Electronic Structure and Defect States of Undoped and (Nb, Ta)-doped Anatase using Density Functional Theory

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ABSTRACT

In this work an overall electronic structure including the position and formation energies of various intrinsic and extrinsic defects are computed for the undoped and (Nb, Ta)-doped anatase using Density Functional Theory aided by Hubbard correction (DFT+U). The intrinsic point defects considered here are, oxygen vacancy (V_O), oxygen interstitial (O_i), titanium vacancy (V_Ti) and titanium interstitial (Ti_i). Additionally, this study investigated the interaction of the dopant atoms with these native defects. Out of all the intrinsic defects considered here, V_Ti and Ti_i are found to be most stable under equilibrium condition. Whereas, conduction band in undoped anatase is consisted of mainly Ti 3d with a minor component of O 2p states, valence band is found to be mainly composed of O 2p with a minor contribution from Ti 3d states. V_O and Ti_i are found to form localized states in the band gap. In Nb- and Ta-doped anatase, hybrid states of Ti 3d and Nb 4d and Ta 5d and Ti 3d are found to form near the conduction band edge along with in the vicinity of conduction band, thereby reducing their band gaps as compared to undoped anatase. Moreover, O_i stabilized near the dopant atom, suggesting higher bond strength
between the dopant and the oxygen atoms. Anisotropy in the effective mass is seen, with the extent of anisotropy being higher for doped anatase. Finally, an alignment of band diagrams for all the intrinsic and extrinsic defect states is performed using vacuum potential from slab-supercell calculation as reference.

Keywords: Electronic structure; density functional theory; native defects; effective mass; formation energy; dopants.

1. INTRODUCTION

Transparent Conducting Oxides (TCOs) are compounds that exhibit high optical transparency and electrical conductivity. These seemingly opposite properties are achieved by doping wide band gap oxides with suitable dopants. Whereas, the large band gap provides the oxide a high optical transparency, the dopants create impurity levels which generate charge carriers responsible for the high conductivity. In general, TCOs find a large number of applications in optoelectronic devices, like, thin film solar cells, light emitting diodes, display panels, etc., the most widely used in the industry being Sn-doped In$_2$O$_3$ (ITO)\(^1\). Although the high optoelectronic properties exhibited by ITO has made it the first choice in optoelectronic industry, its high cost because of the low concentration of indium in the earth’s upper continental crust (~50 ppb)\(^2\) has pushed researchers for designing alternative TCOs.

To this end, TiO$_2$ is a chemically stable, low cost, non-toxic, wide band-gap semiconductor and has been mainly studied in the literature for the photocatalytic applications.\(^3\)\(^4\) Doping introduces additional energy levels, and depending on the position, either it could make this material even more attractive for photocatalytic application (by lowering the conduction band edge) or can make it an effective TCO by adding charge carriers into the conduction and/or the valence bands without compromising on its transmittance. Moreover, it would be interesting to see if anatase can be designed, where both these properties can co-exist. Out of all three thermodynamically stable phases, anatase is favoured both for the photocatalytic and the TCO applications because of its relatively higher activity and lower electron effective mass as compared to others.\(^5\)\(^6\) Though several experimental reports exist in literature, most of these are found to focus only towards fabricating undoped and/or doped anatase for these applications,
Fundamental understanding of this material system is necessary to design high quality materials for respective applications. Moreover, a large number of native point defects can be present in anatase, which then modifies the electronic structure for both the undoped and doped anatase systems, thereby significantly altering the optoelectronic properties. Furthermore, process parameters could significantly vary the microstructure of the synthesized materials, thereby also affecting their optoelectronic properties.

To this end, ab initio (first principle) calculations not only help in the understanding of how the defects (intrinsic and extrinsic) affect the electronic structure of materials at the atomic level (and hence their optoelectronic properties), but also provide insights into how those properties might be improved. Though a range of first principle studies using density functional theory (DFT) have been carried out in the literature for the undoped and doped anatase, the obtained results were found to contradict, which could be attributed to the use of computational methodology in DFT. In this regard, Phattalung et al. computed the native defects in anatase using Local Density Approximation (LDA) exchange correlation functional and found none of these four defect states (i.e., oxygen vacancy ($V_\text{O}$), oxygen interstitial ($O_i$), titanium vacancy ($V_{\text{Ti}}$) and titanium interstitial ($\text{Ti}_i$)) being formed in the band gap. However, experimental data had earlier revealed formation of mid-gap states in these systems, and therefore this discrepancy could be assigned to the incorrect self-interaction error of these functionals in DFT. Note here that, the more advanced methods like DFT + U and hybrid functionals could correctly predict the existence of mid-gap defect levels due to native defects and could also predict the band gap accurately to a certain extent. To this end, Morgan et al. used GGA + U in their calculations and found localized mid-gap states being formed due to the neutral oxygen vacancies and titanium interstitials, both in anatase and in rutile. Delocalized resonant states were predicted for Nb-doped anatase system, thereby suggesting $n$-type TCO for this system. J. Osorio Guillen et al. identified two types of behaviour for transition metal impurities in oxides; (i) in which the delocalized states were formed inside the conduction band thereby making the transparent material conductive and (ii) in which a localized mid gap state could form which then could transform the magnetic properties of the host material, indicating the energy of the outer $d$ electrons of the impurity atom playing a decisive role on the eventual position of this defect state.
Most of the published works till date have either investigated the effect of (neutral) native defects or the effect of dopants on the electronic structure of anatase in an isolated manner. In this paper we used GGA + U approach in DFT to calculate the position and formation energies of various intrinsic (neutral as well as charged) and extrinsic defects for the undoped and of (Nb, Ta)-doped anatase. Apart from understanding the electronic structure of these systems individually, in this study a combination of these two defects (i.e., one native defect and the other extrinsic defect) was used to see the interaction between the native defects with those of the dopants in altering the electronic properties of these systems. Formation energy of all these native defects was calculated to understand the stability of these defects under different conditions. Finally, an alignment of band diagrams for all the intrinsic and extrinsic defect states is performed using vacuum potential from slab-supercell calculation as reference.

