Nature of Chemisorption on Titanium Carbide and Nitride

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Extensive density-functional calculations are performed to understand atomic chemisorption on the TiC(111) and TiN(111) surfaces, in particular the calculated pyramid-shaped trends in the adsorption energies for second- and third-period adatoms. Our previously proposed concerted-coupling model for chemisorption on TiC(111) is tested against new results for adsorption on TiN(111) and found to apply on this surface as well, thus reflecting both similarities and differences in electronic structure between the two compounds.

Keywords: Density-functional calculations, Titanium carbide, Titanium nitride, Adatoms, Adsorption, Chemisorption, Density of states.

I. INTRODUCTION

Within an extensive theoretical study of atomic chemisorption on the Ti-terminated polar TiX(111) (X = C, N) surfaces, we have presented characteristic trends in adsorption energies and geometries for H, second-row elements B, C, N, O, and F, and third-row elements Al, Si, P, S, Cl. The study has both fundamental and technological motivations, as these materials are important in applications in which surface properties are essential, such as growth of alumina on Ti(C,N)(111) and use of TiN as a thin diffusion barrier in integrated circuits or as a biocompatible material.

Our results show similar trends for TiC and TiN, with atomic adsorption energies for the second- and third-period elements varying along the periods in a characteristic pyramid-like way [Fig. 3(a)] and [1, 2]. Within each period, the energies increase from group III to group VI and decrease from group VI to group VII, with overall higher values for period 2. These variations are very large, from ~3.5 eV for Al to ~8.5 eV for O. Also, the preference for adsorption on TiC vs. TiN varies, with a slightly stronger chemisorption on TiN for the remaining adatoms.

Such variations cannot be explained within a simple model, where only one type of coupling mechanism is considered. In a separate study, we propose a concerted-coupling model for adsorption on TiC(111), in which two different types of adatom–substrate couplings are active. This is similar to the d-band model for chemisorption on transition metals [3], however, with very different couplings, due to the more complex electronic structure of TiC. In this contribution, we pursue our investigation further, analyzing the electronic structure of the different adsorbates on TiN(111) and discussing whether our proposed model can be generalized and used to understand the similarities and differences between the TiN(111) and TiC(111) substrates.

II. COMPUTATIONAL METHOD

The computational method used is described in Ref. [2]. In short, the pseudopotential-plane-wave density-functional-theory (DFT) code dacapo is used, with PW91 GGA exchange-correlation potential, ultrasoft pseudopotentials, and slab geometry [4].

In the present paper, the electronic structures of the considered systems are analyzed by calculating and plotting the total and local densities of states (DOS and LDOS, respectively) obtained from the calculated Kohn-Sham (KS) wavefunctions and energy eigenvalues. Atom- and/or orbital-projected LDOS’s are obtained by projecting the KS wavefunctions onto the individual atomic orbitals and then plotting them as functions of the energy relative to the Fermi level, $E - E_F$. The spatial extent of the DOS’s at specific energy intervals is also analyzed in detail by examining the KS-wavefunction amplitudes for the relevant electronic states in three-dimensional real space. Also, the charge localization around individual atoms is analyzed with the “atoms-in-molecule” method of Bader [5].

III. RESULTS AND ANALYSIS

A. Electronic structure of the clean TiX(111) surfaces

Bulk TiC and TiN adopt the NaCl structure. Thus, in the (111) direction, the crystals are composed of alternating Ti and X atomic layers, in an ABC stacking sequence. Our study focuses on the Ti-terminated surfaces, since experiments show this to be the stable termination for TiC(111) [6]. The calculated lattice parameters and surface relaxations are given in Refs. [1, 2].

Both Ti-terminated TiX(111) surfaces are characterized by the presence of strong Ti-localized surface resonances (TiSR’s) [7], pinned at $E_F$ [Figs. 1(a–b)] and consisting of mainly $d_{yz}$ and $d_{xz}$, $d_{xy}$, $d_{x^2-y^2}$ orbitals (where $z$ is perpendicular to the surface). Figure 1(c) shows this symmetry and how the TiSR electron distribution is localized mainly around the Ti atoms (as evidenced also by the small width of the TiSR peaks) and extends toward...
the fcc surface sites.

