
Electronic Properties of Titanium using density functional theory

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Abstract

In the present work, the electronic properties of titanium were studied in three phases of α , β and ω using the Density Function Theory (DFT). The full potential augmented plane wave plus local orbital (FLAPW+lo) method was applied using the generalized gradient approximation. The calculated total energies showed that omega phase was more stable than the two other phases. The largest electrical conductance was related to the β phase. These results were in good agreement with the findings of the previous works. In addition, these results showed that an increase in volume would lead to a decrease in energy; thus, causing an increase in the electrical conduction.

Keywords: Electronic conductivity; Titanium; DFT calculation

1. Introduction

Group IV transition metals including Titanium, Zirconium, Hafnium and their alloys have various applications in industry. Titanium has higher stability and lower density (45%) than steel. Ti($z=22$) with a partially filled 3d shell is in the d^2s^2 configuration and appears in five phases of α (hcp), ω (hexagonal), γ (distorted hcp), δ (distorted bcc) and β (bcc) [1, 2, 3] in which γ and δ are instable phases.

Phases α and ω are at room temperature and atmospheric pressure and phase β is found to be up to 900°C and 8 GPa [4]. Furthermore, theoretical calculations have shown that ω phase is more stable than α phase at 0 K [5-9]. In addition, the observed experimental results of the diffraction have shown that the stability range of α phase varies between room temperature to around 923 K [10].

At room temperature, the transition phases $\alpha \rightarrow \omega$, $\omega \rightarrow \gamma$ and $\gamma \rightarrow \delta$ have been observed in 7.4 GPa, 128 GP and 140 GP [1], respectively; however, transition to β phase occurs at higher temperature. The experimental lattice parameters are as follows: $a=2.957 \text{ \AA}$, $c=4.685 \text{ \AA}$ for α phase [11], $a=4.624 \text{ \AA}$, $c=2.813 \text{ \AA}$ for ω phase [12] and $a=3.31 \text{ \AA}$ for β phase [4]. Based on the Wyckoff notation, space groups of α , ω and β are 194; P63/mmc, 191; P6/mmm and 229; Im-3m, respectively [13]. Moreover, α , ω and β have the structures with 2, 3 and 1 atoms in the unit cells, respectively; their positions are shown in Table.1. Each host atom in

the hcp lattice is surrounded by 12 nearest neighbors and this number is 8 for β phase.

In the hexagonal structure, (ω) atoms in the host B layer (as shown in Fig. 1) have a total of 11 neighbors; in the A layer, they have 14 neighbors.

2. Calculations

All the calculations were performed with wien2k package based on the FLAPW+lo method [14]. The exchange correlation potential was measured by LDA (Local Density Approximation) and GGA (PBE96) (Generalized Gradient Approximation); but it should be considered that these two approximations have negligible changes in calculating the density of state and band structures. The energy cut-off -6 Ryd was used between core and valance electrons and it was found to be sufficient for the convergence of the total energy occurring about 1×10^{-4} e. The optimization showed that the largest value of the charge density in Fourier expansion was $G_{\max}=12 \text{ bohr}^{-1}$. As Ti was paramagnetic in the bulk, spin polarization was neglected. The muffin-tin radius separated electrons to core state (which was treated fully relativistically) and semi-core and valence states were computed by a scalar relativistic approximation. RK_{\max} , k-mesh and k-point for all the phases are mentioned in Table 2.

3. Results and Conclusion

The total energy was calculated for α , ω and β phases. The obtained results indicated that the total energy of β phase was greater than that of the two

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other phases and the total energy of α was quite larger than that of ω (Table 3). The exchange-correlation was performed using both the GGA and LDA methods; since GGA led to lower energy, it was used in this work.