II. COMPUTATIONAL DETAILS

Here the electronic structure of pure anatase, along with those for the various intrinsic and extrinsic electronic defect states were calculated using density functional theory (DFT) implemented in Quantum ESPRESSO software suite.\textsuperscript{17} Whereas, neutral and charged states of the oxygen vacancies (denoted as $V_O$, $V_O^{+1}$, $V_O^{+2}$, thus the charge state varying from 0 to 2), oxygen interstitials ($O_i$), titanium vacancies ($V_{Ti}$) and titanium interstitials (denoted as $Ti_i$, $Ti_i^{+1}$, $Ti_i^{+2}$, $Ti_i^{+3}$, and $Ti_i^{+4}$, with the charge states varying from 0 to 4) were used as the intrinsic defect states, Nb and Ta dopants were used as the extrinsic defects. Here, a $2 \times 2 \times 2$ supercell (constructed from the conventional cell of anatase) with a tetragonal structure [see FIG. 1(a)], which contained a total of 96 atoms (i.e., Ti$_{32}$O$_{64}$) was used for the computation. Moreover, here Generalized Gradient Approximation (GGA) Perdew-Burke-Ernzerhof (PBE) was adopted for the exchange-correlation potential.\textsuperscript{18} Note that, standard DFT functionals tend to delocalize electrons over the crystal and hence, are not represented correctly only by these functionals, particularly for the material systems which contain transition elements with partially filled $d$ or $f$ orbitals. Hence along with GGA-PBE, a Hubbard-like (U) correction term, which accounted for the columbic repulsion of these localized $d$ or $f$ electrons was used here; henceforth denoted as DFT (GGA) + U approach.\textsuperscript{19} The reported U value of 4.2 eV was used here to do the present
calculation.

[Image: FIG. 1. Schematic of undoped (a) and Nb-doped anatase supercell (b), the first brillouin zone of anatase lattice with high symmetry k points (c) and distorted TiO$_6$ octahedron of anatase (d). The two vertical Ti-O (apical) bonds are slightly longer than the other four equatorial Ti-O bonds. The central blue atom is the Ti atom and the red atoms are O atoms.]

Note that this value was used in the literature to calculate the lattice parameter, bulk modulus and defect states of surface oxygen vacancies in anatase using DFT (GGA) + U approach, and these calculated data were found to be in agreement with those of the experimental results and/or those calculated using the hybrid DFT route. Here, projector augmented wave (PAW) type pseudopotentials obtained from PSlibrary were used to model for the core electrons (i.e., [He], [Ne], [Ar]3d$^{10}$ and [Kr]4d$^{10}$4f$^{14}$ for O, Ti, Nb and Ta atoms respectively). Further, 2s$^2$2p$^4$, 3s$^2$3p$^6$3d$^2$, 4s$^2$4p$^6$5p$^6$5d$^3$ and 5s$^2$6s$^2$5p$^6$5d$^3$ were used for O, Ti, Nb and Ta respectively in this computation as their valence electron configuration. Convergence tests were performed to determine the K-Points mesh for Brillouin zone integration and cut off energy for the plane wave expansion. Whereas, Monkhorst-Pack k-point mesh of 3 $\times$ 3 $\times$ 3 was used for the Brillouin zone integration, a cut off energy of 55 Ry (i.e., 748 eV) was used for the plane wave expansion. Note that, increasing the cut off energy from 55 to 60 Ry changed the total
energy of the cell by only about 0.001 Ry (i.e., 0.013 eV), thereby claiming 55 Ry as a reasonable cut off energy value. Moreover all the supercell structures were fully relaxed before proceeding with the calculations. The convergence threshold on energy and forces for ionic minimization were taken as $2.72 \times 10^{-3}$ eV and $5.14 \times 10^{-2}$ eV/Å respectively. Note that after performing the main calculation, a denser mesh of $6 \times 6 \times 6$ was used to compute the density of states (DOS) in order to obtain sharp peaks in the plot.

Whereas intrinsic neutral defects of vacancies and interstitials were created by removing and adding one atom respectively from and to the supercell, charged defect states were created by using the charged supercell and a neutral background charge. For example, to create a neutral O vacancy ($V_O$), one neutral O atom was removed from the supercell, whereas, for creating $V_O^{+1}$, a neutral O atom and one electron were removed from the supercell and similarly for creating $V_O^{+2}$, a neutral O atom and two electrons were removed from the supercell. Likewise to create a neutral interstitial defect, a single interstitial atom was introduced into the supercell, whereas to create the charged interstitials, electrons were added to or removed from the supercell following the above mentioned procedure. To model doping, a Ti or an O atom was substituted with a Nb or a Ta atom to create $\text{Nb}_{Ti}$, $\text{Nb}_{O}$, $\text{Ta}_{Ti}$, and $\text{Ta}_{O}$ defect states [see FIG. 1(b)]. To compare and understand the relative stabilities of various intrinsic and extrinsic defects, formation energy ($E_f^{[X^q]}$) for all these above cases was calculated using the following equation:

$$E_f^{[X^q]} = E_{tot}^{[X^q]} - E_{tot}^{[bulk]} - \sum_i n_i \mu_i + qE_F$$  \hspace{1cm} (1)

where, $E_{tot}^{[X^q]}$ is the total energy of the supercell with defect X, $E_{tot}^{[bulk]}$ is the total energy of an equivalent defect free supercell, $n_i$ represents the number of atoms of type $i$ that have been added to or removed from the supercell to create the defect, $\mu_i$ represents the chemical potential of the defect forming species (Ti or O), $q$ represents the charged state of the defect and $E_F$ is the Fermi level referenced to the valence band maxima (VBM) in the bulk.

To calculate the chemical potential of Ti and O in Ti- or O-rich conditions, the following boundary criteria were considered:

$$\mu_{Ti} + 2\mu_{O} = \mu_{TiO_2, bulk} \hspace{1cm} (2)$$

$$\mu_{Ti} \leq \mu_{Ti, bulk} \hspace{1cm} (3)$$
\[ \mu_0 \leq \frac{\mu_{\text{O}_2\text{ molecule}}}{2} \]  

(4)

where, \( \mu_{\text{Ti}} \) and \( \mu_0 \) are the chemical potentials of the defect forming species of Ti and O respectively; \( \mu_{\text{Ti}_2\text{O}_3\text{ bulk}} \), \( \mu_{\text{Ti} \text{ bulk}} \) and \( \mu_{\text{O}_2\text{ molecule}} \) represent the chemical potentials of bulk TiO_2, Ti, and O_2 molecule respectively.

Note that, here the total energies were calculated for each of these structures per formula unit, which were then used as their chemical potential values. Moreover, \( \mu_{\text{Ti}} \) and \( \mu_0 \) should always be lower than their natural phases of \( \mu_{\text{Ti}_{\text{ bulk}}} \) and \( \mu_{\text{O}_2\text{ molecule}} \) respectively, otherwise which these natural phases of Ti and O_2 would form instead of TiO_2 (see eq. (3) and (4)). Additionally, for O-rich (or Ti-poor) condition, \( \mu_0 = \frac{\mu_{\text{O}_2\text{ molecule}}}{2} \) and for O-poor (or Ti-rich) condition, \( \mu_{\text{Ti}} = \mu_{\text{Ti}_{\text{ bulk}}} \).

