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Tailoring the Energy Band Gap of Transition Metal Doped TiO_2 Thin Film

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Abstract

Water splitting for hydrogen production under sunlight using TiO_2 as photo catalyst provides a better route for solar energy and attracts the attention of many researchers. The photo catalytic activity of TiO_2 under sunlight irradiation depends on the band gap energy. The transition metal doped TiO_2 shows an edge over TiO_2 in optical absorbance and photo catalytic activity. Thin film of Cr doped TiO_2 was deposited by Electron beam evaporation deposition process on glass substrate, the band gap of sample was measured with UV-Vis spectroscopy. In order to provide theoretical ground to our experimental band gap results the first principle (ab-initio) calculation was performed using the computer code WIEN2K with Full Potential Linearized Augmented Plane Wave method (FP-LAPW) based on the density functional theory (DFT).

Keywords: Photo-catalyst, UV-Vis spectroscopy, WIEN2K, FP-LAPW, DFT

1. Introduction

Titanium dioxide is one of the most important semiconductors. It is the 9th abundant element in earth crust. Titanium dioxide also known as titanium (IV) oxide or titania which is the naturally occurring oxide of titanium with chemical formula TiO_2. TiO_2 have many important applications like water purification and conversion of solar energy. Due to electronic structure and chemical stability TiO_2 can be used as photo catalyst in water splitting for hydrogen production [1].

At present time the world is facing two major problems of energy and environment. After the innovatory growth in industry the average concentration of CO_2 in the atmosphere has been increased from 280 ppmv (parts per million by volume) to 387 ppmv by 2009 [2]. Efficient photo catalytic water splitting as

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renewable energy source offer a way of carbon-free, high quality hydrogen to power fuel cells. However, achieving high efficiency hydrogen production system is not an easy task. By year 2007, the photo catalytic water splitting hydrogen production is 5% of commercial hydrogen production while the rest of 95% hydrogen is produce from fusel fuel [3]. The photo catalytic hydrogen production can be a better source of renewable energy as its cost reduces with advancement of technology.

The use of TiO_2 as photo catalyst for water splitting hydrogen production put forward a fine way of clean, renewable, low cost and environment friendly source of energy. The efficiency of photo catalytic activity depends on high optical absorption, proficient formation of charge carriers and proficient use of theses charge carriers in the photo catalytic process. The conversion efficiency of materials is determined by the band gap of the materials because the materials will absorb all photons in the solar spectrum with energies greater than or equal to the band gap, resulting in excited electron-hole pairs available for initiating photochemistry. A large amount of created electron hole pairs recombine without taking part in any type of reaction and released the energy in heat or some other form. Most oxide semiconductors have band gap values greater than 3.0 eV, for example TiO_2 have band gap 3.2 eV for anatase and 3.0 eV for rutile structure phases [4,9] which lies in the near ultra-violet (UV) and far visible portion of the spectrum (λ<387 nm) respectively.

Several methods have been proposed for extending the absorption edge of TiO_2 to visible region of the solar spectrum in which doping is considered to be more superficial. The preceding study gives an idea that doping with Cr results large red shift in the absorption.

Computational research has provided opportunities in condensed matter Physics, as the modern material science is demanding in term of expertise, resources and time so one cannot rely on the hit and try method. One opportunity to study complex material is to carry out the computer simulation. Most of ab-intio calculations are based on density-functional theory (DFT) employing the local-density approximation.WIEN2k is one of the most accepted and consistent package for first-principles computation [10]. In our calculation we have used Full Potential Linearized Augmented Plain Wave (FP-LAPW) method within GGA approximation as implemented in WIEN2k code [11].

In this paper Cr doped TiO_2 have been studied experimentally as well as theoretically and their results have been compared.