Table 1. Atomic position for α , β and ω structures

| | α | β | ω |
|---|-------------------------------------------|---------|-------------------------------------------|
| 1 | $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ | (0,0,0) | (0,0,0) |
| 2 | $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$ | | $(\frac{1}{3}, \frac{2}{3}, \frac{1}{3})$ |
| 3 | | | $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$ |

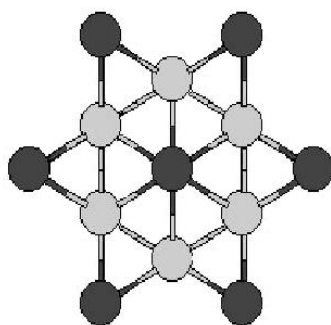


Fig. 1. Hexagonal structure, dark points show A-layer and light points show B-layer

Table 2. Optimized k-point and RMT radius for all three phases

| Phase | RMT(Å) | k-point | k-mesh | RKmax | |
|----------|--------|---------|--------|-------|-----|
| α | 2.6 | 764 | 64 | 8.5 | |
| ω | 2.6 | 2.47 | 2460 | 171 | 8.5 |
| β | 2.6 | | 512 | 26 | 8 |

Table 3. The total energy for all three phases

| Method | E_{α} (Ryd/atom) | E_{ω} (Ryd/atom) | E_{β} (Ryd/atom) |
|--------|-------------------------|-------------------------|------------------------|
| LDA | -1704.01012 | -1704.01241 | -1704.00033 |
| GGA | -1707.6357 | -1707.63600 | -1707.5023 |

Total DOS and partial DOS of d, s and p-bands are shown in Figs. 2 and 3; they were in good agreement with the previous works [15].

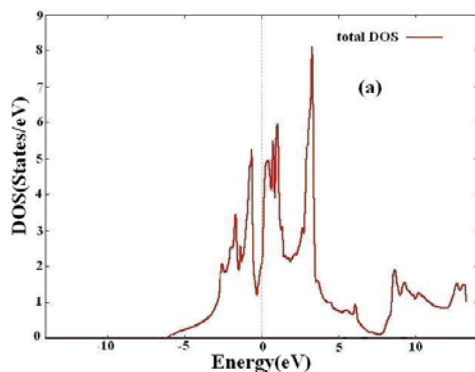


Fig. 2. (a)

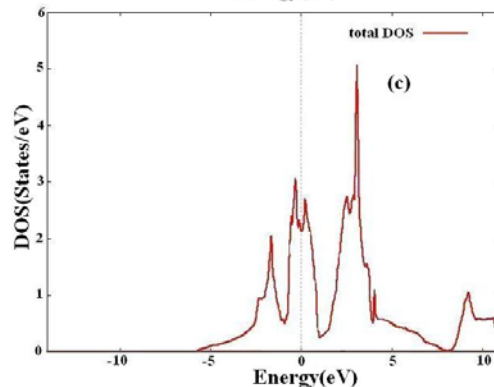
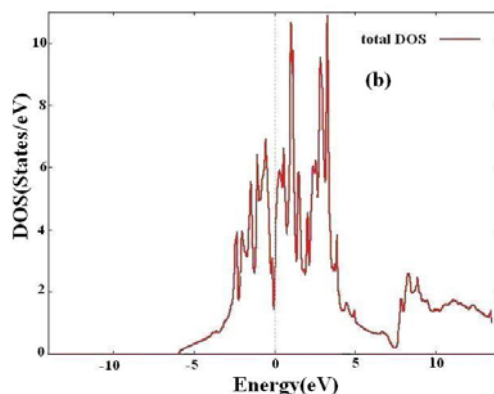


Fig. 2. Total DOS of (a) α -phase, (b) β -phase and (c) ω -phase

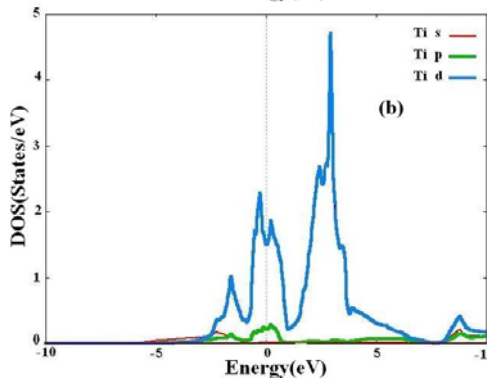
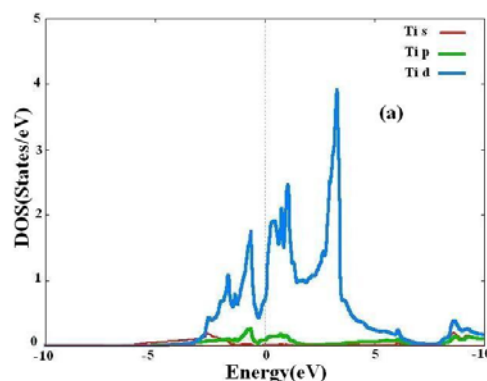