The high symmetry points of the first brillouin zone which were used to plot the band structure (i.e., \( \Gamma \) at the centre of the brillouin zone, A at a vertex, R and M at the edge centres, X and Z at the face centres) are shown in FIG. 1(c). Next, the effective masses \( (m^*) \) of the electron and the hole were calculated by respectively fitting (parabolically) the bottom of the conduction band and top of the valence band along \( \Gamma - X \) and \( \Gamma - Z \) directions of the brillouin zone with the following relation:

\[ m^* = \hbar \left( \frac{d^2E}{dk^2} \right)^{-1} \]  

(5)

where, \( E \) is the energy of the electron at wave vector \( k \) in a particular band, \( \frac{d^2E}{dk^2} \) represents the curvature of that band and \( \hbar \) is the reduced Planck’s constant \( (1.054 \times 10^{-34} \text{ J.s}) \).

Finally, for aligning the band diagrams for different systems, vacuum level calculations were performed using the slab-supercell model. Slabs with nine layers of atoms (with the atomic layers of (001) miller plane) and vacuum of 20 Å width on both the sides were used here. Convergence for the work function of pure anatase was checked with respect to the length of the vacuum and was found to be same up to the second decimal places irrespective of vacuum lengths of 19 and 20 Å, thereby making 20 Å a reasonable choice for vacuum level calculations. The work function of pure anatase was found to be 5.80 eV which is close to the experimentally measured value of 5.35 eV, indicating these calculations to have sufficient accuracy.\(^{23} \) Since all
the systems should have the same vacuum energy level, this level was used as the reference for band alignments.

III. RESULTS AND DISCUSSIONS

A. Electronic structure of pure anatase

The lattice parameters of anatase as well as that of Ti-O bond lengths of the distorted TiO$_6$ octahedron [see FIG. 1(d)] computed in this work are provided in TABLE I, which were found to be in agreement with the literature reports. This close agreement of the present data with those of the existed theoretical and experimental reports suggested reliability of the present computational work to predict the electronic structure and defect states of this system.

TABLE I. Lattice parameters and Ti-O bond lengths for anatase (in Å)

|                  | Lattice parameter | Ti-O bond length |
|------------------|-------------------|------------------|
|                  | \(a\) | \(b\) | \(c\) | Apical | Equatorial |
| Current work     | 3.84 | 3.84 | 9.84 | 1.99 | 1.95 |
| Other computational work (GGA + U)$^{24}$ | 3.89 | 3.89 | 9.53 | 2.01 | 1.98 |
| Experimental value$^{24}$ | 3.78 | 3.78 | 9.50 | 1.98$^{25}$ | 1.93$^{25}$ |

FIG. 2. Band structure (a) and PDOS (b) of anatase. Points P1 and P2 correspond to the CBM and VBM respectively and \(E_g\) is the indirect band gap (2.44 eV). \(E_F\) represents the fermi level.
The band structure of pure anatase is shown in FIG. 2(a). Whereas, the conduction band minima (CBM) was found to lie at Γ or the centre of the first brillouin zone (marked as P₁ in FIG. 2(a)), the valence band maxima (VBM) lied in between the K Points of Γ and M (marked as P₂ in FIG. 2(a)), indicating that anatase has an indirect band gap ($E_g$) of 2.44 eV. This is an underestimation with respect to the experimentally reported value of 3.4 eV for this system.²⁶ Note that, this mismatch arises primarily from the self interaction error in DFT for using the highly localized $d$ and $f$ orbital electrons. Although this error can be reduced by using the GGA+U approach, depending on the type of calculation (i.e., DFT, DFT+U, or DFT using hybrid functionals) and the choice of the empirical parameters like $U$ and mixing parameter ($\alpha$ which defines the amount of exact Hartree-Fock exchange to be mixed with the standard DFT functional), the computed values in the literature widely range from 2.1 to 3.5 eV.²⁷,²⁸ Moreover, the Fermi level ($E_F$) was found to be at the valence band edge, indicating the highest occupied energy states for the electrons [see FIG. 2(a)].

Projection of the density of states onto the atomic orbitals (known as projected or partial DOS; PDOS) revealed the valence band of anatase being mainly comprised of O 2p orbitals along with minor contribution from Ti 3d orbitals [see FIG. 2(b)]. Similarly, the conduction band was found to primarily consist of Ti 3d orbitals along with a small contribution from O 2p orbitals. Moreover, the charge density plots [see FIG. 3(a)-3(b)] of the valence and the conduction band edges (VBE and CBE) showed the former being mainly composed of the dumbbell shaped O 2p orbitals, whereas the latter comprised of four lobed Ti 3dx_y orbitals. Moreover, the band structure of anatase revealed the conduction band edge on an average having a higher curvature than that of the valence band edge which was rather flatter [see FIG. 2(a)]. This asymmetry in curvature was particularly visible in the band structure drawn along Γ − $X$ direction of the brillouin zone [see FIG. 4(a)], thereby giving rise to increased disparity in the effective masses of the charge carriers; i.e., effective masses of electrons at CBM and holes at VBM along Γ − $X$ direction (denoted as $m_{ex}$ and $m_{hx}$ respectively and similarly $m_{ez}$ and $m_{hz}$ for charge carriers along Γ − $Z$ direction), which were found to be 0.59 $m_e$ and 1.72 $m_e$ respectively ($m_e$ being the rest mass of an electron). The difference in curvature of the valence and the conduction band edges is due to the localized oxygen $p$ nature (O 2p states) of the valence band edge, which makes those bands very flat; a trend observed in many transparent conducting oxides (TCOs).²⁹,³⁰ This is probably the reason why anatase is generally not used as a $p$-type TCO because the generated holes would...
have a very high effective mass due to the flat nature of the valence band and thus an extremely low mobility.\textsuperscript{29}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{charge_density.png}
\caption{Charge density plots (at $\Gamma$ point) of VBE (a) and CBE (b) for a single (but different) slice of atoms along (001) plane of pure anatase. The dumbbell structures (around O atoms) are the O 2p orbitals (seen here at different orientations) while the four lobed structures (around Ti atoms) represent Ti 3d<sub>xy</sub> orbitals. The charge isosurface is shown at a density of 0.01 e/Å\textsuperscript{3}.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{band_structure.png}
\caption{Band structure of pure anatase along $\Gamma$-X direction (a) and $\Gamma$-Z direction (b) showing the difference in the curvature of the bands along these directions.}
\end{figure}

Moreover, anisotropy in the band structure and hence in the effective mass values along different directions of the brillouin zone were also observed [see FIG. 4(a)-4(b)]. $m_{ex}$ ($\sim 5.10$ m\textsubscript{e}) was found to be about ten times higher than $m_{ex}$ ($\sim 0.59$ m\textsubscript{e}), which would give rise to anisotropy in the mobility and conductivity values. A similar anisotropy in the effective mass of electrons in anatase was also observed by Kamisaka et al.\textsuperscript{31}

Finally, bader charge analysis showed the average partial charges on Ti and O atoms in anatase to be +2.25 and -1.15 respectively, indicating some amount of covalent characteristic to
Ti-O bond rather than a complete ionic characteristic, in which case the charge states on Ti and O would have been +4 and -2 respectively. These results are found to be in close agreement with those of the data reported by Koch et al, where partial charges of +2.5 and -1.3 were obtained respectively for Ti and O in anatase.32

**B. Native Defect States in Anatase**

1. **Geometrical distortion and Charge redistribution due to neutral native defects**

Here, the original bond lengths of the anatase crystal (i.e., of the undistorted lattice) were found to alter because of the creation of (neutral) native defects of Vₐ, Tiᵢ, Vₜ, and Oᵢ, thereby bringing geometrical distortion to the vicinity of the defect sites [see TABLE II and FIG. 5(a)-5(d)]. The directions in which the attractive and the repulsive forces were found to act on the neighbouring atoms of the native defects are shown in FIG. 5(a)-5(d) and thus are known as defect-associated atoms.

