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To cite this article: V V Ilyasov *et al* 2018 *J. Phys.: Conf. Ser.* **1109** 012001

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Physics of surface carbon ceramics by laser nanostructuring with 5d-metal componentry

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Abstract. Using density functional theory, we have carried out an ab initio simulation of 5d-metal adsorption on the polar (111) titanium carbide surface terminated by Ti. We have carried out a systemic study of the local atomic reconstructions of the W/TiC_x(111), and their electronic and thermodynamic properties. The bond length and the adsorption energy have been found for different reconstructions of the surface atomic structure in W/TiC_x(111) systems.

1. Introduction

The carbon ceramics, such as titanium carbide (TiC) have attracted considerable interest as a potential material for nuclear reactors, aerospace application, and electronic devices due to its unique properties. We systematically investigate the atomic structure, electronic and thermodynamic properties of adsorbed tungsten atoms on the polar TiC (111) surface using first principle calculations. The bond length, adsorption energy, and formation energy for different atomic surface reconstructions of the W/TiC (111) systems were established. The effect of tungsten coverage on the electronic structure and the adsorption mechanism of tungsten atom nucleation on the TiC (111) are also investigated. We also suggest the possible mechanism of tungsten nucleation on the TiC (111) surface. Our results show that the nucleation of tungsten on the polar TiC (111) surface can be realized by three reconstruction mechanisms, which are responsible for the change in physical properties of material.

2. Model and Method

A theoretical model of the W/TiC (111) system is represented by three-dimensional periodic slab. The vacuum gap was chosen to be at 1,2 nm to avoid any interaction between translations in the [111] directions of the slab. In Fig. 1(a) we illustrate a fragment of the TiC (111) slab. The potential positions of the adsorbate atom are shown in Fig. 1(b). We have considered five different configurations of tungsten atom placed on a TiC (111) surface. The configurations presented as



follows: (i) The binding site A corresponding to W atom placed above the topmost Ti atom in the TiC surface, (ii) in binding site B the W atom placed above Ti atom of third Ti layer (fcc hollow), (iii) the binding site C the tungsten atom placed above C atom of second Ti layer (hcp hollow), (iv) A_{vac} the tungsten atom placed above the surface vacancy of the Ti atom of layer 1, and (v) C_{vac} the tungsten atom placed above of the vacancy of C atom of layer 2.

All the calculations in the work were performed within the DFT using pseudopotential approximation [1]. Exchange-correlation energy was calculated using Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation [2]. For the plane waves used in the expansion of the pseudo-wavefunctions the cutoff energy of 400 eV was chosen. All surfaces were calculated using the Monkhorst-Pack method generation of flat ($6 \times 6 \times 1$) k-point mesh. The total energy convergence threshold of 10^{-6} Ry/cell was used. In order to consider the interaction between the valence electrons and the core, Vanderbilt ultrasoft pseudopotentials were used. The adsorption energy of tungsten atom on the TiC (111) systems was determined similar as in paper [3].

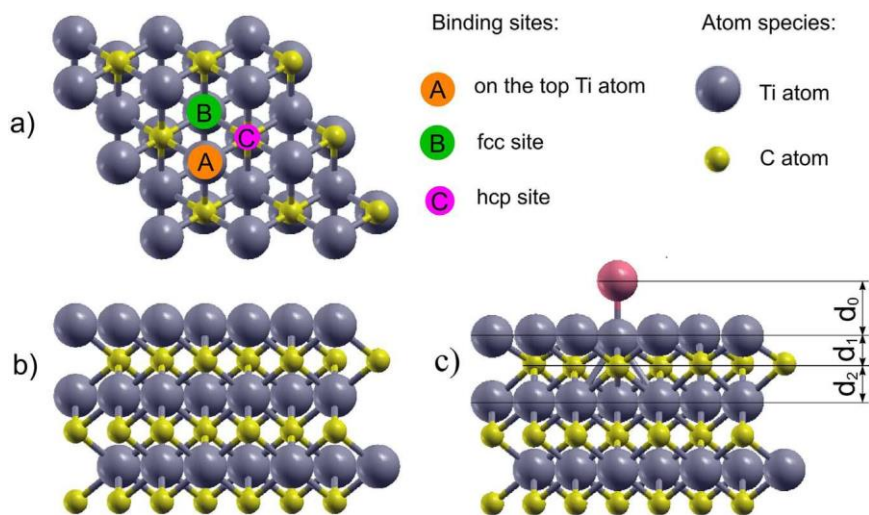


Figure 1. The models of TiC (111) surface in different directions; (a) top view, (b) side view, and (c) binding sites of tungsten adsorption on TiC (111) surface.

