHLIGHTS

- *Ab initio* calculation of O-atom adsorption on non-stoichiometric polar TiC(111) and TixCy (111) with Ti/C vacancies surface are performed.
- We also have examined the effects of oxygen adsorption upon the band and electron spectra of TiC(111) surface in its various reconstructions
- Bond length and adsorption energy for various reconstructions of $O/Ti_xC_y(111)$ have established.
- Effective charges of the oxygen atom and the titanium and carbon atoms nearest to it were identified.