**TABLE II.** Distances (in Å) of the neighbouring atoms from the defect site

|                | X = V₀ | X = Tiᵢ | X = Vₜ | X = Oᵢ |
|----------------|--------|---------|--------|--------|
|                | X-O₁,₂ | X-O₂,₃,₅,₆ | X-O₄ | X-Tiₗ₁,₂ | X-Tiₗ₂ | X-Tiₗ₃ |
| Pure anatase (undistorted lattice) | 1.95 | 1.99 | 2.48 | 1.84 | 2.25 | 2.42 | 1.99 | 1.95 | 3.06 | 1.95 | 1.99 | 1.95 |
| Anatase with X (distorted lattice) | 1.97 | 2.10 | 2.41 | 2.02 | 2.10 | 2.65 | 2.47 | 2.02 | 2.95 | 1.97 | 2.05 | 2.12 |

Three broken Ti-O bonds (i.e., Ti₁, Ti₂ and Ti₃ in FIG. 5(a)) were formed due to the creation of one V₀. Further, this V₀ in anatase was found to push these three nearest Ti atoms outwards because of their mutual strong repulsion, which could be associated to the higher oxidation state of Ti (see TABLE II). The two nearby O atoms (labelled in FIG. 5(a)) were found to move towards V₀ in order to minimize the total energy of the system.
FIG. 5. A conventional cell of anatase showing various neutral native defects (denoted by X) such as V\textsubscript{O} (a), Ti\textsubscript{i} (b), V\textsubscript{Ti} (c) and O\textsubscript{i} (d). The approximate direction of forces acting on the neighbouring atoms is also depicted. The atoms in the neighbourhood (defect associated atoms) have been labelled.

Usually in literature, Ti\textsubscript{i} was seen to be placed at the centre of the distorted octahedron of the oxygen atoms in the anatase lattice. However, we used two approaches in our calculation. In the first approach, Ti\textsubscript{i} was placed at a random location inside the crystal [position X in FIG. 5(b)] and allowed to relax to reach its lowest energy configuration. The second one followed the widely adopted literature approach, where the total energy calculation for anatase with Ti\textsubscript{i} at the centre of the distorted octahedron was carried out. The total energy of the first configuration was found to be slightly lower (by 0.23 eV) than that of the second one, suggesting increased stability of the first configuration over the second one. Hence, all further calculations here were carried out using the first configuration only. The neighbouring Ti atoms near Ti\textsubscript{i} (Ti\textsubscript{1}, Ti\textsubscript{2}, Ti\textsubscript{3} and Ti\textsubscript{4}) were found to move outwards due to mutual repulsion among Ti atoms (see TABLE II). Whereas, the two O atoms present in the apical positions [i.e., O\textsubscript{1} and O\textsubscript{4} in FIG. 5(b)] were seen to be pushed away from the interstitial site, the other four oxygen atoms in the neighbourhood (i.e., O\textsubscript{2}, O\textsubscript{3}, O\textsubscript{5} and O\textsubscript{6}) were found to move towards this interstitial site due to attraction from Ti\textsubscript{i} (see TABLE II).

Moreover, removing a neutral Ti atom from anatase to create V\textsubscript{Ti} resulted in the six oxygen atoms in the neighbourhood (i.e., O\textsubscript{1}-O\textsubscript{6}) to relax outwards due to their strong mutual repulsion [see FIG. 5(c) and TABLE II]. Here, the oxygen atoms present at the apical positions (i.e., O\textsubscript{1} and O\textsubscript{4}) were found to relax outwards by the maximum distance (~ 0.5 Å away from V\textsubscript{Ti};
see TABLE II) than those of the others. Ti atoms in this neighbourhood were found to be displaced inwards only slightly probably because of the missing repulsive force from the removed Ti atom.

Introducing O\(_i\) in anatase resulted in the formation of a dimer with that of the lattice oxygen atom [see FIG. 5(d)]. Note that, relaxation of atomic positions automatically resulted into this configuration even when we did not assume O\(_i\) to form a dimer with a lattice oxygen atom. The O-O bond length of the dimer was found to be 1.47 Å, which is close to the O-O bond length in \([\text{O}_2]^{2-}\) as calculated for BaO\(_2\) (1.49 Å), indicating the existence of the dimer in the form of \([\text{O}_2]^{2-}\). The geometry in its neighbourhood was only found to be slightly affected, with the neighbouring Ti atoms (Ti\(_1\), Ti\(_2\), Ti\(_3\)) being moved slightly outwards (see TABLE II).

### Table III

Partial charges on atoms at various positions near defect X obtained from bader charge analysis.

| Atoms                                          | Partial charge |
|------------------------------------------------|----------------|
|                                                | System with X = \(V_0\) | System with X = \(\text{Ti}_1\) | System with X = \(V_{\text{Ti}}\) | System with X = \(O_i\) |
| Defect atom X                                  | -              | +1.83                     | -                      | -            |
| Ti atoms in the neighborhood of the defect X (defect associated atoms) | \(\text{Ti}_1\) | +2.01                     | +2.19                   | -            | -            |
|                                                | \(\text{Ti}_2\) | +2.01                     | +2.19                   | -            | -            |
|                                                | \(\text{Ti}_3\) | +1.98                     | +2.19                   | -            | -            |
|                                                | \(\text{Ti}_4\) | -                         | +2.19                   | -            | -            |
| O atoms in the neighbourhood of defect X (defect associated atoms) | \(\text{O}_{1-6}\) | -                         | -                       | -0.93        | -            |
| Ti atoms far away from defect X (average partial charge) | +2.28          | +2.27                     | +2.25                   | +2.30        |
| O atoms far away from defect X (average partial charge) | -1.15          | -1.17                     | -1.14                   | -1.15        |

\(^a\)Both the atoms in the dimer had the same charge of -0.58

Bader charge analysis was performed to know the distribution of charge on the neighbourhood atoms of native defects (labelled for all cases in FIG. 5(a)-5(d); see TABLE III). In anatase with \(V_0\), this analysis showed a reduction in the positive charge on defect associated
Ti atoms (Ti_{1-3}) from +2.28 to ~ +2.01, indicating the unpaired electrons of the dangling bonds being localized over these atoms, adjacent to the vacant site (see TABLE III). Charge density plot for the defect state clearly showed the extra charge being localized on the three nearby Ti atoms on Ti 3d_{z^2} orbitals for anatase with V_{O} [see FIG. 6(a)]. A significant amount of charge density was also observed in the position of V_{O}. Using GGA PW-91 functional in DFT for anatase with V_{O}, Kamisaka et al. had also found the electron density of the defect state to comprise of Ti 3d orbitals for the surrounding three Ti atoms.\textsuperscript{31}

Similarly, for anatase with Ti\textsubscript{i}, the partial positive charge on the interstitial atom and that of the nearby Ti atoms (Ti_{1-4}) were found to be +1.83 and +2.19 respectively, as compared to that of +2.27 for Ti atoms, which were far away from the defect site, indicating the excess charge (due to the unpaired electrons) being primarily localized on the interstitial Ti atom and on the four Ti atoms in the neighbourhood of the interstitial site on the four-lobed Ti 3d orbitals [see TABLE III and FIG. 6(b)].