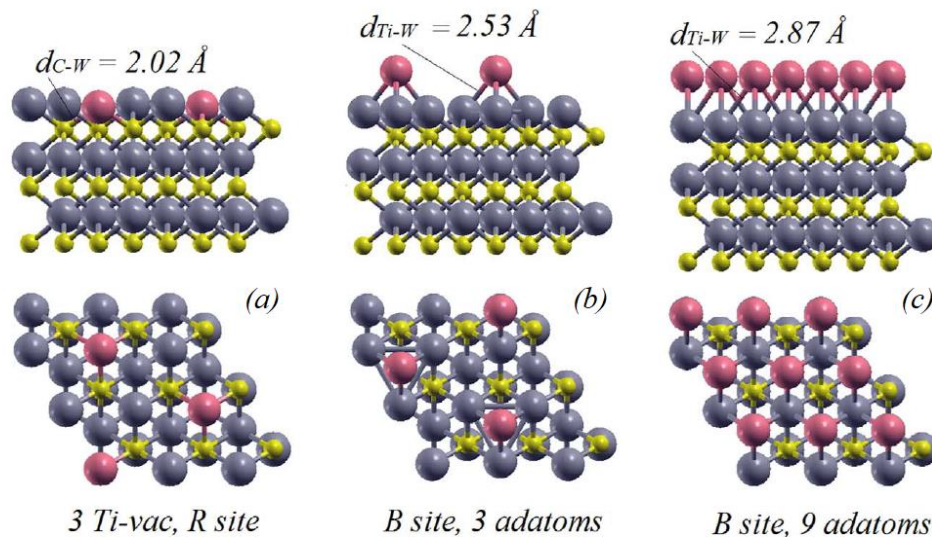
3. Results and Discussion

As we suggest, when laser radiation is applied to the TiC (111) surface, three possible surface reconstruction mechanisms are responsible for the formation of novel properties of the material. First mechanism consists in the fact that Ti atoms in topmost layer of TiC (111) surface can be partially replaced by tungsten atoms. This crystal lattice symmetry breaking and adsorption processes of W atom lead to a significant reconstruction of the local atomic structure of the surface. The second mechanism is the reconstruction of the local atomic W/Ti_xC_y structure, making W atom as a vacancy by diffusion during laser evaporation of C atoms at the subsurface layer TiC (111). The formation energy of C and Ti vacancies differ by 28%, i.e., more energy is required for evaporation of C atom. For example, using Nd:YAG laser radiation with a wavelength of $1.06 \mu\text{m}$ and a pulse during of 40 nm at generation frequency of 2000 Hz, the radiation energy density in the TiC surface is in the range from 2.0 to 6.4 J/cm^2 . In this range of laser radiation density, the observed difference in the formation energy of C and Ti vacancies is insignificant. The third mechanism is that, under laser evaporation, the position of C and Ti atoms in the two upper layers of TiC (111) surface can be replaced by W atom, or W atom can take the binding position at the TiC (111) surface. Thus, the crystal lattice symmetry breaking leads to a change in the Ti–C bond length, as shown in Table 1.

Table 1. The relaxed Ti–W, Ti–C, and W–C bond lengths in different positions of W atom adsorbed on TiC (111) and $Ti_x C_y$ (111) surfaces, in Angstrom (θ – cover degree)

Bond length	TiC	Position of W atoms in surface			
		A	B ($\theta=1$)	C	A, Ti_{vac}
Ti-W	-	2.17	2.87	2.53	-
Ti-C	2.05	2.09	2.12	2.07	2.05
W-C	-	-	-	-	2.03

In order to study the adsorption of W atom on the TiC surface, we performed the relaxation of one upper Ti–C layer with atomic adsorbate at the 2D W/TiC (111) and W/ $Ti_x C_y$ (111) systems. Initially, W atom was placed at a distance of 2.5 Å from TiC (111) surface. The two lower Ti–C layers in the W/TiC (111) system were fixed. The relaxation was carried out until the sum of all forces in the system was reduced below 0.001 eV/Å. The relaxed atomic structures of W atom adsorbed on TiC(111) and $Ti_x C_y$ (111) with different configurations are illustrated in Fig. 2. We also calculated the lattice parameters of the tungsten atom and the atoms of the upper layer of TiC and bond lengths between W atom and nearest atom in the stoichiometric and non-stoichiometric TiC slab (see Table 1).

