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Effect of oxygen adsorption on structural and electronic properties of defective surfaces (001), (111), and (110) TiC: Ab initio study

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ABSTRACT

A model of the oxygen adsorption on the defective surfaces (001), (111) and (110) of titanium carbide with different reconstructions is investigated by ab-initio calculations. In the framework of DFT calculations, the relaxed atomic structures of the surfaces (001), (111), and (110) of O/Ti_xC_y systems with titanium and carbon vacancies are studied. The structural and electronic properties of these systems are also investigated. The bond length and the adsorption energy for different reconstructions of the atomic structure of the surfaces (001), (111), and (110) of O/Ti_xC_y systems were established. The influence of the oxygen adatoms on the band structure and the electronic spectra of the O/Ti_xC_y system with different reconstructions was studied. Our calculations of effective charge per oxygen and nearest atoms show that the observed charge transfer from the titanium atoms to the oxygen and the carbon atoms is due to the reconstruction of local atomic and electronic structures and it correlates with processes of chemisorption. The physical nature and mechanisms of nanostructuring of the surfaces (001), (111) and (110) of titanium carbide are also discussed.

1. Introduction

Due to its unique properties [1–9], titanium carbide (TiC) is a currently interesting candidate for applications in nanoelectronic devices, coating in nuclear reactors and aerospace [10–15]. Studies of the atomic structure of the TiC surface represent an essential aspect for understanding the properties of transition metals carbides [13,14] and offer an opportunity to look inside the properties of materials [15]. Under the nanosecond lasers, the melting, high-gradient cooling, and crystallization of the surface layer occur [16,17]. The nanostructuring of the material surface at the stage of growth crystallization can be controlled by using of energy density and laser pulse duration. By using atomic resolution scanning tunneling microscopy [14], it was found that there is formation of the structure TiC(001) - (1×1) in TiC under the reiterated heating at a temperature up to 1300 °C in high vacuum, and then it transfers to the TiC(001)- $\sqrt{2} \times \sqrt{2}$ structure at the annealing at temperature of 1150 °C [14]. Kuramochi et al. [14] have also shown that, the high reactivity of carbon vacancies to oxygen can lead to the replacement of surface position carbon vacancies by oxygen.

It is known that [18] the chemical activity of the (111) surface for gas adsorption is significantly higher than that of the (001) surface. Therefore, study of the "gas-surface" interaction under laser irradiation is also important to understand the TiC(111) surface. Experimental and theoretical studies of the TiC(111) atomic structure show that the polar surface is terminated by titanium atoms [18–20] and can be represented by two atomic structure types being (1×1) and $(\sqrt{3} \times \sqrt{3})R30$ [21]. Besides, the atomic oxygen adsorption on the TiC(111) surface at room temperature forms the TiC(111)—O structure [21], which is experienced reconstruction into the TiC(111)-$(\sqrt{3} \times \sqrt{3})R30$—O type with increasing temperature up to 1000 °C [22,23]. However, the structural and electronic properties of the different TiC surfaces, which are lack of studies in previous works [13,24], should be studied further details. The above reconstruction of the various TiC surfaces is the result of local interatomic interactions (including oxygen) and their effects on the electron spectrum of titanium and carbon subsystems. Recently, the dependence of the structural and electronic properties of the TiC (110) surface on plate thickness has been studied [13]. The studies of the atomic and energy structures of the TiC(110) and TiC(001) surfaces show that the surface energy of TiC(110) is two times higher than that of the TiC(001) surface [13]. In an ab-initio study, the electronic properties of

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TiC(001) and TiC(111) surfaces have been investigated [25,26]. It is shown that the reconstruction of the local atomic structure correlates with the electron energy spectrum and surface properties. In addition, the electronic and structural properties of titanium oxycarbides (TiC_xO_{1-x}) [27] and hydroxylated Ti_2C and Ti_3C_2 [28] nanotubes have been also investigated by density functional theory (DFT).

In the process of nanostructure formation with laser in air, oxygen adsorption on the TiC(001), TiC(111) and TiC(110) surfaces, i.e. the O/Ti_xC_y system, should be studied first of all. DFT calculations show that the maximum value of the energy of O-adsorption on the non-polar TiC(001) surface is observed in the position above C atom (4.96 eV/atom [20], 6.68 eV/atom [25]). The maximum value of the energy of O-adsorption on the polar TiC(111) surface is from 9.0 eV/atom to 10.25 eV/atom [20,26]. It is higher than that in the non-polar TiC(001) surface case. The nature of O-adsorption on the TiC(001), TiC(111) surfaces with C- and Ti- surface vacancies was studied in previous works [25,26]. However, data of atomic oxygen adsorption on the surface (110) of titanium carbide plate is not published. In the available literature, there are no data on the systematic study of the surface properties of titanium carbide as a result of laser nanostructuring in the air.

As mentioned above, the effects of O-adsorption on nonideal substrates, which control electronic and structural properties of the O/Ti_xC_y systems with Ti- and C-surface vacancies, are still lack of study. Therefore, in the present work, we use density functional theory (DFT) to systematically study the effects of O-adsorption on the structural and electronic properties of atomic Ti_xC_y (001), (111) and (110) surfaces with Ti and C vacancies.