![FIG. 6. Charge density plots (at Γ point) for anatase with V_{O} (a), Ti\textsubscript{i} (b). The charge density has been plotted for the mid gap defect state. The isosurface around Ti atoms near V_{O} and Ti\textsubscript{i} are shaped like 3d_{z^2} and 3d_{xy} orbitals respectively. The charge isosurface is shown at a density of 0.01 e/Å\textsuperscript{3}.](image)

For anatase with V_{Ti\textsubscript{i}}, the partial charge on the six O atoms (O_{1-6}) in the neighbourhood of the vacancy was found to be -0.93 as compared to the charge of -1.14 on O atoms away from the vacant site. This is expected because in a normal Ti-O bond, oxygen atom (because of its high electronegativity compared to Ti) would attract the bonding electrons towards itself which would create a partial negative charge on O atoms. So, when V_{Ti\textsubscript{i}} was created, the bond was broken,
which decreased the partial negative charge on O atoms near the vacancy. Thus, these six O atoms were the primary defect associated atoms. In case of anatase with O_i, it was found that the partial charge on O atoms forming the dimer was \(~-0.58\) as compared to the partial charge of \(-1.15\) on O atoms, that were far from the defect site. O atoms in the dimer together had a partial charge of \(-1.16\) which was found to be closer to the charge of \(-1.15\) on O atoms away from the defect site, indicating charge similarity between O_i defect site in its dimer state with that of a normal O lattice site, the only difference being the two oxygen atoms in O_i instead of one.

2. Neutral and Charged Oxygen vacancies (\(V_O, V_O^+, V_O^{+2}\))

As oxygen atom has the valence state of two, \(V_O\) in anatase would create two unpaired electrons in its vicinity. The electron band diagram and the DOS plot of anatase with \(V_O\) showed the formation of a mid-gap defect state [see FIG. 7 and FIG. 8(a)-8(b)]. Further, this defect state was found to spread over a very small energy range, indicating this to be highly localized. Moreover, DOS plot of anatase with \(V_O\) clearly showed the defect state being associated to Ti 3d orbitals, suggesting the states being localized on a few Ti atoms [see FIG. 8(b)]. In this case, \(E_F\) was found to lie at the edge of the defect state on the side of the conduction band, indicating this mid-gap states being occupied.

![Band diagram of anatase with V_O clearly showing the mid-gap defect state. VBM of pure anatase has been taken as the reference energy value. Fermi level (\(E_F\)) has also been shown.](image)

FIG. 7. Band diagram of anatase with V_O clearly showing the mid-gap defect state. VBM of pure anatase has been taken as the reference energy value. Fermi level (\(E_F\)) has also been shown.
FIG. 8. DOS of pure anatase (a) and anatase with $V_0, V_0^{+1}, V_0^{+2}$ (b) – (d) respectively with Ti 3d states also shown. The mid gap defect state can be seen shifting towards the CBM as the charge on the vacancy increases. Dotted line represents the $E_F$ and VBM of pure anatase has been chosen as the reference for all the plots.
Whereas, for \( V_O \) the defect states were found to form \( \sim 0.56 \) eV below the conduction band edge, the gap states were found to move closer to the conduction band edge with increasing charge on the vacancy from 0 to +2 [see FIG. 8(b)-8(d)]. The gap state became very close to the conduction band edge (\( \sim 0.07 \) eV) for anatase with \( V_O^{+1} \). Additionally, \( E_F \) in this case was found to be around the middle of the defect state [see FIG. 8(c)], hence, increasing the excitation probability of the electrons in the gap state to the conduction band and thereby providing \( n \)-type conductivity to anatase. For anatase with \( V_O^{+2} \), the defect state was found to form inside the conduction band near the CBE (seen as a distinct peak near CBE in FIG. 8(d)) with \( E_F \) being located at the VBM. The band gap values for anatase with \( V_O, V_O^{+1}, V_O^{+2} \) were found to be 2.55 eV, 2.48 eV and 2.35 eV respectively. Note here the reduced band gap of anatase with \( V_O^{+2} \) as compared to pure anatase, because of the formation of these defect states at the conduction band edge [see FIG. 8(d)].

### 3. Neutral and Charged Titanium interstitials \((Ti_i, Ti_i^{+1}, Ti_i^{+2}, Ti_i^{+3}, Ti_i^{+4})\)

A neutral Ti atom has a valence state of four, hence one Ti\(_i\) in anatase would result into four unpaired electrons. The band diagram of anatase with Ti\(_i\) clearly showed the formation of mid-gap defect state which was found to spread over a very small energy range indicating a higher degree of localization [see FIG. 9]. However, \( E_F \) was found to lie in the conduction band, which is adjacent to CBE, indicating some of these excess charge carriers (or unpaired electrons of Ti\(_i\)) being delocalized, while the rest could be localized and present in the mid gap defect state.

**FIG. 9.** Band diagram of anatase with Ti\(_i\) clearly showing the mid-gap defect state. VBM of pure anatase has been taken as the reference energy value. Fermi level (\( E_F \)) has also been shown.
FIG. 10. (a) DOS of pure anatase (a) and anatase with $Ti_i, Ti_i^{+1}, Ti_i^{+2}, Ti_i^{+3}$ and $Ti_i^{+4}$ (b) – (f) respectively with Ti 3d states also shown. Dotted line represents the $E_F$. VBM of pure anatase has been taken as the reference for all energies.
DOS plots of anatase with different charge states of Ti interstitial clearly showed that this defect, in all its charged states created mid-gap defect states in the band gap which were associated with Ti 3d orbitals [see FIG. 10(a)-10(f)]. For Ti$_i^{+1}$, $E_F$ was still found to lie in the conduction band, however, the distance between it and the CBE decreased as compared to that of Ti$_i$ (i.e., 0.34 eV for Ti$_i$ and 0.21 eV for Ti$_i^{+1}$; see FIG. 10(b)-10(c)). Further, in case of Ti$_i^{+2}$, $E_F$ was found to locate at the edge of the mid gap state [see FIG. 10(d)], indicating the two electrons which were removed from Ti$_i$ to create Ti$_i^{+1}$ and Ti$_i^{+2}$ successively being present in the conduction band, hence suggesting the presence of the two defect states in the conduction band because of Ti$_i$. Moreover, when one more electron was removed to create Ti$_i^{+3}$, $E_F$ shifted to the middle of the mid gap defect state and finally for Ti$_i^{+4}$ it was found to coincide with the VBM [see FIG. 10(e)-10(f)]. These observations indicate that the two electrons which were removed to create Ti$_i^{+3}$ and Ti$_i^{+4}$ successively from Ti$_i^{+2}$ occupied the localized mid gap defect states. Thus, Ti$_i$ was found to create two localized defect states in the band gap of anatase, whereas two delocalized states were formed in the conduction band, hence causing anatase with Ti$_i$ and/or Ti$_i^{+1}$, intrinsically $n$-type.