Our calculated surface DOS’s [Figs. 1(a–b)] show that the TiSR is more filled on TiN(111) than on TiC(111). This is confirmed by a Bader analysis of the surface charges, yielding a surface-Ti ionicity of +1.09 for TiC and of +0.96 for TiN. This can be understood by considering the filling of the TiSR’s as the mechanism that compensates the electrostatic instability of the polar TiX(111) surfaces [3]. As bulk TiN is more ionic than bulk TiC (Ti → X charge transfers of 1.62 eV for TiC and 1.62 eV for TiN, according to our Bader analysis) [2], a larger compensating surface charge is needed on TiN(111).

The bulk electronic structure of TiX [inserts in Figs. 1(a–b)] consists of (i) a lower valence band (LVB), of only X2s character, (ii) an upper valence band (UVB), characterized by bonding Ti3d–X2p states in its high-energy part and by X2p–X2p bonding interactions in its low-energy part, and (iii) a conduction band (CB), of mainly Ti3d character, corresponding to antibonding Ti3d–X2p states [1, 2]. The ionicity of bulk TiX is evidenced by a predominance of Ti (X) character in the CB (UVB).

Both TiX(111)-surface UVB’s [Figs. 1(a–b)] are composed of one main peak, three smaller peaks at lower energies, a shoulder on the high-energy side of the main peak, and a small peak at the upper edge of the UVB. For both surfaces, our detailed analysis of the individual KS wavefunctions composing the UVB (Fig. 2) shows that, similarly to the bulk UVB, the main UVB peak and the high-energy UVB region consist of Ti–X bonding states [Fig. 2(c)]. On the other hand, the three low-energy peaks consist almost exclusively of X–X bonding states that are mainly localized to the surface region [Figs. 2(a–b)], that is, they are X-localized surface resonances (XSR’s).

Like for the bulk DOS [2], several differences exist between the TiN(111) and TiC(111) surface DOS’s [Figs. 1(a–b)]: (i) the UVB and CB of TiN(111) lie at lower energies, due to the partial filling of the CB with the extra electron per formula unit present in TiN; (ii) the pseudogap between the UVB and the TiSR is larger for TiN(111); and (iii) the UVB DOS is considerably larger than for TiC. The TiSR’s around the TiN(111) plane possesses a larger DOS than the TiSR’s around the TiC(111) surface. This can be understood by considering the filling of the TiSR’s as the mechanism that compensates the electrostatic instability of the polar TiX(111) surfaces [3]. As bulk TiN is more ionic than bulk TiC, a larger compensating surface charge is needed on TiN(111).

The appearance of the TiSR’s arises from the energetical lowering of Ti-localized antibonding Ti–X states (indeed, for both compounds, a closer inspection of the CB reveals the quenching of a bulk CB peak located right above the TiSR’s). The TiSR’s can thus be interpreted as dangling bonds extending toward the fcc sites (which in the bulk would be occupied by X atoms) [Fig. 1(c)]. Similarly, the appearance of the XSR’s in the low-energy UVB region is caused by the breakage of X–X bonding interactions, which dominate at these energies.

B. Electronic structure of fcc adatoms on TiX(111)

In a separate study, we have proposed a model for the description of the exceptionally strong atomic chemisorption on TiC(111) [1]. In this concerted-coupling model, based on the Newns-Anderson (NA) model [3], the adsorption is understood to arise from the concerted action of two different types of adatom–substrate coupling: a strong adatom–TiSR coupling and weaker adatom–CSR couplings.

Briefly, the NA model for chemisorption on metal surfaces yields two limiting cases: weak and strong chemisorption, corresponding, respectively, to small and large coupling matrix elements between adatom and substrate states, compared to the substrate band width. In the weak chemisorption, the adsorbate level is shifted and broadened (if it lies in the energetical region of the substrate band). In the strong chemisorption, the adatom level is replaced by two levels that lie on each side of the substrate band. These are usually interpreted as the bonding and antibonding states of the “surface molecule” formed by the adatom and its neighboring substrate atoms. These bonding and antibonding states appear gradually, as the adatom level is broadened. As h increases, this level broadens further and splits gradually into two separate levels [4].

