A DFT study of Au deposition on (001) surface of TiN

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Abstract. The surface and local electron properties of Au atoms deposited on the (001) surface of TiN have been theoretically analysed using a periodic slab model and density functional based calculations. The surface was described by a 2x2 cell five layers thick, on which gold atoms are added. Deposition of single atoms on the surface, (thickness = 0.25 monolayers), shows that the preferred site is on-top of Ti atoms, with a metal-surface distance of 2.49 Å. The computed adsorption energy for this site is -1.92eV, which is only slightly lower than that between two Ti surface atoms (-1.90eV). On-top nitrogen sites are less favorable by about 0.4eV. The calculations were carried out using the Perdew-Wang 91 exchange correlation functional and ultra soft pseudopotentials, with electronic states represented by a plane-wave expansion.

Introduction

Transition-metal carbides and nitrides possess an unusual combination of physical and chemical properties which make them attractive from both a fundamental and technological point of view [1]. They have high melting points and extreme hardness, properties which are typical of covalent crystals, as well as metallic conductivities comparable to those of pure transition metals. These materials have good corrosion resistance and some of them have shown high superconducting transition temperatures [2]. They have also attracted considerable interest as potential catalysts [3].

Most investigations on carbide and nitride compounds have been aimed at their bulk properties, while work devoted to the study of their surfaces is relatively scarce. The interest in the structural properties of these surfaces was stimulated by an analysis of the diffraction pattern of TaC which revealed the existence of a rippled relaxation on the (001) surface [4]. Similar relaxation characteristics on the (001) surface were also observed in HfC [5] and VN [6]. To generalize these surface observations and state that they are representative for this whole class of materials is somewhat premature since only two carbides and one nitride of transition-metals have been reported. Such surface relaxations will be analyzed for a series of nitrides in a forthcoming paper [7].

From a theoretical point of view, several works have been devoted to the analysis of the electronic structure of carbides and nitrides [8]. In particular band structure calculations for TiN have been reported using a wide variety of theoretical approaches [9, 10]. Properties such as lattice parameters and bulk modulus have also been theoretically estimated [11-13]. With respect to the TiN surface, two recent studies have been reported, both of them using density functional theory (DFT) based methods. The electronic structure of the (001) face was carefully examined by Li et al. [13] from periodic slab calculations (Crystal95 [14]) in which the surface was kept fixed. The structure of the low index (001), (110) and (111) surfaces, including relaxation effects, were analyzed by Marlo et al. [12] from DFT calculations including generalized gradient approximation (GGA) and using plane waves (CASTEP [15]) to expand the electronic states.

Because of their very special properties, these materials have also been considered as supports for the deposition of metal transition clusters, both for engineering purposes (sensors, electronic
devices) and for catalysts. However, as far as can be ascertained, no theoretical results concerning transition metal deposition on TiN surfaces have been reported. In this paper, a theoretical analysis of the Au/TiN interface based on DFT periodic GGA calculations is reported. Gold has been selected as the transition metal due to the good catalytic properties recently reported for this material.

Computational Details

In order to model the extended nature of the Au/TiN system, periodic three dimensional (3D) DFT calculations were carried out using the VASP 4.4.3 code [16, 17]. In these calculations, the energy was obtained using the GGA implementation of DFT proposed by Perdew et al [18]. Ultrasoft pseudopotentials [19] were employed to remove the core electrons from the calculation and a plane-wave basis set was used. The cut-off energy used for the plane waves was 225 eV and the Monkhorst-Pack set of four k points was used. Forces on the ions were calculated through the Hellmann-Feynman theorem as the partial derivatives of the free energy with respect to the atomic position, including the Harris-Foulkes [20] like correction to forces. This calculation of these forces allows geometrical optimization using the conjugate-gradient scheme. Iterative relaxation of atomic positions was stopped when the change in total energy between successive steps was less than 0.001 eV. With this criterion, forces on the atoms were generally less than 0.1 eV / Å.

Titanium nitride is an instance of a diatomic solid AB having a rock salt structure, with an experimental unit cell parameter of 2.119 Å [21]. In order to test the reliability of the DFT approach, the first step was to perform an optimization of the cell parameter. For this purpose a cube containing 4 Ti atoms and 4 N atoms was selected as a supercell. The optimization of such a cell gave a lattice parameter of 4.253 Å, in agreement with the experimental value (4.238 Å). The nitride surface was then represented by a 2x2 supercell, 5 layers thick, on which periodic 3D boundary conditions were applied, allowing a vacuum space of 20 Å between the slabs (fig. 1). In the optimization of both the surface and surface + gold adatoms, only the three outermost layers were allowed to relax. This choice, as well as that concerning the thickness of the slab, is justified later.