4. Neutral Titanium vacancies ($V_{Ti}$) and Oxygen interstitials ($O_{i}$)

In this calculation, no mid-gap defect states because of the presence of $V_{Ti}$ and/or $O_{i}$ in anatase were found to form [see FIG. 11(a)-(d)]. DOS plot for the defect associated O atoms showed O 2p states being formed inside the valence band and spread over a wide energy range indicating these as delocalized states [FIG. 11(c)-11(d)].
FIG. 11. Total DOS (a) and PDOS (b) of anatase. DOS of anatase with $V_{Ti}$ (c) and $O_i$ (d). Red coloured portion represents O 2p states (scaled by 5 times) due to the defect associated atoms. Dotted line represents the $E_F$. VBM of pure anatase has been taken as the reference for all energies.
C. Stability of native defects

The dominant defect types under various conditions were identified here by comparing their formation energies. FIG. 12(a)-(b) show the formation energies of native defects for O-poor and O-rich conditions respectively, obtained as a function of $E_F$, the upper and lower limits of which correspond to the CBM and VBM respectively. The charge transition levels (denoted by $\varepsilon$) of various native defects are shown in

TABLE IV. Note that, these transition levels are $E_F$ values where multiple charged states of a defect state are stable.

![FIG. 12. Defect formation energies of native defects as a function of fermi level ($E_F$) in O-poor (a) and O-rich (b) conditions. The lower and upper limits of fermi level correspond to VBM and CBM respectively.](image)
TABLE IV. Charge transition levels (in eV) of various native defects with respect to the VBM.

| Defect | Charge states (q, q') | Transition level $\varepsilon(q, q')$ |
|--------|-----------------------|---------------------------------------|
| $V_O$  | +2/+1                 | 2.27                                  |
|        | +1/0                  | 2.28                                  |
| $Ti_i$ | +4/+3                 | 2.33                                  |
|        | +3/+2                 | 2.34                                  |
|        | +2/+1                 | 2.73                                  |
|        | +1/0                  | 2.74                                  |
| $V_{Ti}$ | 0/-1               | 0.01                                  |
|         | -1/-2                | 0.02                                  |
|         | -2/-3                | 0.03                                  |
|         | -3/-4                | 0.04                                  |
| $O_i$  | 0/-1                 | 2.36                                  |
|        | -1/-2                | 2.37                                  |

For a wide range of $E_F$ (from 0 to ~2 eV), the most stable charged states of Ti vacancies, O vacancies, Ti interstitials and O interstitials were found to be -4, +2, +4 and 0 respectively [see FIG. 12(a)-(b)], suggesting Ti vacancies, O vacancies and Ti interstitials being acted as quadruple acceptor, double donor, and quadruple donor respectively. Both in O-poor and in O-rich conditions, the most stable defect states were found to be $Ti_i^{+4}$ and $V_{Ti}^{-4}$. Moreover, in O-poor condition [see FIG. 12(a)], $Ti_i^{+4}$ was found to be the most stable defect state for $E_F$ between 0 and 2 eV, which altered when $E_F$ got close to the CBM (i.e., for n-type semiconductors), where $V_{Ti}^{-4}$ became more stable. Furthermore, in this region, the stability of O vacancies was found to be higher than that of Ti interstitials. In our calculation, O interstitials were found to have a positive formation energy for both these conditions and thus were unlikely to form spontaneously under equilibrium conditions. For a wide range of $E_F$ values (from 0 to ~2.4 eV), neutral state of O interstitials was found to be more stable as compared to its other charged states and hence were likely to bind with a lattice oxygen atom and form a dimer configuration.
Although oxygen vacancies were not the most stable defect states in any of the two conditions, these in the form of $V_O^{+2}$ were found to have a negative formation energy for $E_F$ ranging between 0 to 1.2 eV in O-poor conditions [FIG. 12 (a)], and hence are likely to form.

The charge transition levels of O vacancies ($\varepsilon(+2, +1)$ and $\varepsilon(+1, 0)$) were found to lie only slightly below the CBM ($\sim 0.16$ eV; see TABLE IV) indicating these as shallow donor defects, hence making these electrons ionize easily and thereby leading to intrinsically $n$-type conductivity in anatase. Similarly, out of four transition levels of Ti, two (i.e., $\varepsilon(+4, +3)$ and $\varepsilon(+3, +2)$) were found to locate close to the CBM, whereas the other two (i.e., $\varepsilon(+2, +1)$ and $\varepsilon(+1, 0)$) lied in the conduction band, thereby clearly indicating Ti interstitial to provide $n$-type conductivity to anatase. Note that, the transition levels of Ti vacancies (from $\varepsilon(0, -1)$ to $\varepsilon(-3, -4)$) were found to lie almost at the valence band edge, indicating these as shallow acceptors. Finally, the transition levels of O interstitials ($\varepsilon(0, -1)$) and $\varepsilon(-1, -2)$ were found to lie $\sim 0.08$ eV below the CBM. Moreover the stability of -2 charged state of O interstitials near the CBM could imply O interstitials being present as the acceptor states, however note that these would be very unlikely to form due to their high formation energy.

Note that, in O-poor condition, donor type defects (O vacancy and Ti interstitial) were found to have a lower formation energy than those of the acceptor type defects (Ti vacancy and O interstitial) for $E_F$ in the range of 0-1.8 eV [see FIG. 12(a)]. This could then lead to an incomplete compensation of the electrons (induced by the donor-type defects) by the holes (induced by the acceptor-type defects), thereby making anatase intrinsically $n$-type, reason behind the growth of intrinsically $n$-type anatase for oxygen deficient samples. However, in O-rich conditions, the acceptor-type defect states (mainly Ti vacancy) was found to be more stable, which could make anatase $p$-type [see FIG. 12(b)] under these conditions.