Our concerted-coupling model for TiC(111) is based on an analysis of the difference in DOS (∆DOS) before and after adsorption (thus, the ∆DOS shows the appearance and quenching of states due to the adsorption of an adatom as positive and negative peaks, respectively) [1]. For all considered adatoms on TiC(111), our ∆DOS’s show: (i) the appearance of Ti-dominated states at ∼ +1.0 eV; (ii) a strong quenching of the TiSR; (iii) the appearance of states below $E_F$, whose energies decrease with increasing adatom number $Z$ within each adatom period (due to the decreasing free-atom energy as $Z$ increases).

Within the NA model, these results are interpreted as evidence for a strong adatom–TiSR coupling, giving rise to antibonding and bonding states above and below, respectively, $E_F$. At the same time, our calculated ∆DOS’s show also that the bonding adatom–TiSR level below $E_F$ is successively broadened and split into subpeaks as its energy approaches the middle of the substrate UVB re-
FIG. 1: (a–b) Total and atom-projected DOS for the top TiX bilayer of the clean (a) TiC(111) and (b) TiN(111) surfaces. The inserts in (a) and (b) show the total DOS for bulk TiC and TiN, respectively. (c) Real-space contour plot (from above the surface and showing only the top TiC bilayer) of the total charge density of the electronic states above −0.6 eV on TiC(111), showing the TiSR (C atoms: green balls; Ti atoms: inside the electron clouds, as marked in the figure).

FIG. 2: Real-space contour plots of the KS wavefunctions for the clean TiN(111) surface at selected energies, viewed perpendicularly to the surface, illustrating: (a–b) typical bonding N–N interactions, with and without coupling to bulk states, in the lower UVB region; (c) a typical Ti–N bonding state, with high N-localization, in the main UVB peak. Ti (N) atoms are grey (green) balls, or lie inside the electron clouds, as marked in the figures.

This indicates, within the NA model, an additional, weaker, coupling between the TiSR-modified adlevel and the substrate UVB peaks, which are characterized by CSR’s. Thus, the subpeaks correspond to combinations of the bonding and antibonding solutions that arise from adatom–CSR couplings. This is confirmed by (i) the presence, in the substrate-projected ∆DOS’s, of negative peaks that are almost exclusively localized around the C atoms and that lie at energies in between the subpeaks and (ii) our state-resolved, real-space, analysis of the DOS, which shows that the subpeaks are dominated by adatom–C bonding states at lower UVB energies and by adatom–Ti bonding states at higher energies. The adatom–C states are only present at energies lower than the main substrate UVB peak and can only be interpreted as bonding solutions of adatom–CSR couplings. This analysis shows also that the adatom–C bonding states get successively stronger as the energetical overlap between the TiSR-modified adlevel and the substrate CSR’s increases. Maximum overlap is achieved for the O adatom, for which all bonding adatom–TiSR states lie in the lower half of the substrate UVB.

Our new calculations for atomic adsorption on TiN(111) show that the ∆DOS’s [Figs. 3(b)–(k)] behave in a similar way on this substrate. Figure 4 illustrates schematically the concerted-coupling model for TiN(111), using the calculated ∆DOS for fcc H on TiN(111), which provides the most complete illustration of the different types of adatom–substrate couplings. As can be seen, the results for adsorption on TiN(111) show strong similarities to those described above for TiC(111). However, a closer comparison reveals differences: (i) the antibonding peak above $E_F$ lies at a lower energy than on TiC(111), +0.4 eV; (ii) the TiSR quenching is stronger than on TiC(111) and involves a larger number of TiSR electrons; (iii) the coupling between the TiSR-modified adlevel and the XSR’s occurs at lower energies than on TiC(111). Points (i) and (ii) can be understood from the
facts that the TiN(111) TiSR lies at a lower energy than on TiC(111) and that this causes a larger filling of the TiSR on TiN than on TiC. Point (iii) is caused by the lower energy of the TiN(111) UVB, compared to that of the TiC(111) UVB.