**Figure 2.** Top and side views of the models of W/ $Ti_x C_y$ (111) surface

From Table 1 we can see a significant restructuring of the local atomic structure caused by the bonding position of adsorbate W atom at the 2D TiC (111) surface. In the position A of adsorbate, the Ti–C bond length in the surface is maximal, and it is about 1.8% relative to the Ti–C bond length in the clean 2D TiC (111). The interatomic distance between adsorbate W atom and Ti atom in the surface in this configuration is minimal in comparison with the covalent Ti–C bond length in 2D TiC (111) surface. In the case of positions B and C of atomic adsorbate, the interatomic distance W–Ti increases by 15% relative to the position A. Especially, in the position B, the interatomic distance W–Ti increases by 32% relative to the position A with increasing coverage degree of tungsten atom to $\theta = 1.0$ monolayer (ML). In the position C, the Ti–C distance in the (111) surface increases by 3% relative to the clean TiC (111) surface.

The local atomic structure of 2D W/ $Ti_x C_y$ (111) system has attracted considerable interest to study W nucleation on non-stoichiometric $Ti_x C_y$ (111) surface. The atomic structures of W/ $Ti_x C_y$ (111) system with different adsorption configurations were shown in Fig. 2. It is shown the possibility to replace upper surface Ti atom by W atom with an appearance of one (two or three) atomic vacancy in

the upper surface Ti atom, resulting in the formation of W–C bond. In this case, the W–C bond length is $d_{W-C} = 2.03 \text{ \AA}$. In the case of with both Ti and C vacancies, W atom will take a position of Ti atom. We can deeply understand the nature of the reconstruction of the atomic structure of ultrathin film TiC, which is associated

Based on the stable binding site, we establish the adsorption energy of atomic tungsten adsorbate on stoichiometric TiC (111) surface in three different binding sites A, B, and C. The adsorption energy data and the vertical distances between adsorbate and topmost atomic layer are listed in Table 2. We can see that the W adsorbate atom in the binding site B (fcc site) is most stable. In this position, one W atom is bonded to three other Ti atoms of the TiC (111) surface as a metal bond type. The W–Ti bond length is $d_{W-Ti} = 2.52 \text{ \AA}$ and it characterized by an adsorption energy of -8.33 eV/atom . The adsorption energy of W atom is comparable to the adsorption energy of oxygen atom ($E_{ads} = -8.75 \text{ eV}$ [4] or $E_{ads} = -10.68 \text{ eV}$ [5]) in the site B on the stoichiometric surface TiC (111). The adsorption energy of $E_{ads} = -8.33 \text{ eV/atom}$ indicates that the binding site B can be the center of nucleation of W atoms in the W/TiC(111) system. In the binding site A, one W atom is strongly bonded to other topmost Ti atoms of the TiC (111) surface with the adsorption energy of $E_{ads} = -7.28 \text{ eV/atom}$. In order to compare with other similar systems, in Table 2, we have also cited the previous results of the systems of O/TiC, Fe/TiC, Fe/NbC, and Fe/TaC [4-9].

Table 2. The distance (\AA) between the adsorbate W atom and the TiC (111) layers after relaxation, adsorption energy (eV) of W atom for various binding sites on the TiC (111) surfaces

2D phase	d_0	d_1	d_2	E_{ads}	Adsorption type
TiC(111)	-	1.04 [5]; 1.01 [4]	1.35 [5]; 1.39 [4]	-	-
W/TiC(111)	2.02	1.05	1.35	-7.28	Site A
	1.87	1.07	1.35	-8.33	Site B
	1.87	1.06	1.35	-8.19	Site C
W/Ti _x C(111)	-0.08	1.05	1.35	-12.21	Ti-vacancy
	1.88	1.05	1.34	-8.04	Bridging to 2 Ti
W/Ti _y C(111)	1.79	1.06	1.35	-9.12	Site C
	1.79	1.06	1.35	-8.89	Bridging to 2 Ti
O/TiC(111)	1.71 [5]	1.03 [5]	1.36 [5]	-8.38 [5]; -6.6.5 [4]	On top Ti atom
	1.68 [6]	-	-	-4.94 [6]	
	1.71 [8]	-	-	-2.95 [4]	On top Ti atom
O/TiC(001)	1.75 [9]	-	-	-3.44 [9]	
	2.80 [7]	-	-	-3.80 [7]	On top Ti atom
Fe/TiC(001)	2.74 [7]	-	-	-4.40 [7]	On top Nb atom
Fe/NbC(001)	2.83 [7]	-	-	-4.14 [7]	On top Ta atom
Fe/TaC(001)					