Fig. 3. (a) and (b)

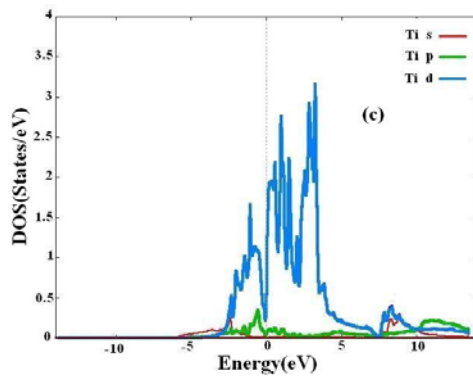


Fig. 3. Partial DOS of (a) α -phase, (b) β -phase and (c) ω -phase.

The band structure related to three phases is presented in Figs. 4-a, 4-b and 4-c, respectively. The electrical properties were determined by the location of the Fermi level and the DOS per atom at Fermi energy ($n(\epsilon_f)$).

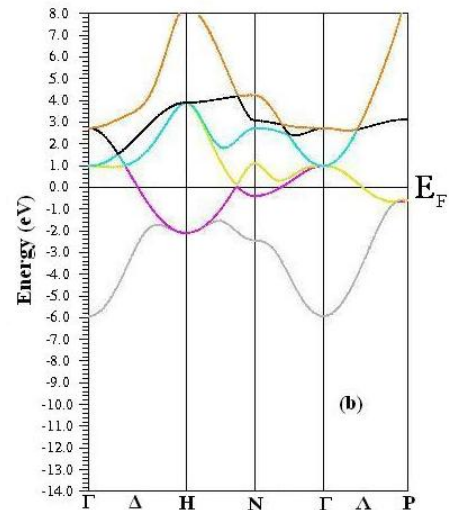


Fig. 4. (a) and (b)

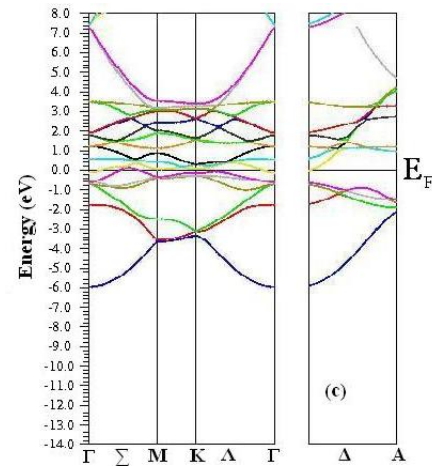
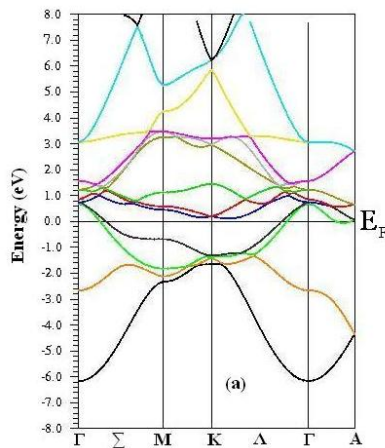


Fig. 4. Band structure of (a) α -phase, (b) β -phase and (c) ω -phase

Table 4. The number of state at the Fermi level and for s, p and d-orbitals

| Phase | $n(\epsilon_f)$ (State/Ryd) | $n_s(\epsilon_f)$ (State/Ryd) | $n_p(\epsilon_f)$ (State/Ryd) | $n_d(\epsilon_f)$ (State/Ryd) | ϵ_f (Ryd) |
|----------|-----------------------------|-------------------------------|-------------------------------|-------------------------------|--------------------|
| α | 26.35 | 0.09 | 1.14 | 9.19 | 0.51304 |
| ω | 23.26 | 0.37 | 0.66 | 2.10 | 0.537 |
| β | 29.51 | 0.13 | 2.92 | 19.83 | 0.48751 |

Considering the fact that conductivity is related to the number of states at the Fermi level $n(\epsilon_f)$ and according to the mentioned values in Table 4, the sequence of electrical conductivity was obtained as $\sigma_\beta > \sigma_\alpha > \sigma_\omega$.

This statement can be clearly observable in Fig.5. According to this figure, for all three phases, an increase in volume led to a decrease in the energy; therefore, it caused an increase in the electrical conduction.

