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SYNTHESIS AND CHARACTERIZATION OF Mg DOPED TiO_2 THIN FILM FOR SOLAR CELL APPLICATION

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Abstract

In order to achieve high conductivity and transmittance of transparent conducting oxide (TCO), we attempted to fabricate Mg doped TiO_2 ($Mg_xTi_{1-x}O_2$) thin films and characterized them for their structural and optical properties. The $Mg_xTi_{1-x}O_2$thin films have been deposited on glass substrate by doctor's blade technique. The structure of the films were confirmed to be tetragonal and particle size were estimated to be ≈11.1 nm from XRD analysis. The Optical property study in the same range shows higher value of absorbance in comparison to the pure TiO_2 film after the wavelength 425 nm. The band gap is estimated to be 1.78 eV much lower than pure TiO_2 (3.2 eV). So the study shows that doping a small amount of Mg can enhance the visible light absorption in the epitaxial thin film which can be a suitable material for use in solar cell to trap the solar-radiation.

Keywords: Mg doped TiO_2 Nano particles; Band gap; Optical properties.

1. Introduction

In this era of nano technology, nano materials have been the subject of enormous interest for the scientists and academicians. Due to their very small size, nano materials are known to have unique mechanical, thermal, biological, optical and chemical properties, and becoming a potential candidate for versatile industrial applications.

TiO_2 nano materials are one of the potential candidates for solar energy application due to TiO_2's unique optoelectronic and photochemical properties. Especially, as a photovoltaic performance to efficient energy conversion for solar radiations, TiO_2 nano materials have been receiving a great deal of attention. TiO_2 is a wide band-gap semiconducting materials and it is of much interest due to its various applications like water and air purification through utilization of solar energy [1-3], nano size TiO_2 as anode of dye sensitized solar-cell [4] . However, the large band gap (≈3.2 eV) restrict most of the solar spectrum unutilized. So now several approaches are being adopted so that visible light active TiO_2 photocatalytic material can be produced. The efficiency of TiO_2 can be improved by morphological modifications or by incorporation of additional components in the TiO_2 structure. The morphological modification includes formation of small crystallite size. The visible light active TiO_2 has been produced by doping it with non-metals as well as metals [5-7]. To extend the optical absorption of TiO2 to the visible region, various dopants have been added to the oxide to improve its solar efficiency [8-9]. To improve the quality of film as well as the physical and chemical properties of thin films, the addition of some metal ions as impurities is expected to play an important role in changing the charge carriers concentration of the metal oxide matrix, catalytic activity, the surface potential, the phase composition, the size of crystallites, and so on [10-11]. Doping a metal or nonmetal into TiO_2 could change the band edge or surface states of TiO_2 [12]. Usually the modification is done by doping transition metals . But the transition metal doping cause thermal instability to the anatase phase of TiO_2[13]. The main demerit of metal doping is that, if the metal does not incorporate into the TiO_2 frame work and remains on the surface it blocks the reaction site. The incorporation of transition metals in TiO_2 crystal lattice may result in the formation of new energy levels between valence band and conduction band. Mg is an alkaline earth metallic material which is used to dope into TiO_2 anatase to improve photo activities [14]. It is found that Mg is the best one in the series which can replace for Ti in bulk because its ionic radius. Doping of Mg won't change the crystal structure. Several methods are adopted to dope Mg to TiO_2. Here, sol-gel technique is adopted because of its simplicity and reproducibility. Basically, the sol-gel process designates a type of solid materials synthesis procedure by chemical reactions in a liquid at low temperature. The sol-gel process has become a widely used method during the last several decades. in this method it is usually easy to maintain nanoparticles(np) in a dispersed state in the solvent which subsequently formed the sol. Further these colloidal particles can be linked together by condensation to get the gel.