2. Computational model and method

In this work, a three-dimensional periodic slab scheme has been used for modeling the reconstruction of the O/Ti_xC_y(001), (111), and (110) surfaces with Ti and C vacancies. We used a supercell containing unit cells of (2×2) TiC(001), (110) and (3×3) TiC(111). Fig. 1(a), (c), and (e) illustrate a fragment of the TiC(001), TiC(111), TiC(110) slabs, respectively. The potential positions of the adsorbate atom are shown in Fig. 1(b), (d), and (f). In recent work, we have considered 17 different atomic configurations of the O/Ti_xC_y(001), (111) and (110) with Ti, C vacancies and O/TiC without vacancies. We also considered the ideal TiC surface for comparison [25,26].

The TiC(001), TiC(111), and TiC(110) slabs consist of 6 non-equivalent planes in the [001], [111] and [110] directions. The basic supercell consists of 48, 54 and 72 atoms, respectively. The vacuum gap width was selected at 15 Å in order to avoid any interaction between the slab translations in the [001], [111] and [110] directions.

In this paper, we performed the self-consistent total energy calculations based on density functional theory (DFT) using a pseudopotential approximation (Quantum Espresso code) [29]. Exchange and correlation energy were calculated using the Perdew-Burke-Ernzerhof revised for solids (PBEsol) functionals within the GGA approximation [30,31]. The cutoff energy of the plane waves used in the expansion of the pseudo wave functions was 400 eV. Therefore, we calculated all surfaces using a $(3\times3\times1)$ flat k–point mesh generated by the Monkhorst-Pack method. The accomplished total cell energy convergence was at least 10^{-6} Ry/cell. To describe the interaction between the valence electrons and the core, we used the Vanderbilt ultrasoft pseudopotentials. The pseudopotentials were based on the Trullier–Martins scheme [32]. The electronic configurations were used for the Ti, O, and C atoms as follows: Ti – $[Ar]4s^23d^2$, O – $[He]2s^22p^4$, C – $[He]2s^22p^2$. The states of [Ar] and [Ne] attributed to the core.

The adsorption energy of an oxygen atom on the TiC(001), TiC(110), and TiC(111) surfaces can be written as follows [15,20]:

$$E_{ads} = E_{tot} - E_{ref} - E_0, \quad (1)$$

where E_{tot} stands for the total energy of the O/TiC(001), O/TiC(110), O/TiC(111) systems, E_{ref} is the total energy of the relaxed respective surface without oxygen, and E_0 is the energy of an isolated oxygen atom.

A Löwdin population analysis [33] allows to determine the effective charges on the oxygen atom and the nearest atoms on the surface of titanium and carbon atoms in 17 O-adsorbed O/Ti_xC, O/TiC_y, and O/TiC models.

3. Results and discussion

3.1. Atomic structure of (001), (111) and (110) surfaces of O/Ti_xC_y

In order to study the adsorption of oxygen atoms on non-stoichiometric surface with (001), (111) and (110) configuration planes of the titanium carbide system O/Ti_xC_y, relaxation was performed for the upper double atomic layer (Ti, C) of the titanium carbide plate with adsorbate. Initially, the oxygen atom was placed

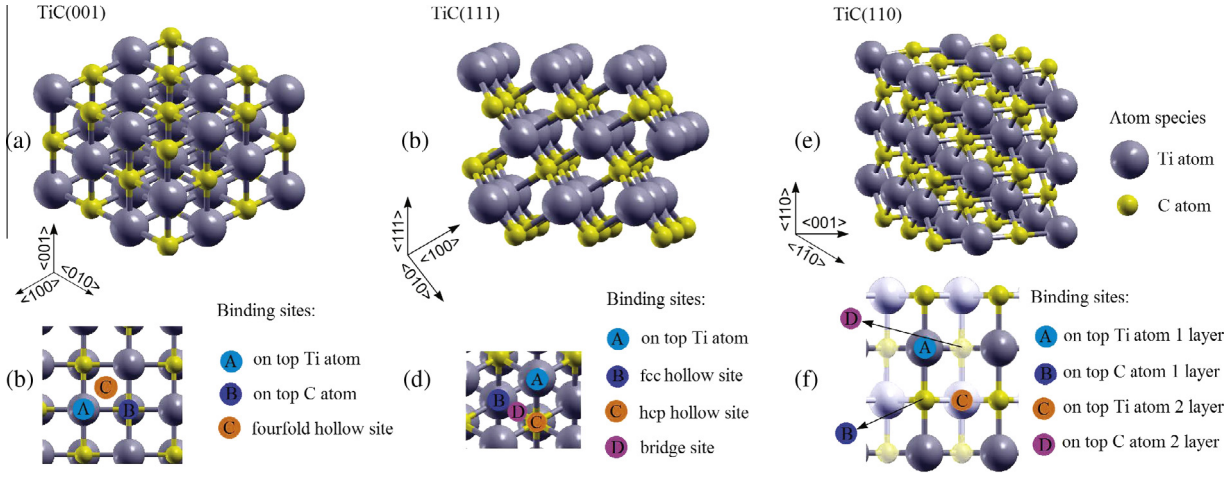

Fig. 1. Computational supercell for different surfaces in TiC (a, c, e) and binding sites of an oxygen atom (b, d, f) on the surfaces (001), (111) and (110), respectively (top view). Fcc hollow site – face-centered cubic hollow site, hcp hollow site – hexagonal closed packed hollow site.