Furthermore, as shown in our previous work [16], increases in pressure led to a decrease in the lattice constant and inter atomic space.

In the comparison of $n(\epsilon_f)$ for s, p and d-orbitals (as shown in Table 4), d-orbitals played an important role [17] in conductivity. Thus, $n_d(\epsilon_f)$ instead of total $n(\epsilon_f)$ was compared in the current study.

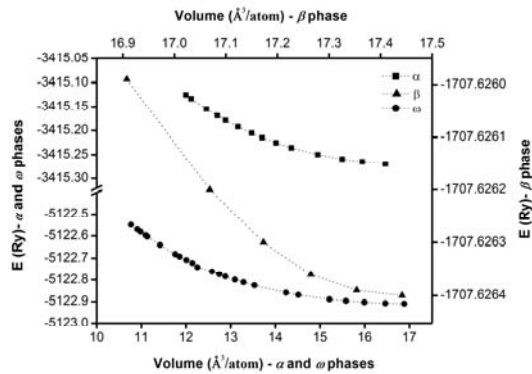


Fig. 5. Energy vs. volume per atom of α , β and ω phases

As could be expected from the band structure of all phases of Titanium, there were no band gaps between conductance and valence bands and all three phases were metallic. In addition, there was no band in less than -7.0 eV. The density of bands around the Fermi energy level increased from β to α and α to ω because of the increase in the number of atoms per unit cell [18].

Moreover, the X-ray photoelectron spectroscopy (XPS) spectra (Fig. 6) were calculated. The same results were stated for the comparison of the energy value corresponding to the peak in this figure. As shown in the figure, the energy value corresponding to the peak in Fig. 6a ($E_{\alpha}=2.792792$ eV) was smaller than the one in Fig. 6b ($E_{\beta}=2.840795$ eV) and that in Fig. 6c was greater than the energy value of the peak demonstrated in Fig. 6c ($E_{\omega}=2.588588$ eV); meaning that, β phase was more localized than α phase and the latter was more localized than ω phase. The reason can be that, if the peak of XPS is located on greater energy, the orbitals will be more localized.

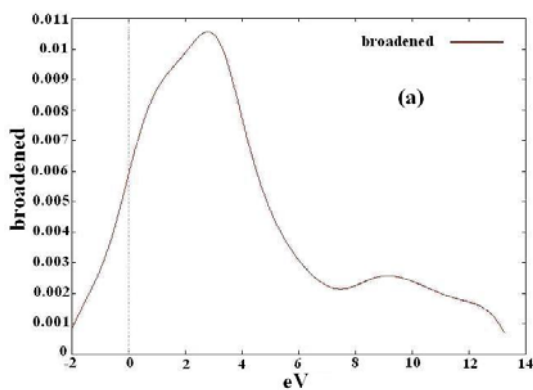


Fig. 6. (a)

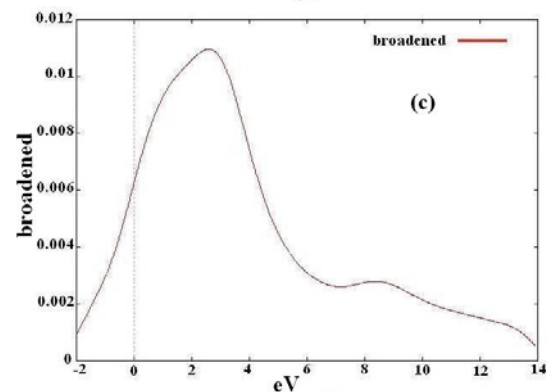
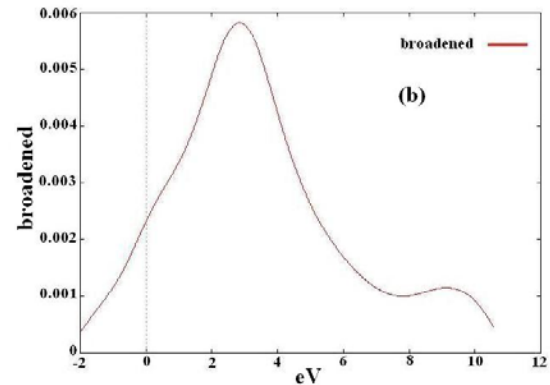


Fig. 6. XPS of (a) α -phase, (b) β -phase and (c) ω -phase

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