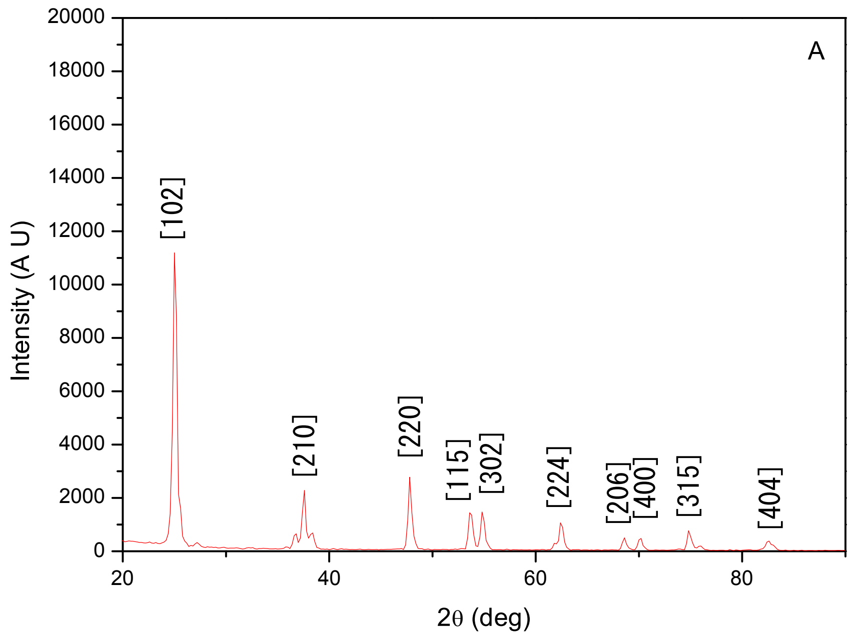
Usually light of energy greater than the band-gap value of the material excites the electrons to jump from the valence band to the conduction band. The band-gap value of anatase TiO_2 is 3.2eV so UV light is required to excite its electron from valence band to conduction band creating a hole. But UV light only constitutes 5% of solar radiation so maximum part of solar radiation is unused. So it is attempted to produce visible light active TiO_2 nano thin films which will be able to use almost 40% of solar-radiation. In this paper, preparation of Mg doped TiO2 thin film and its optical properties is studied by UV Vis spectro photometer within a wavelength range 300-900nm. From X-ray diffraction it is found that there is almost no change in the particle size between pure TiO2 and Mg doped TiO2 thin films but, the strongest peak is oriented towards the a-axis corresponding to the lattice plane (300). The band-gap of the film is calculated by Tauc plot method which is found to be appreciably low i.e.2.63eV**.** Usually, recombination is facilitated by impurity or defect. Prevention of recombination is usually done by doping with ions or hetrojunction coupling. So here we have doped the alkaline earth metal Mg to the TiO_2 thin film in the ratio (0.01M :0.99M).

2. Materials and Methods

Mg-doped TiO_2 ($Mg_xTi_{1-x}O_2$) thin film for x=0.01have been prepared by the sol-gel method. Starting reagent materials were taken as MgO(99.99% pure Merck) and TiO_2 (99.99% pure Merck).DI water and Acetic acid were used as the solvent. Stoichiometric proportionate powders of MgO and TiO2 were mixed with suitable amount of acetic acid to form a uniform lump free paste. Then the DI water was added drop wise with continuous stirring at room temperature until a homogeneous transparent sol is formed. There after 0.1M HNO_3 was added to the sol. The refluxing was done at 180°C for 6-7 hrs. The prepared gel was kept for one day. Mg-doped thin films were deposited on the glass slide by doctor blade technique. The film was annealed at temperature 300°C. The crystal structure of the annealed film was investigated by X-ray diffracton (XRD, Shimandzu-6100) with CuKα radiation (λ=.1540nm). Optical transmittance spectra of the thin films were measured by UV-Vis spectrometer (Shimadzu-2540) in the wavelength range 300-900nm.The resistivity is measured by the Hall measurement.