The adsorption energy in the binding site C has a transition state (see Table 2). To better understand the nature of chemisorption, we identified the effective charge distribution of W atom and its nearest neighbors atoms in the different binding sites. Our DFT calculations of the effective charges of the W, Ti, and C atoms (in the topmost and second layers of the surface) with different binding configurations are provided in paper [10]. The charge transfer is determined by the chemisorption processes of the adsorbate on the polar surface TiC (111) due to a significant difference in the Pauling electronegativity of W atom ($2.36X$), Ti atom ($1.54X$), and C atom ($2.55X$) [11]. The charge transfer between the W atom and the (111) surface can be controlled by work function. The calculations of the work function in different binding configurations of TiC and Ti_xC_y surfaces are listed in [10]. We can see that, by an

adsorption of W atom on the polar stoichiometric W/TiC (111) surface for the binding configurations A, B, and C, the work function reduces up to 10%. This change of the work function correlates with increasing the local charge transfer from Ti to W in the binding configurations B and C.

Next, we studied the adsorption energy of W atom on the defective surface Ti_xC_y (111). The Ti atoms in the topmost layer of TiC surface are replaced by the W atoms. These configurations of W/ Ti_xC_y (111) surface are characterized by a high adsorption energy (see Table 2). The binding site A with the adsorbed atom replacing the position of Ti vacancy has the highest adsorption energy of -12.21 eV/atom, and therefore, it can be the center of nucleation W atoms in the W/ Ti_xC_y (111) system. It should be noted that after relaxation, W atom may be displaced to the position of Ti vacancy from site C or stay above of the vacancy of C atom for W/TiC_y system. In the binding site A, the adsorption energy of W/ Ti_xC_y system increases by 1.2 times according to the symmetry lowering lattice of Ti and C vacancies. Here, the Ti-vacancy in the topmost layer is replaced by the adsorbed atom with the high probability of the first mechanism of the surface structuring. The adsorption energy of the W atom in the site A of stoichiometric and non-stoichiometric surfaces in comparison with other calculations is listed in Table 2. From Table 2 we can see that the adsorption energy of the d-metal on the polar TiC (111) surface is 1.9 times higher than that on the TiC(001) surface. In paper [10] reveal, that with increasing tungsten coverage to $\Theta = 1.0$ ML in the position B (fcc site) on TiC (111) surface, the adsorption energy increases by 1.2 times. It should be noted that the W nucleation on the polar TiC (111), Ti_xC (111) and TiC_y (111) surfaces can be realized by three possible mechanisms of the surface reconstruction, as suggested above, which are responsible for the creation of novel properties of materials.

4. Conclusion

It was shown that the adsorption of W atom on small defective surfaces Ti_xC_y (111) surfaces with different binding configurations leads to a rearrangement in its local atomic structure and band spectrum. The Ti atoms in the topmost layer in the presence of one (two or three) Ti-vacancy can be replaced by the W atom, forming a W–C bond length of 2.03 \AA . In the case of both Ti and C vacancies, the positions of Ti-vacancies will be occupied by the tungsten atom. Our results show that the nucleation of W on the polar Ti_xC_y (111) surface can be realized by three reconstruction mechanisms, which are responsible for the change in physical properties of the material.

References

- [1] Giannozzi P, Baroni S, Bonini N et al. 2009 *J. Phys.: Condens. Matter.* **21** 395502.
- [2] Perdew J, Burke K, Ernzerhof M 1996 *Phys. Rev. Lett.* **77** (18) 3865.
- [3] Ilyasov V, Popova I, Ershov I et al. 2017 *Diamond & Related Materials* **74** 31.
- [4] Roberto C 2007 *Phys. Rev. B* **75** 235438.
- [5] Ilyasov V, Pham K, Yalovega G et al. 2016 *Surf. Sci.* **649** 20-26.
- [6] Ilyasov V, Pham K, Holodova O, Ershov I 2015 *Surf. Sci.* **351** 433-444.
- [7] Lekakh S, Medvedeva N 2015 *Comp. Mater. Sci.* **106** 149-154.
- [8] Vines F, Sousa C, Illas F et al. 2007 *J. Phys. Chem.* **111** 1307-1314.
- [9] Didziulis S, Butcher K, Perry S 2003 *Inorg. Chem.* **42** 7766-7781.
- [10] Ilyasov V, Pham K, Zdanova T et al. 2017 *Physica B* **526** 28-36.
- [11] Allred A 1961 *J. Inorg. Nucl. Chem.* **17** 215-221.