2. Experimental and Computational Details

The high vacuum Torr international deposition system was used for thin film deposition. This system consists of vacuum system comprising of turbo molecular pump roughed by a dry scroll pump. Vacuum was adjusted by the pc control system and maintained at $1x10^{-6}$ torr in the experiment. Dry Nitrogen gas was used for the venting process after deposition of thin film. To avoid contamination a thin foil of aluminum was used for protecting the vacuum chamber from unnecessary coating built up with an inexpressible disposable material. The temperature more than 3500^{o}C can be obtained easily by direct evaporation .The melting point of TiO_2 is 1400^{o}C .To produce the trouble free evaporation the cleanliness is extremely importance. It is better to use a separate crucible for each material; in this experiment the crucible cleaned with distal water and then treated with the acetone was used. The substrate glass was first given ultrasonic bath for twenty minutes and then it was cleaned by hot air. Different deposition parameters are summarized in table. 1

Table 1. Different deposition parameters.

Vacuum	$1x10^{-5}$ torr
Crucible filled	75 %
Ventilator temperature	18^{o}C
Electron beam angle	270^{0}
Substrate revolution	20 r/min
Deposition time	30 second

For the computational study of TiO_2 the following data was used: The Rutile TiO_2 have tetragonal structure belong to the space group of $P4_2/mmm$, with lattice parameters a=4.593A^0, b= 4.594A^0 and c= 2.959A^0, where the position of the Ti atoms is (0, 0, 0) and O atoms is at (0.3053, 0.3053, 0).The unit cell have four Ti atoms and two O atoms [12]. The band calculations were performed with the Full Potential Linearized- Augmented Plain Wave method (FP-LAPW) based on Density Functional Theory (DFT) with Generalized Gradient Approximation (GGA) used in WIEN2K code developed by Blaha *et al*. In LAPW the unit cell of a crystal divide in two parts one is the atomic sphere and the second is the interstitial space. The wave function also has to deal with two base sets. For atomic space

$$\mathbf{V(r)} = \sum_{l,m} \mathbf{V_{lm}}\,(\mathbf{r})\,\mathbf{Y_{lm}}(\mathbf{r}) \quad (1)$$

For the interstitial space

$$\mathbf{V(r)} = \sum_{\mathbf{k}} \mathbf{V_k}\,\mathbf{e^{ikr}} \quad (2)$$

Integration was taken in a reciprocal space by taking 100 k-points in the first brillouin zone.

3. Result and Discussions

The optical properties of thin film are measured with lambda 950 spectrometer in the wavelength range of 250 nm to 1200 nm. The band gap is determined by the reflection UV-Vis spectra of Cr doped TiO_2 shown in the figure 1.

The reflectance data is analyzed by the Kubelka–Munk [13] formalism which converts the reflectance to equivalent coefficient of absorption "α" which is proportional to the Kubelka–Munk function "$F\,(R_\infty)$".The band gap is assumed to be indirect and determined from the graph by plotting the $[F(R_\infty)h\upsilon]^{1/2}$ versus $h\upsilon$, as the intercept of the extrapolated linear part of the plot at $[F(R_\infty)h\upsilon]^{1/2}=0$, assuming that the absorption coefficient "α" is proportional to the Kubelka–Munk function $F(R_\infty)$.The intercept come at 1.9 eV so the band gap determined is 1.9 eV which have some reasonable ratio with previous studies [14-17]. Pure TiO_2 has absorption edge around 3.3eV. It is noted that TiO_2 shows a large red shift in the absorption edge when doped with 12.5% of Cr. This red shift is due to the localized energy level introduced by the Cr in the forbidden energy range of TiO_2.

The figure 2 shows the calculated density of states (DOS) for Rutile TiO_2. In the valence band, the O-2p (blue lines in figure) and Ti-3d (pink lines in figure) orbitals have large contribution. In this region the pd-hybridization take place, this is due to the covalent bonding nature for TiO_2. Below the upper valence at around 18eV another band appeared in which the main contribution came from the O-2s (Green lines in figure). Above the Fermi level was the conduction band in which Ti-3d states majorly contribute.