In addition, our state-resolved, real-space, analysis of the DOS shows that also on TiN(111) there is a successively increasing dominance of adatom–X bonding states [Fig. 3(b–k)] with decreasing energy. Again, however, differences can be detected: (i) compared to the adatom–Ti coupling, the adatom–X coupling is generally stronger on TiN(111) than on TiC(111); (ii) while no adatom–Ti coupling can be detected in the TiSR energetic region on TiC(111), such adatom–Ti bonding states are found in the TiSR energetic region on TiN(111). Point (i) can be understood from the higher ionicity of TiN, which results in a stronger LDOS on the N atoms, compared to the C LDOS in TiC, and thus a stronger adatom–X overlap on TiN(111) than on TiC(111). Point (ii) can be interpreted as the presence of a weak coupling, similar to the adatom–UVB coupling, between the Ti-localized CB and the antibonding adatom–TiSR states. Due to the CB being partially filled in TiN, this adatom–CB coupling results here in filled states, in contrast to TiC, where the CB is empty.

Our results show thus that the atomic chemisorption on TiN(111) can be understood and analyzed in a way similar to that on TiC(111). Both types of interaction of our concerted-coupling model (adatom–TiSR and adatom–XSR’s) appear to be active on both substrates, due to the similarities between the electronic structures of the two surfaces. However, some differences are detected, which can be related to the higher ionicity and higher energy of $E_F$ in TiN, compared to TiC. In particular, the results indicate that a weak adatom–CB coupling is also present.

IV. DISCUSSION AND CONCLUSIONS

Our previous analysis shows that, from the DOS perspective, our concerted-coupling model is applicable also to adsorption on TiN(111). In the following, we discuss how this model can be used to account for the essential features of the calculated trends in $E_{ads}$ [1, 2], which varies in a characteristic pyramid-like manner for the second-period adatoms B, C, N, O, and F, peaking at O, and the third-period adatoms Al, Si, P, S, and Cl, peaking at S, on both TiC(111) and TiN(111) [Fig. 3(b–k)].

Given the strong quenching of the TiSR, a strong contribution to the bonding can be expected to come from the first component of the concerted coupling, the adatom–TiSR coupling. Indeed, the adsorption energy for O on the TiSR-deficient TiC(001) surface is 43% weaker than on TiC(111) [1]. The strong bonding contribution of the TiSR arises from the fact that the antibonding adatom–TiSR solution lies above $E_F$, thus remaining empty for all adatoms.

Our calculated $\Delta$DOS’s [Figs. 3(b–k)] show that, within each adatom period, the TiSR quenching decreases from group-IV to group-VII adatoms, while it increases from group III to group IV. These trends could indicate an increase in adatom–TiSR coupling strength from group III to group IV and a successive decrease from group IV to group VII. These trends agree with the calculated $E_{ads}$ trends for B → C, for Al → Si, for O → F, and for S → Cl. Also, the smaller TiSR quenching in period 3 than in period 2 indicates a weaker adatom–TiSR coupling for period 3, in agreement with our $E_{ads}$ results.

However, this trend in adatom–TiSR coupling strength disagrees strongly with the calculated $E_{ads}$ trends for C → N → O and for Si → P → S. On the other hand, our state-resolved DOS’s (see Sec. III.B) show that the second component of the concerted coupling, the adatom–XSR couplings, gets successively more active as the energetic overlap between the adlevel and the substrate XSR’s increases. As Z increases within each adatom period, the adlevel energy decreases, thus increasing the overlap between the adlevel and the energetic region of the XSR’s (that is, the lower half of the substrate UVB). Therefore, the adatom–XSR coupling strengths can be expected to increase as Z increases within each adatom period, providing an explanation for the overall increasing $E_{ads}$ values from group III to group VI. In addition, this provides further explanation for the stronger chemisorption of the second-period adatoms, compared to the third period, due to the lower free-atom energy, within a given group, of the second-period adatoms.