3. Result & Discussion

The diffraction profile of pure and Mg doped TiO_2 thin film was fitted to the Pseudo-Voigt function using *pro-fit* software. The programme *Pro-fit* has been used to decompose the diffraction pattern into it's constituent Bragg reflections by fitting analytical profile function to obtain the various parameters like intensity, position, breadth and shape of each reflection. The phase crystallinity and x-ray diffractogram of plain and Mg doped TiO_2 thin films are shown in Figure-1. There is no evidence of secondary phase in either case. Both the x-ray micrograph matched with the anatase phase of nanocrystalline TiO_2. For both the films all the planes are identified and leveled properly. For plain and Mg doped TiO_2 thin films the highest intensity occurs at the plane (102) and (300) respectively. The lattice parameters of TiO_2 thin film changes from a=b=5.358 Å, c= 9.541 Å to a=b=10.639Å, c=7.576 Å due to Mg doping. Here, it is seen that, magnesium modified titanium dioxide thin film is stretched more along the a axis. This can be attributed to local lattice distortion induced by impurity site. The structure of TiO_2 anatase is described as a coordination of TiO_6 octahedrons in which there are double octahedron layers stacking alternatively along c-axis and having more empty spaces between layers than within layers. So, the crystal is more compressible along c-axis. C-axis is called as the soft axis of TiO_2 because the Young's modulus value in this direction is more than twice smaller than that along in plane direction [15]. When the impurity is added the size of the MgO_6 octahedron reduce causing the change in internal strain which in turn changes the value of bond length. The particle size also changes from 11.416nm to 11.419nm by addition of Mg. The different estimated parameters as obtained from the xrd analysis are presented in table-1.



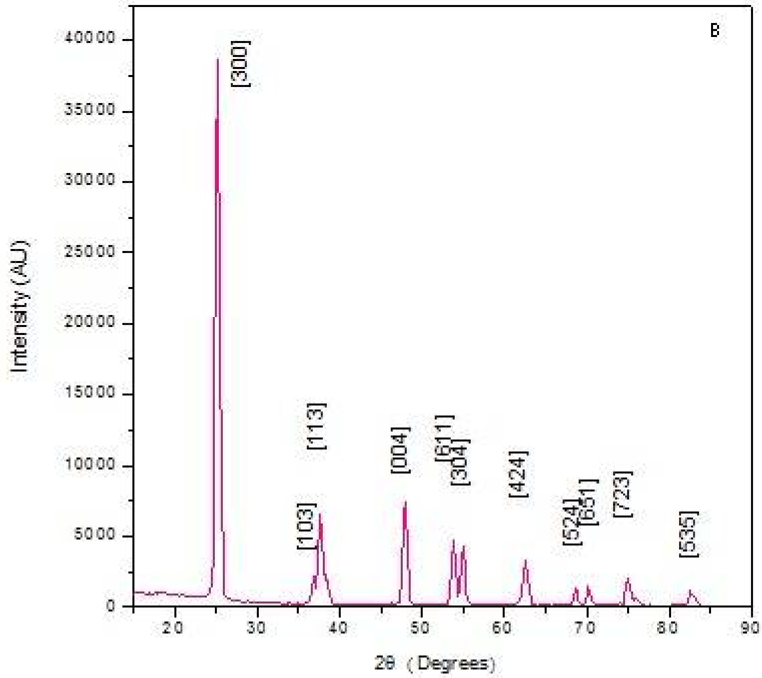


Figure-1: X-ray diffractogram of (A)TiO_2 and (B)$Mg_{0.01}Ti_{0.99}O_2$ Thin film

Table-1: Estimated Structural parameters of pure & Mg doped TiO_2 thin films

Sample	a in Å	b in Å	c in Å	(hkl)	Crystallite size in nm	Strain
TiO_2	5.358	5.358	9.541	(102)	11.41	-1.508
$Mg_{0.01}Ti_{0.99}O_2$	10.639	10.639	7.576	(300)	11.419	-1.506