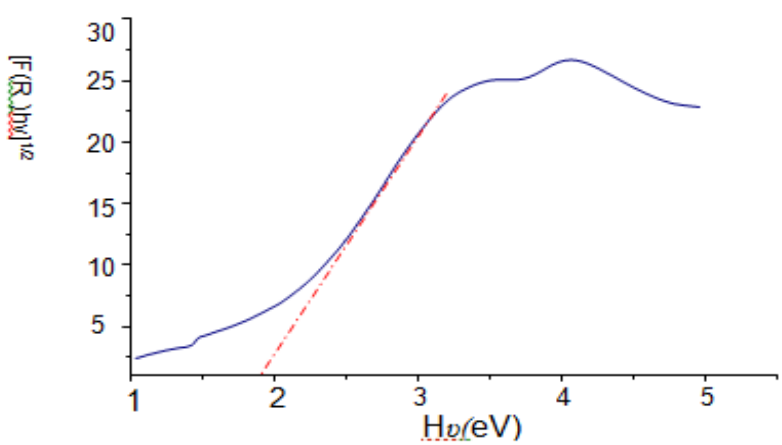

Figure 1. UV-Vis defuses reflectance spectra.

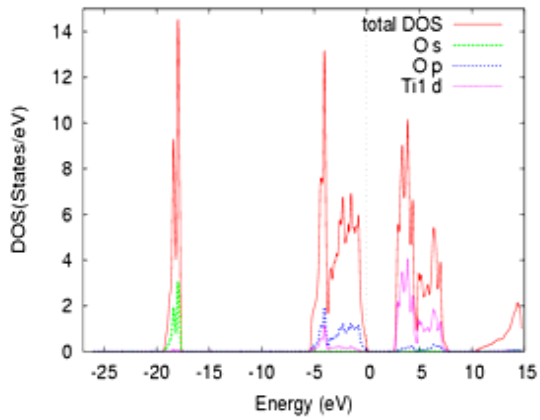

Figure 2. Density of states of TiO_2 (Rutile phase).

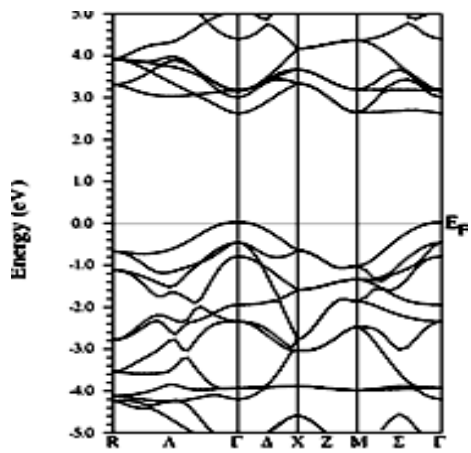

Figure 3. Band structure of TiO_2 along high symmetry Directions.

The figure 3 shows the band structure of TiO_2. In this figure the maxima of the valence band occur at the Γ point and the minima of the conduction band is also on the same point which exhibits that the TiO_2 in Rutile phase has direct band gap. The band gap noted from the figure is 2.6eV which is lesser than the experimental value. The experimentally measured band gap of TiO_2 in Rutile phase is 3eV. This band gap underestimation is due to the short coming of GGA. Theoretical band gap calculations of TiO_2 using different approximation are also done in past. [18-23].

The figure 4 shows the density of state for the doped TiO_2. The spin calculation for the doped TiO_2 is performed. The figure 4a shows the density of states for the spin up calculation and the figure 4b shows the density of states for the spin down calculation.

In figure 4a the valence band has only one main peak in the region 6.3eV to 11.2eV .In which the oxygen and Ti have contributions. While the conduction band occurs touching to the Fermi level in which the Ti and Cr have main contribution and O have very little contribution to the total density of states.

The density of states for the spin down calculation is shown in figure 4b, in which like the spin up calculation the valence band has one large band in range of about 4eV to 9eV. In this band the O, Ti and Cr all have contribution to the total density of states .In the conduction band Ti and Cr have main contribution and the O have very little contribution .The contribution of the Cr shows the effect of the doping . The spin up calculation shows totally metallic nature from density of state for Cr doped TiO_2 while the spin down show a large band gap .In such a case the band gap of material is estimated from the density of states which show some gap, the band gap is the minimum energy from the Fermi level which is in the spin down calculation case is about 1.1eV. The result found in this paper is in good agreement with the reported results [18], [24-25].