![Diagram](image)

**Fig. 1** View of the 2 x 2 cell five layer thick used to represent the TiN (001) surface.

**Fig. 2** Schematic view of the rippled relaxation.
Results and discussion

Relaxation of the isolated surface is considered first. In a binary material the surface charge distribution is not the same for both species and therefore the ionic cores exhibit different forces in the surface region. In consequence, the surfaces tend to rumple to a greater or lesser extent. The relaxation involves an outwards displacement of (011) rows of a species and inwards movements of the other. This rippled relaxation has been experimentally observed in some metal carbides [5] and nitrides [6] where the non-metal atoms are found to move outwards and the metal atom rows inwards with respect to a bulk-truncated layer. The present DFT calculations agree with this kind of surface relaxation as shown in fig. 2, where a schematic description of the phenomenon is depicted. In Table 1, the rippling parameters for the first layers, computed using several surface models are reported. In these models, some of the layers are allowed to relax (free) and others are kept fixed (fix). As can be seen the rippling parameter, \( r \), for the first layer ranges between 0.178 and 0.193Å. The actual value oscillates as the model becomes larger. Initial values of 0.178Å for the 2/2 model, grows for the 3/2 and 3/3 models, smoothly converging to 0.188Å for the 5/5 super cell. Rippling for the inner layers is also observed, but is an order of magnitude smaller. It is also worth noting that for the 5/5 model the deepest rippling parameter is practically nil (0.002Å), i.e. it almost reaches the bulk value, indicating that the rippled relaxation is almost completely attenuated beyond the fifth layer.

Table 1 Rippling parameter \( r \) (Å) for the TiN (001) surface computed from periodic GGA DFT calculations and different slab models.

<table>
<thead>
<tr>
<th>Model</th>
<th>2 free/ 2 fix</th>
<th>3 free/ 3 fix</th>
<th>4 free/ 4 fix</th>
<th>5 free/ 5 fix</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_1 )</td>
<td>0.178</td>
<td>0.188</td>
<td>0.193</td>
<td>0.191</td>
</tr>
<tr>
<td>( r_2 )</td>
<td>0.014</td>
<td>0.013</td>
<td>0.032</td>
<td>0.018</td>
</tr>
<tr>
<td>( r_3 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( r_4 )</td>
<td>0.034</td>
<td>0.061</td>
<td>0.035</td>
<td>0.034</td>
</tr>
<tr>
<td>( r_5 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

When the different models are compared, it is observed that, as far as the first layer rippling parameter is concerned, the surface model consisting of 3 free layers and 2 fixed ones, gives a suitable representation at a moderate size, and therefore that is why this surface model has been chosen for the calculations in this work.

Next, the deposition of Au atoms on the surface for a coverage of 0.25 i.e. one Au per cell) was performed. Three sites were considered, as depicted in fig. 3. Sites A and B correspond to on-top of Ti and N atoms, respectively. Model C refers to the fourfold hollow site in which the Au atom is in the vertical of the centre of the square ring. An additional site corresponding to the centre of the Ti-N bond was also considered, but calculations showed it to be unstable.

Adsorption energies, \( E_{ads} \), and distances of gold atoms to the surface computed from spin-polarized DFT GGA calculations are reported in Table 2 (because of the rumpling, the surface here represents the outermost surface atoms, i.e. the nitrogen subplane). Calculations showed that the preferred sites are on-top of surface Ti atoms, with an adsorption energy of -1.92eV. The on-top N
sites are less favourable by about 0.4eV. Furthermore, adsorption energy on hollow sites (-1.90eV),
appear to be virtually identical to that of A sites, suggesting that for low coverage, Au atoms could
migrate easily between neighbouring Ti surface atoms, providing a possible mechanism for surface
diffusion of gold atoms exists. Compared to other gold/surface systems the interaction energy for
the Au/TiN interface appears to be relatively low. Thus, for the Au/TiO₂ (110) interface, the
adsorption energy is computed to be 0.99eV from ab initio embedded cluster DFT calculations, i.e.
almost half that of the Au/TiN system [22]. These results suggest a significantly larger binding
energy for gold atoms on TiN even taking into account the different theoretical approaches used.
(Actually, for the Cu/TiO₂ (110) system, the adsorption energies computed from ab initio
embedded cluster DFT calculations and periodic GGA DFT calculations are 2.85 and 2.39eV
respectively [22].)

