Research Article

Structural and Electronic Properties of Pure Ta, TaNO, and TaZrNO with Ab Initio Calculations

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This paper presents the results of self-consistent first-principle calculations for the crystal structure and electronic structure of pure tantalum, TaNO, and TaZrNO within density functional theory (DFT) for the sake of comparison and shows the influence of allowing elements on the interatomic distance and the Fermi level. The large total densities of states (TDOS) value for TaZrNO implies the highest electronic conductivity. The difference in values is due to the Zr metallic atoms presence in TaZrNO compound. There is a strong interaction between Ta and (N, O) (Ta–N = 0.39, Ta–O = 0.21) in TaON compound, and Zr presence increases this interaction (Ta–N = 1.74, Ta–O = 0.30) in TaZrON compound.

1. Introduction

The elemental tantalum Ta crystallizes in three crystalline phases, bcc-Ta (α -phase), f.c.c-Ta, and a new phase which is now generally referred to as β -tantalum. The discoverers of the tetragonal tantalum β -Ta (a metastable phase), in 1965 are Read and Altman [1]. It has been attracting much interest in most applications because of its high resistivity (170–210 $\mu\Omega$ cm) [2–5]. It is preferred for fabricating capacitors and resistors. The chemical stability and robust mechanical properties of Ta make it a particularly desirable material. Numerous crystal structures have been reported for β -Ta. A tetragonal unit cell Ta was proposed by Read and Altman [1] Das [6] proposed a bcc-based superlattice structure, while Burbank [7] proposed a hexagonal hcp structure and β -uranium model that was also proposed by Arakcheeva et al. [8, 9] on the basis of X-ray diffraction (XRD) study on single crystals of β -Ta produced through electrolytic crystallization, and in the end, the anomalous f.c.c-Ta structure was observed in very thin films of tantalum [10, 11].

On the other hand, nitride formation is common to most transition elements. Many compositional and structural

forms exist, with many transition elements forming several different nitride phases. In many of these compounds, nitrogen atoms occupy interstitial lattice sites because they are smaller than the metal atoms. For this reason, they are often referred to as interstitial compounds. Transition metal nitrides are refractory metals that possess technologically useful properties including superconductivity and ultrahigh hardness, and they combine various physical and chemical properties, such as high melting points (around 3000°C). They also possess electronic and magnetic properties that make them useful as electronic and magnetic components and as superconductors [12].

Although monometallic nitrides have been the object of considerable studies [13–15], bimetallic transition metal nitrides have attracted only limited attention. Van Dover et al. [16] investigated the Ternary Transition-Metal Nitride Y-Nb-N and Gd-Cr-N Systems by reactive sputtering, providing evidence for a new superconducting (Nb,Y) N solid solution.

Similarly, the literature on oxynitrides has been scarce. Oxynitrides of transition metals are a new exciting class of materials [17] that possess interesting refractory behaviour,

higher elastic modulus, and hardness. They also offer great potential for their optical properties and recently have received much attention because of their potential use as pigment materials [18]. It has been known that oxygen atoms can substitute nitrogen atoms in monometallic nitrides due to the similarity in their radius. In many of the oxynitrides compounds, the N and O atoms are found in interstitial lattice positions in between the metal atoms. For this reason, their phases can exist over broad composition ranges with appreciable vacancy concentrations (both metal and nonmetal) and their physical properties are quite sensitive to composition. Yashima et al. [19] investigate neutron diffraction for confirmation of anion ordering and synchrotron powder diffraction for high-precision analysis of the crystal structure and electron density of an active TaON photocatalyst sample under visible-light excitation. Yashima et al. [20] employ the density functional theory (DFT) for theoretical calculations of the electron density distribution and partial density of states of TaON compound.

Our primary aim was therefore to present the results of a theoretical investigation of the structural and electronics of metastable β -Ta, bcc-Ta, and f.c.c-Ta. The bcc-Ta ((f.c.c-Ta)) structures are cubic; the space group is $Im\bar{3}m$ (no.229) ($Fm\bar{3}m$ (no.225)) with two (four) formula units per unit cell, the metastable β -Ta (β -uranium, Distorted A15, and Hexagonal) structures are (tetragonal $P4_2/mnm$ (no.136), distorted $Pm\bar{3}m$ (no.223), and hexagonal $P6_3/mmc$ (no.194)). The bimetal (monometal) transition metal oxynitride TaZrNO (TaNO) structures are hexagonal (cubic), and the space group is $P6m2$ (no.187) ($F43m$ (no.216)) with one (four) formula unit(s) per unit cell. Until now, there has been no report on the electronic properties of pure tantalum, TaNO, and TaZrNO.