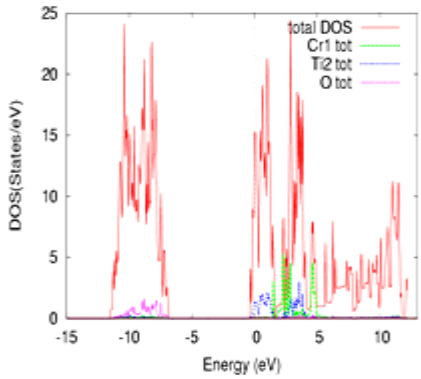

Figure 4a. Density of states for spin up calculation.

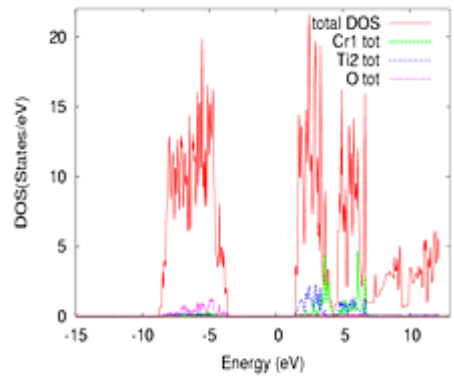

Figure 4b. Density of states (DOS) for spin down calculation

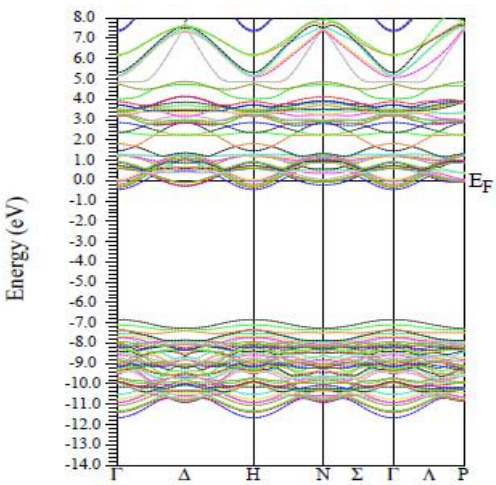

Figure 5a. Band structure of Cr doped TiO_2 in spin up calculation.

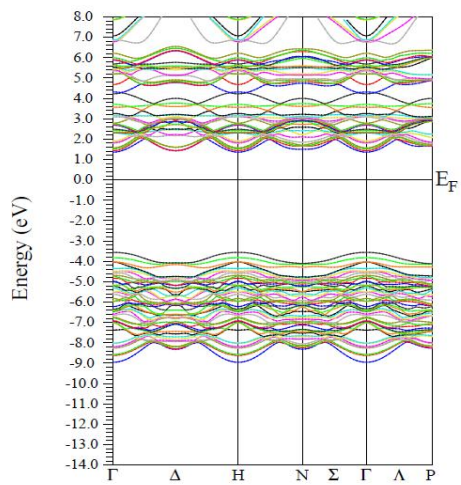

Figure 5b. Band structure of Cr doped TiO_2 in spin down calculation

As the band gap of un-doped TiO_2 calculated by ab-initio method in this work was 2.6eV so the reduction of the band gap in doped TiO_2 is due to the doping of chromium.

The figure 5a shows the band structure of Cr doped TiO_2 calculated by ab-initio spin calculation .This band structure is for spin up calculation which show no band gap, but when we perform the spin down calculation, it gives a band gap of 1.1eV as shown in figure 5b.

The minima of the conduction band occurs it r and H symmetry points. While the maxima of the valence band occur at the same points which shows that Cr doped TiO_2 have a direct band gap nature. Since it is mentioned in the discussion that when the material have a half metallic nature and show two different band gap structure in the spin up and spin down then minimum energy difference between the Fermi level and the minimum of conduction band is considered as the energy band gap of material. So from the figure 5 it is clear that Cr doped TiO_2 have 1.1eV direct band gap.

4. Conclusion

The literature available on the band gap of TiO_2 and first principle calculation in this paper suggests that pure TiO_2 is a wide band gap material. When TiO_2 is doped with a 12.5% Cr. It was observed experimentally as well as by theoretical calculations that band gap is decreased from 3.3 eV to 1.9 eV and 2.6 eV to 1.1 eV respectively. The difference in values of experimental and theoretical results is due to short comings of GGA. This doped TiO_2 can be used as photo catalyst in water splitting for hydrogen production and this hydrogen can further be used as fuel and in other useful applications.

5. References

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