**D. Extrinsic defect states in anatase and their interaction with native defects**

In this computational work, Nb and Ta were chosen as the extrinsic dopant atoms. Note that, these dopant atoms can substitute either Ti or O atom in the anatase lattice to create the substitutional defects of $\text{Nb}_\text{Ti}$, $\text{Nb}_\text{O}$, $\text{Ta}_\text{Ti}$, or $\text{Ta}_\text{O}$ respectively. Whereas, the formation energies of $\text{Nb}_\text{O}$ and $\text{Ta}_\text{O}$ were found to be 10.14 and 11.54 eV respectively, these for $\text{Nb}_\text{Ti}$ and $\text{Ta}_\text{Ti}$ were
found to be -3.46 and -4.42 eV respectively, hence leading substitution of these dopants at Ti lattice site only. Moreover, the formation energy of Ta\textsubscript{Ti} (i.e., -4.42 eV) was found to be lower than that of Nb\textsubscript{Ti} (i.e., -3.46 eV) indicating higher solubility of Ta in anatase lattice than that of Nb. Introducing a single Nb or Ta dopant atom in anatase lattice (supercell with 96 atoms) as a substitutional defect led the dopant atom concentration to be approximately 1 at.%.

These dopant atoms were found to change the positions and the bond lengths of their surrounding atoms only slightly with both Ti and O atoms in the neighbourhood being relaxed outwards (see TABLE V) to accommodate the larger sized dopant atoms than the host Ti atoms (atomic radii of Ti, Nb and Ta being 1.40, 1.45 and 1.45 Å respectively).\textsuperscript{34} This suggested easy incorporation of Nb and/or Ta atoms in the anatase lattice, which was also evident from their negative formation energies. In our calculation, Ti atoms were found to relax more than O atoms, which could be because of the repulsion between these positive dopants and the host Ti atoms.

|                           | X = Nb |       | X = Ta |       |
|---------------------------|--------|-------|--------|-------|
|                           | X - O\textsubscript{1} | X - O\textsubscript{2} | X - Ti  | X - O\textsubscript{1} | X - O\textsubscript{2} | X - Ti  |
| Pure anatase (undistorted | 1.99   | 1.95  | 3.06   | 1.99  | 1.95  | 3.06   |
| lattice)                  |        |       |        |       |       |        |
| Anatase with X (distorted| 2.03   | 1.96  | 3.18   | 2.01  | 1.96  | 3.18   |
| lattice)                  |        |       |        |       |       |        |

Note that, \textit{d} orbital energy of a transition metal dopant is responsible in determining the position and the nature of the defect states, i.e., whether the delocalized resonant states would form in the conduction band and produce free electrons, or a gap state is introduced in the band diagram.\textsuperscript{16} In this work, both Nb and/or Ta dopant atoms were not found to form any mid-gap localized defect states [see FIG. 13 and FIG. 14]. Nb dopant was found to create delocalized Nb 4d states, whereas Ta dopant formed delocalized Ta 5d states inside the conduction band [see FIG. 13 and FIG. 14].
$E_F$ for Nb$_{Ti}$ and Ta$_{Ti}$ was found to lie at 0.31 and 0.28 eV above CBE respectively indicating the excess electrons from these dopants being occupied at the bottom of the conduction band, thereby making doped anatase a metal-like system. These observed induced $n$-type conductivity in (Nb, Ta)-doped anatase system in the present study were found to be in agreement with the data reported in the literature.$^{27,35}$ The corresponding $E_g$ for these systems was found to reduce to 2.35 eV and 2.40 eV respectively as compared to that of pure anatase (2.44 eV). Charge density plots revealed the CBE being composed of a hybrid of $d_{xy}$ ($4d_{xy}$, $5d_{xy}$ for Nb$_{Ti}$ and Ta$_{Ti}$ respectively) states for the dopants and Ti $3d_{xy}$ states for the host atoms [see FIG. 15(a)-15(b)].
FIG. 15. Charge density plots (at Γ point) of CBE for a single slice of atoms along (001) plane of anatase with NbTi (a), and TaTi (b). The four lobed structures around the Nb and Ta atoms at the centre represent the Nb 4d_{xy} and Ta 5d_{xy} orbitals respectively. Ti 3d_{xy} orbitals can also be seen around the Ti atoms. The charge isosurface is shown at a density of 0.01 e/Å^3.

In section 3.1, it has already been shown that anatase intrinsically has anisotropy in effective mass values. The anisotropy became even higher in doped (NbTi, TaTi) anatase systems as compared to that of pure anatase because of the presence of d_{xy} orbitals of the dopant atoms in CBE (see TABLE VI). m_{ex} was found to remain unaffected indicating the band curvature along Γ − X direction not being changed noticeably due to doping (see TABLE VI). However, along Γ − Z direction, the bands became almost flat for both the doped systems indicating a very high value of m_{ez}. This theoretically calculated anisotropy in the effective mass of electrons was found to be in agreement with that of the experimentally observed anisotropy for Nb-doped anatase. Addition of these dopant atoms was also found to increase the effective mass of holes, m_{hx} and m_{hz} along Γ − X and Γ − Z directions respectively as compared to those of pure anatase (see TABLE VI). Increasing dopant concentration (from 1 to 2 at.% in this case) was found to alter m_{ex} only insignificantly, though m_{hx} and m_{hz} were found to be significantly affected (see TABLE VI). Though increasing dopant concentration was found to increase m_{hx}, however for m_{hz} no such pattern was seen.
TABLE VI. Effective masses of charge carriers (in terms of rest mass of electron, \( m_e \)) along specific directions in the brillouin zone.

| System            | Charge carrier effective mass |          |          |
|-------------------|-------------------------------|----------|----------|
|                   | Electrons (CBM)               | Holes (VBM) |
|                   | \( \Gamma - X \) (\( m_{e\alpha} \)) | \( \Gamma - Z \) (\( m_{e\alpha} \)) | \( \Gamma - X \) (\( m_{h\alpha} \)) | \( \Gamma - Z \) (\( m_{h\alpha} \)) |
| Pure anatase      | 0.59                          | 5.10     | 1.72     | 1.07     |
| Ta doped anatase  |                               | *        | 1.89     | 2.21     |
| (1 at. %)         |                               | *        | 1.92     | 4.98     |
| Nb doped anatase  |                               | *        | 2.17     | 2.12     |
| (2 at. %)         |                               |          | 2.10     | 1.93     |

*Effective mass could not be calculated because the bands became extremely flat giving a curvature value of zero at CBM indicating a very high value of effective mass.