This paper presents the results of self-consistent first-principles calculations for the crystal structure and electronic structure of pure tantalum, TaNO, and TaZrNO within DFT for the sake of comparison and shows the influence of allowing elements on the interatomic distance and the Fermi level.

The paper is organized as follows. The computational method is described in Section 2. In Section 3, the results are presented and compared with available experimental and theoretical data. Conclusion is given in Section 4.

2. Computational Method

All calculations were performed by using the CASTEP (Cambridge Serial Total Energy Package) simulation program [21] that solves the Schrodinger-like Kohn-Sham equations according to the formalism of the density functional theory (DFT) [22, 23]. We used the Generalized Gradient Approximation (GGA) and a Perdew-Burke-Ernzerhof (PBE) scheme [24] for handling the electronic exchange-correlation potential energy. Also, the pseudopotentials constructed using the ab initio norm conserving scheme describe the valence electron interaction with the atomic core, in which the Ta ($4f^{14} 5d^3 6s^2$), Zr ($4d^2 5s^2$), N ($2s^2 2p^3$), and O ($2s^2 2p^4$) orbitals are treated as valence electrons. Using

FIGURE 1: (Ta) β -uranium structure.

FIGURE 2: (Ta) Distorted A15 β -structure.

for all structures high cut-off energy (280 eV) even at the price of spending long computational time is the condition to obtain accurate results. Brillouin zone (BZ) sampling is carried out using a $6 \times 6 \times 6$ Monkhorst-Pack mesh set [25]. For Ta (distorted A15) and hexagonal (type Cd or Zn) structures, the BZ sampling is carried out using a $10 \times 10 \times 6$ Monkhorst-Pack mesh and a cut-off energy of (280 eV). Atomic positions are relaxed and optimized within a density mixing scheme, based on a Conjugate Gradient (CG) method for eigenvalues minimization. Actually, the equilibrium lattice parameter is determined from a structural optimization, using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization technique. This technique provides a fast way of finding the lowest energy structure, with the

FIGURE 3: TaZrNO structure.

FIGURE 4: Total and partial densities of states for β -Ta (β -uranium).

following thresholds for converged structures: (i) energy change per atom less than 2×10^{-5} eV, (ii) residual force less than 0.05 eV/Å, (iii) atom displacement during geometry optimization less than 0.002 Å, and (iv) maximum stress within 0.1 GPa. The crystal structures of Ta: β -uranium, Ta: Distorted A15 β -structure, and TaZrNO structure are given in (Figures 1, 2, and 3).

3. Results and Discussion

3.1. Structural Properties. Results for the lattice parameter a , c and c/a are reported (Table 1) and compared with experimental and theoretical calculations. Our calculated GGA values for a for pure tantalum are in good agreement with the experimental data [1, 3, 7]. We have obtained the same value for a of TaNO as experimental [26] one. For TaZrNO, our computed lattice constant (a) is bigger

FIGURE 5: Total and partial densities of states for β -Ta (distorted A15). FIGURE 6: Total and partial densities of states for β -Ta (hexagonal model).

than the experimental one, within 7.4% [27]. Also, for both structures, the calculated lattice parameter ratio c/a (0.523, 1.978, and 1.792 for 0020 β -uranium, distorted A15, and hexagonal, resp.) is in reasonable accord with the previously considered data (0.531, 1.860, and 1.890, [1, 7, 28–31] and 1.098 for TaZrNO that is also in reasonable accord with of 1.064) [27]. In order to attempt an understanding the interatomic distances of the various compounds, we have found excellent agreement between our calculated

FIGURE 7: Total and partial densities of states for α -Ta.

FIGURE 8: Total and partial densities of states for f.c.c-Ta.

and available experiment interatomic distances for different phases of pure tantalum. The results of distances are reported in Table 1.

3.2. Electronic Structures. Density of states and electronic band structure often provide sufficient information for a thorough characterization of the electronic properties of the material. Total density of states (DOS) of all β -Ta (metastable phase), α -Ta, and f.c.c-Ta structures were calculated in order to understand differences in the chemical bonding between them. The DOS for β -Ta structure, shown in Figures 4 and 5, is concentrated in two peaks. The low energy peak, between -9 and -3 eV (the zero of energy is taken at the Fermi energy E_f), is comprised mostly of s and d states. The other broad

peak, lying at and above E_f , has d character with small admixture of p characters and is responsible for the $N(E_f)$ of 26.024 and 18.268 states/eV $\text{\AA}^3$ for β -uranium and distorted A15 models, respectively. For the hexagonal model, the DOS is mainly due to the d states, with small s characters at around -5 and 10 eV (Figure 6). Figures 7 and 8 shows respectively the density of states for α -Ta and fcc-Ta that are mainly dominated by d states and little s contributions especially around -5 eV. Both structures are metallic because of the finite DOS at the Fermi level (E_f). The DOS values at E_f of all structures are shown in Table 2. Let us mention a large DOS at the Fermi level; this implies a high electronic conductivity and various applications to electronic conductors. Figures 9 and 10 show the total density of states (TDOS) and partial density of states (PDOS) for TaNO and TaZrNO compounds. The TDOS of TaNO (TaZrNO) can be mainly distributed in the following three energy regions in the valence bonding region.