On the other hand, such a trend is in contrast to the $E_{ads}$ trends for O → F and S → Cl. However, F and Cl have ionic bonds, as shown by our calculated Bader charges, which yield a charge transfer from the surface Ti atoms to the F and Cl adatoms of 0.75–0.80 electrons, and by our calculated electron distributions, which show negligible bond charges for F and Cl [2]. This implies almost fully occupied outer electron shells for the F and Cl adatoms, which can therefore be considered to be almost inert toward further chemical interaction, that is, toward a coupling with the UVB states. Indeed, our $\Delta$DOS’s show that the F and Cl adlevels do not broaden as significantly as the levels of other adatoms with the same amount of overlap with the UVB region [cf., for example, Cl and O on TiN(111)], indicating a weaker adatom–UVB coupling. For all the other fcc adatoms, the electron densities show a clear covalent character for the adatom–substrate bond, with the ionic character increasing successively with increasing Z within each adatom period. This is confirmed by our calculated Bader charges for the adatoms: −1.07, −1.31, −1.34, −1.20, and −0.80 for the second-period adatoms B, C, N, O, and F, respectively (corresponding to 21%, 33%, 45%, 60%, and 80% of their empty outer electron shells) and −0.40, −0.89, −1.08, −1.05, and −0.74 for the third-period adatoms Al, Si, P, S, and Cl, respectively (corresponding to 8%, 22%, 36%, 52%, and 74% of their empty outer electron shells).
FIG. 3: Adsorption of the second-period adatoms B, C, N, O, and F and of the third-period adatoms Al, Si, P, S, and Cl in fcc site on TiX(111). (a) Calculated trends in adsorption energies $E_{\text{ads}}$ (excerpt from Ref. 2). (b)–(k) Calculated densities of states (DOS’s) for adsorption on TiN(111). Thin line: adatom-projected DOS. Thick line: difference in total DOS ($\Delta$DOS) before and after adsorption for the surface TiN bilayer, including adatom. Dashed (dot-dashed) line: $\Delta$DOS projected onto N (Ti) atoms of the surface bilayer. Shaded area: energetical location of the substrate UVB. Dashed vertical lines: energetical location of the six substrate-UVB peaks. (l) Contour plot of the KS wavefunction at $E = -6.8$ eV for the fcc O adatom on TiN(111), illustrating a typical bonding adatom–N interaction.
Thus, the concerted-coupling model, which well describes the calculated DOS results, provides also a way for understanding the main features of the calculated $E_{\text{ads}}$ trends for both TiX(111) surfaces. In particular, our analysis points toward a greater role for the adatom–XSR couplings in this understanding than what has been suggested so far in the literature.

Our results show also a small but interesting difference between TiC and TiN: for adatoms with low $Z$ (B and Al) chemisorption is slightly stronger on TiN(111), while for adatoms with higher $Z$ it is stronger on TiC(111). For B and Al, the adlevels lie above the UVB region. The adatom–XSR contributions to their bonding strengths are therefore negligible and their chemisorption is dominated by the adatom–TiSR coupling. Hence, our $E_{\text{ads}}$ results imply that the bonding contribution from the adatom–TiSR coupling is somewhat stronger on TiN(111) than on TiC(111), which is in agreement with our previous observation that the TiSR quenching is stronger on TiN than on TiC. Now, as stated above, as the adlevel energy shifts down and overlaps with the UVB region, the adatom–XSR couplings get successively stronger. However, for the same adlevel shift, this overlap is stronger on TiC than on TiN, due to the smaller UVB–CB energy gap of TiC. Therefore, for the same adatom, the adatom–XSR contributions to the bonding strength are stronger on TiC than on TiN. As $Z$ increases within each adatom period, this effect grows strong enough to “neutralize” the stronger adatom–TiSR coupling for TiN and invert the chemisorption preference between TiN and TiC.

In summary, the application of our concerted-coupling model, originally proposed for adsorption on TiC(111), can be generalized to TiN(111). However, the quantitative differences in electronic structures between the two compounds must be taken into account. This shows that adsorption on TiC and TiN is more complex and versatile than on, for instance, pure metal surfaces and that the combination of several different mechanisms must be taken into account, giving a potential for variations, very useful in applications.

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