Abstract

TiO_2 (anatase polymorph) is a wide band gap semiconductor, studied for its interesting optoelectronic properties. Intrinsic (or native) defects and extrinsic defects (dopants) can alter the band structure of TiO_2 in interesting ways, which can render this material suitable for certain optoelectronic applications like photocatalysts and transparent conducting oxides.

In this work, we perform a comprehensive *ab initio* electronic structure analysis of undoped and doped anatase systems using density functional theory aided by the Hubbard correction (DFT+*U*). Such an analysis could help in selecting better dopants for transparent conducting oxide (TCO) and photocatalytic applications. To avoid fitting *U* parameter to properties like band gap, we use the linear response *ansatz* to systematically compute *U* for the dopant atoms. The dopants considered are Nb, Ta, Mo, V, W, Cr, Co, Cu, La and Ce. Electronic structures of anatase with intrinsic defects are also reported. The intrinsic point defects considered are oxygen vacancies (V_O), oxygen interstitials (O_i), titanium vacancies (V_{Ti}) and titanium interstitials (Ti_i).

Out of all the intrinsic defects considered, V_{Ti} and Ti_i were found to be the most stable under equilibrium condition. V_O and Ti_i were found to form localized states in the band gap. In case of V_O, the localized states were formed close to the conduction band. Ti_i also formed mid gap defect states. Electron transition from the defect states to the conduction band could impart intrinsic *n*-type conductivity to anatase.

In the case of the dopant atoms considered, dopants like Nb, Ta, V and Ce formed states in the conduction band with no mid gap states. Dopants Nb, Ta and W were found to have the Fermi levels positioned near the conduction band edge, indicating these systems to exhibit *n*-type conductivity. Other dopants like Mo, W, Cr, Co, Cu formed states in the band-gap. Mid gap states could be undesirable for TCO applications because the electron transitions to/from the mid gap states would reduce the transparency. Dopants which form states close to the conduction or the valence band affect the curvature of these bands. Effective masses of charge carriers are defined by band curvatures and hence are altered when dopants peturb the band structure. Effective mass of electrons at the conduction band edge was found to be higher in doped systems than in pristine TiO_2. Dopants also reduced the parabolicity of bands in general which leads to differences in effective mass values computed using different algebraic definitions.

This study provides an insight into how native defects and dopants affect the electronic structure of the host anatase material by forming impurity states and/or altering the band curvature, which in turn affects the optoelectronic properties of the material. Based on

electronic structure and effective mass analysis, Nb, Ta and W are identified to exhibit higher transparency and conductivity as compared to the other dopants considered here. The theoretical results presented here, increase our understanding and show the potential of dopants to alter the properties in anatase TiO_2.

Keywords: *ab initio*, *TiO_2*, *transparent conducting oxide*, *effective mass*, *formation energy*