Note that, in all real experimental conditions with doped semiconductors, native defects are always present along with those of the dopants. These dopants can then interact with the native defects, thereby tuning the optoelectronic properties of these materials. FIG. 16 shows the variation in the total energy of the supercell with respect to the separation of the dopant atoms from the native defects. In case of both Nb- and Ta- doped anatase, the energy was found to increase with decreasing separation distance of \( V_O \) to those of the dopant atoms, thereby making the overall system unstable [see FIG. 16(a)-16(b)], indicating a reduced oxygen vacancy concentration near the vicinity of these dopant atoms. On the other hand, \( O_i \) was found to stabilize the dopant atoms [see FIG. 16(c)-16(d)], which could be because of the stronger Nb-O and Ta-O bonds than that of Ti-O (the bond energies of Nb-O, Ta-O and Ti-O being 726, 839 and 666 kJ mol\(^{-1}\))\(^{37}\). However, unlike Ta-doped anatase, for the case of Nb-doped anatase, when the O interstitial came very close to the dopant atom, the total energy started to increase [FIG. 16 (c)]. This could be because of the repulsion between the electron clouds of the dopant atom and \( O_i \) at this very small separation distance, which led an overall increase in the overall energy. The
minima in the total energy could then correspond to the equilibrium separation distance between these atoms. However presence of Ti in the vicinity of Nb and Ta dopants was found to destabilize these dopants, which could be because of the strong repulsion between these positively charged dopant and Ti atoms [see FIG. 16(e)-(f)]. On the other hand, V was found to stabilize the dopant atoms [see FIG. 16(g)-16(h)], which could be because the missing Ti atom near the dopant led to less repulsion and hence lowered the overall energy as V came closer to the dopant. However in case of Nb doped anatase, when V came very close to the dopant atom, the total energy started to increase [FIG. 16(g)].

![Graphs showing energy variation](image)

**FIG. 16.** Variation of total energy of the supercell with respect to the separation between dopant atom and a native defect. Total energy computed for the closest separation has been chosen as zero for each case.
FIG. 17. DOS for anatase with NbT_i along with V_O (a), Ti_i (b), O_i (c) and V_Ti (d). Nb 4d states have been scaled up by five times. Dotted line represents $E_F$. VBM of pure anatase has been taken as the reference energy.

FIG. 17 and FIG. 18 show the DOS plots for the native defects (V_O, Ti_i, O_i, and V_Ti) placed close (about 2 Å for V_O, Ti_i, O_i and 3 Å for V_Ti) to the dopant atoms (NbT_i, TaT_i). A small separation was chosen here to capture any interaction between the dopant atom and the native defect, as a higher separation distance between these would eventually reduce any chances of interaction between these [see FIG. 16]. Whereas, mid gap defect states were seen for the configurations when dopant atoms were present along with V_O or Ti_i, no such gap states were found to form for the dopant and O_i or V_Ti pair [see FIG. 17 and FIG. 18].
In case of anatase with dopant atoms and $V_{Ti}$, $E_F$ was found to lie close to the VBM [see FIG. 17(d) and FIG. 18(d)], implying extra electron introduced by the dopant atom being combined with a hole in the valence band thereby pinning $E_F$ near the VBM. These observations agree well with the corresponding configurations of anatase, when associated individually with those of the native and/or extrinsic defects. No new states which could be attributed to the interaction between these dopant atoms and the native defects were found to form.
FIG. 19. Band line-up diagram for bulk systems of pure anatase, anatase with V_O, Ti_i, V_Ti, O_i, Nb_Ti and Ta_Ti. The positions of band edges and the band gap value have been shown. Both the localized and delocalized defect states are shown. Dotted line represents $E_F$. Vacuum level calculated using the slab configuration was used as the reference ($V_{\text{ref}}$) for energies for different bulk systems.

E. Shifts in VBE and CBE due to neutral native defects and dopants

FIG. 19 shows the band line-up diagram for various bulk systems using vacuum (calculated from slab configuration) as the reference potential ($V_{\text{ref}}$). The conduction band edge (CBE) and the valence band edge (VBE) of pure anatase were found to lie at 4.66 eV and 2.22 eV respectively. For anatase with V_O, VBE was found to shift downward by 0.13 eV, whereas the CBE shifted upward very slightly. The downward shift of the VBE could be attributed to the less band width of O 2p states because of the removal of one oxygen atom (see Sec. 3.1). For anatase with Ti_i, CBE was found to shift downwards as in addition to forming localized mid gap state, Ti_i also formed delocalized defect states at the edge of the conduction band (see Sec. 3.2.2). For anatase with V_Ti and also with O_i, VBE shifted upward because both these native defects formed O 2p delocalized states in the valence band. In these cases, the CBE was also found to move upward. The upward shift of CBM in V_Ti could be because of less band width of Ti 3d states because of the removal of one Ti atom. In the doped systems (Nb- and Ta- doped anatase), CBE
was found to move downward due to the formation of additional delocalized dopant states (Nb 4d and Ta 5d states respectively; see Sec. 3.4) in the conduction band.

IV. CONCLUSIONS

In this work an overall electronic structure including the position and formation energies of various intrinsic and extrinsic point defects were computed for the undoped and doped anatase using DFT+U. Whereas V_{O}, O_{i}, V_{Ti} and Ti_{i} were considered here as the native defects, Nb and Ta were studied as the extrinsic defects. Additionally, in this study the interaction of these dopant atoms with those of the native defects was investigated. Finally effective mass of the electrons and holes both for the undoped and doped anatase were calculated from the curvature of their E-K diagram.

Whereas, the conduction band in undoped anatase was found to consist of mainly Ti 3d states with a minor component of O 2p states, the valence band was found to be mainly composed of O 2p states with a minor contribution from Ti 3d states. In Nb- and Ta-doped anatase, hybrid states of Ti 3d and Nb 4d and Ta 5d and Ti 3d were found to form near the conduction band edge of the conduction band, thereby reducing their band gap (2.35 eV and 2.40 eV respectively) as compared to that of undoped anatase (2.44 eV). These hybrid states were the primary reason for the high conductivity observed in doped anatase. Anisotropy in the band structure was found to exist, which led to widely different values of effective masses of electrons moving along different directions in the brillouin zone. The anisotropy became even larger for the doped systems studied here.

Calculations for the native defects showed that O vacancies (for charged states 0, +1) and Ti interstitials (for all charged states) were associated with localized Ti 3d defect states in the band gap, whereas Ti vacancies and O interstitials formed delocalized O 2p states in the valence band. The gap state was quite close to the conduction band edge in case of V_{O}^{+1} and along with localized states, Ti interstitials also formed delocalized states in the conduction band (with fermi level located inside the conduction band for Ti_{i} and Ti_{i}^{+1}). These factors explained the intrinsic conductivity in anatase. The most stable charged states for Ti and O vacancies, Ti interstitials were found to be -4, +2 and +4 respectively, indicating these as quadruple acceptor, double donor and quadruple donor respectively. O interstitial was found to form a stable dimer configuration with a lattice O atom. Moreover, oxygen deficient anatase was predicted here to be
intrinsically n-type, whereas p-type anatase was predicted in O-rich conditions. Moreover, here O$_i$ was found to stabilize near the dopant atom, suggesting higher bond strength between the dopant and the oxygen atoms. Finally, an alignment of band diagrams for all the intrinsic and extrinsic defect states was carried out using slab-supercell calculation and employing vacuum as the reference potential.
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