- (1) In the region one from approximately -26 eV to -23 eV (-25 eV to -22 eV). In this region, the DOS mainly consists of s orbitals of O, together with a small portion of s orbitals of Ta (s orbitals of O, together with a small portion of s orbitals of Ta and Zr). These states represent the electronic core structures;
- (2) In region two, it is from -18.0 eV to -16.0 eV (-19 eV to -17 eV). In this region, the DOS is contributed mainly from the hybridized s orbitals of N, d orbitals of Ta, together with a small portion of s orbitals of Ta for TaNO, and the same behavior is observed for TaZrNO compounds;
- (3) In region three; it is from -14 eV to 0 eV (-12 eV to 0 eV). This is due to the p -O, p -N, and d -Ta orbitals (p -O, p -N, d -Ta, and d -Zr with a small portion of s -Ta and s -Zr contributions). Above the Fermi energy level, the DOS is predominated by d -Ta and p -N orbitals with a small portion of p -O contribution (d -Ta, d -Zr, p -N, and p -O orbitals with a small portion of p -Ta and p -Zr contributions), corresponding to the electronic anti-bonding states. The two TDOS have some similarities, however, in Figures 9 and 10.

TDOS at the Fermi level is 1.493 for TaNO.

TDOS at the Fermi level is 2.010 for TaZrNO, and the large value for TaZrNO implies the highest electronic conductivity.

The difference in values is due to the Zr metallic atoms presence in TaZrNO compound.

The pure tantalum has the highest (E_f), and generally speaking, the smaller the (E_f) is, the unstable the compound will be.

3.2.1. Bond Orders between Atoms. Bond order is the overlap population of electrons between atoms, and this is a measure of the strength of the covalent bond between atoms. If the overlap population is positive (+), a bonding-type interaction is operating between atom, whereas if it is negative (−), an antibonding-type interaction is dominant between

FIGURE 9: Total and partial densities of states for TaNO.

FIGURE 10: Total and partial densities of states for TaZrNO.

TABLE 1: Lattice constant, shortest Ta-Ta, density, and atomic/unit cell of the all metastable phase.

Materials	Lattice constant a_0 (Å)	c/a	Shortest Ta-Ta (Å)	Density (g/cm ⁻³)	Atom/unit cell	Reference
β -uranium	9.9345	0.523	2.608	17.582	30	[28, 29]
	10.194	0.531	2.650	16.330	30	
Distorted A15	5.1551	1.978	2.550	17.736	16	[1, 30, 31]
	5.3400	1.860	1.890	16.960	16	
Hexagonal	2.804	1.792	2.805	17.605	2	[7]
	2.830	1.890	2.830	16.230	2	
α -Ta	3.217	—	2.786	18.050	2	[3]
	3.31	—	2.860	16.550	2	
f.c.c-Ta	4.108	—	2.905	17.329	4	[11–31]
	4.390	—	3.100	14.21	4	
TaNO	4.827	—	3.031	17.798	12	[26]
	4.827	—	—	—	—	
TaZrNO	3.373	1.098	3.707	13.733	4	[27]
	3.645	1.064	—	—	—	

TABLE 2: Fermi level E_f of the all metastable phase.

	β -uranium	Distorted A15	Hexagonal	α -Ta	f.c.c-Ta	TaNO	TaZrNO
E_f	26.272	18.268	2.418	2.579	4.704	1.493	2.010

atoms. It is apparent that the bonding-type interactions are operating between the metal M (M = Ta, Zr) ($4d$ and $5d$) and the nonmetal (N, O) $3d$ electrons. Thus, there is a strong interaction between Ta and (N, O) (Ta – N = 0.39, Ta – O = 0.21) in TaON compound, and Zr presence increases this interaction (Ta – N = 1.74, Ta – O = 0.30) in TaZrON compound.

4. Summary and Conclusion

Using the first principles based on the DFT, we studied the total (partial) density of states TDOS (PDOS) of pure tantalum, TaNO, and TaZrNO. The large value for TaZrNO implies the highest electronic conductivity. The difference in values is due to the Zr metallic atoms presence in TaZrNO compound. A bonding-type interaction is operating between atoms, and thus there is a strong interaction between Ta and (N, O) (Ta – N = 0.39, Ta – O = 0.21) in TaON compound, and Zr presence increases this interaction (Ta – N = 1.74, Ta – O = 0.30) in TaZrON compound.

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