Fig. 3 Top view of the relaxed surface. The labels for the three different sites for adsorption are A:
on-top of Ti atoms; B: on-top of N atoms and C: fourfold hollow.

An analysis of the density of states (DOS) as well as the electron density maps for the most
stable site was carried out with the aim of understanding the type of metal – surface interaction. In
fig. 4 DOS curves for both isolated Au and the TiN surface are represented (in these diagrams, as
usual, alpha spin is represented as positive and beta spin as negative). DOS for an isolated Au atom
(top of the fig.) clearly shows the d⁵ˢ¹ configuration of the gold ground state. In the case of the TiN
surface, the most relevant feature is the metallic character of this material in agreement with
previous calculations and experiment. The covalent contribution to the Ti-N bond is reflected by the
strong mix of Ti d and N p orbitals clearly observed in the DOS. After adsorption, the gold d band
splits into four main components whose energies coincide with those of new peaks appearing in the
d component of the DOS projected on the surface Ti atoms as shown in fig. 5. The analysis of
electron density maps reported in fig. 6 appears to be a truer reflection. These maps correspond to
the (100) containing Ti, N and Au atoms. The total electron density, reported at the top of fig. 6
shows that the electron density around N atoms is larger than that near Ti centers. Taking into
account that the core of both N and Ti atoms is described through a pseudopotential, the number of
valence electrons for these centres is 5 and 4 respectively. Therefore this larger electron density
around N atoms reveals that the Ti-N bond is considerably polarized, and therefore some ionic
character is still present this in bond. Of special interest in this kind of analysis, is the evaluation of
the difference between the total electron density of the Au/TiN system and that of the isolated
fragments. This difference is reported in the middle and bottom of fig. 6. The isolines of the middle
correspond to the region where the difference is positive, and therefore there is an increment in the
electron density. The isolines at the bottom are negative and show the regions where there is a
lowering of electron density. The analysis shows that there is an electron density increment in the
Au-Ti interatomic region indicating that some covalent bonding arises. When these maps are compared it can be seen that for a Ti atom, the increment of density along the z direction involves population of the $d_{z^2}$ orbital, which is accompanied by a lowering in the density for the $d_{xy}$ orbital. A similar repolarization is found for the gold atom. For this centre, there is a decrease in the inner electron density ($d_{z^2}$ orbital) with an increase in the outer region falling between the Ti and Au atoms. This is also likely to involve some hybridization of 6s and 6p orbitals. Both repolarizations give rise to a reinforcement of the overlap between the two transition metal atoms.

Finally, a careful analysis of these maps does not make it clear if some net charge transfer between the surface and the deposited transition metal takes place. It is therefore concluded that the main contributions to the metal-surface adsorption energy arise from polarization and covalent interactions.

Fig. 4 DOS curves for Au atom (top) and a slab of TiN (001) surface (middle and bottom).
Fig. 5 DOS curves for Au adsorbed on-top of Ti surface atoms obtained from periodic GGA DFT calculations. Top: projected on Au; middle: projected on Ti; bottom: projected on N.

Conclusions

A theoretical analysis of the Au/TiN interface using a periodic slab model has been conducted. The calculations are based on a GGA density functional theory approach using plane waves to expand the electronic states. The (001) surface of TiN was represented as a 2x2 cell, five layers thick, that has been found to adequately reproduce the surface relaxation observed in thicker layers. The relaxation involves a rumpling of the surface atoms in which the nitrogen subplane moves outwards while the titanium rows move inwards.

The preferred site for adsorbed Au atoms is directly above Ti atoms, with an adsorption energy of -1.90eV. The on-top N atom sites are less stable (Eads=-1.54eV), while the fourfold hollow site has an interaction energy close to the Ti on-top sites, suggesting easy diffusion of gold atoms over the surface at low coverage.

The analysis of DOS and electron density maps indicates that the main contributions to the adsorption energy come from polarization and covalent bond contribution, with low net charge transfer between the surface and the gold atoms.
Fig. 6 Electron density maps for Au adsorbed on-top of Ti surface atoms obtained from periodic GGA DFT calculations. Top: total density: levels: 100, 300, 400, 500, 1000, 1500, 2000. Difference between the total density and those of the fragments, i.e. (Au+TiN)-(Au)-(TiN), is reported at the middle (positive) and at the bottom (negative). For density difference the positive levels are: 10, 30, 40, 50, 100, 150, 200, and the negative: -100, -50, -40, -30, and -10.
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References