The optical parameters were calculated from the optical absorption spectra measured by Shimadzu-2540 UV–Vis photo spectrometer in 300–900 nm wavelength range. Usually light of energy greater than the band-gap value of the material excites the electrons to jump from the valence band to the conduction band. UV light is required to excite electron from valence band to conduction band creating a hole in anatase TiO_2 as band gap is 3.2eV. But, UV light only constitutes 5% of solar radiation so maximum part of solar radiation is unused. But, in $Mg_{0.01}Ti_{0.99}O_2$ thin film the absorption % increases compared to pure TiO_2 thin film. So it is can be said that $Mg_{0.01}Ti_{0.99}O_2$ is a visible light active TiO_2 nano thin films which will be able to use extra % of solar-radiation. The absorbance of both the films are compared and found that, absorption of the Mg-doped TiO_2 thin film is more after the wavelength range 422nm i.e. the Mg doping enhances the absorbance of TiO_2 thin film in the visible light range. The extended absorbance of Mg doped sample can be explained as excitation of electron of dopant to the conduction band of TiO_2. The metal dopant used here has different valence state than Ti^{4+} and hence may induce the oxygen deficiencies during synthesis. So the generation of new energy levels due to the injection of impurities within the band-gap coupled with generation of oxygen vacancies by metal ion doping may contribute to the observed visible light absorption of Mg doped TiO_2thin film. The comparative absorption spectra are represented in Figure-2.

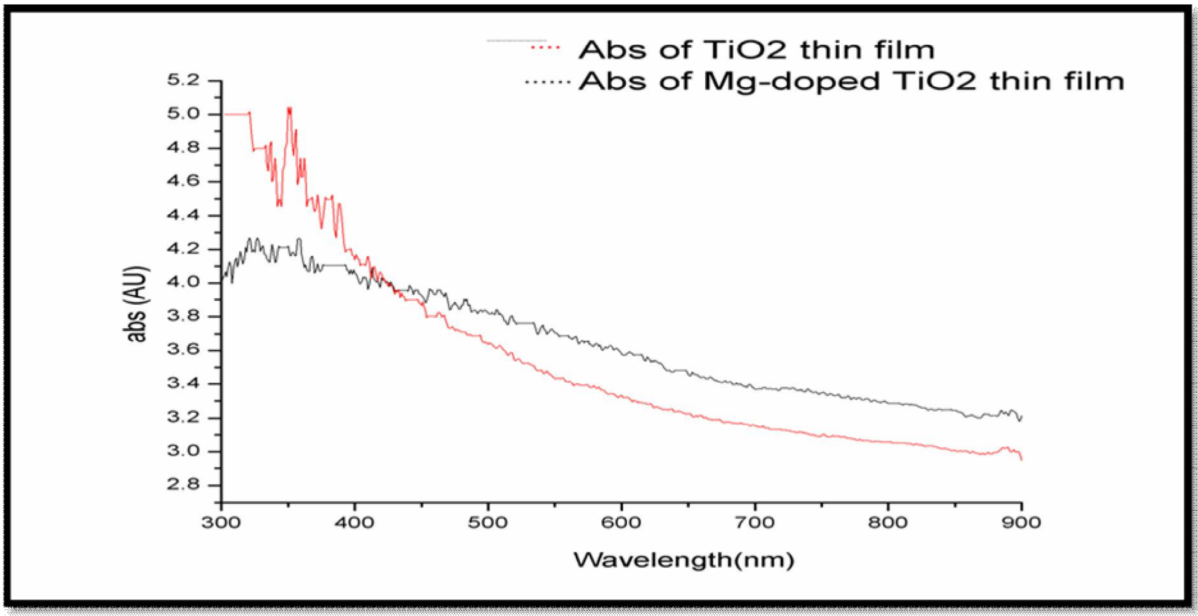


Figure2 : Absorbance spectra of TiO_2 and $Mg_{0.01}Ti_{0.99}O_2$ Thin film

The band-gap of both the films are calculated from Tauc plot that is a plot between $(\alpha h\nu)^n$ and $h\nu$, where $h\nu$ is the incident photon energy. Here α represents the absorption co-efficient and power coefficient n can have different values depending on the type of electronic transition. n=2 for allowed direct and n=1/2 for allowed indirect transition. The extrapolation of linear region of the graph to α=0 gave the band-gap value [16-17]. The band gap of both the pure and Mg-doped TiO_2 thin films are calculated by considering the direct transition since it is more favourable for anatase TiO_2 according to Reddy'paper [18]. The comparative band-gap calculation for both the films is shown in figure3.

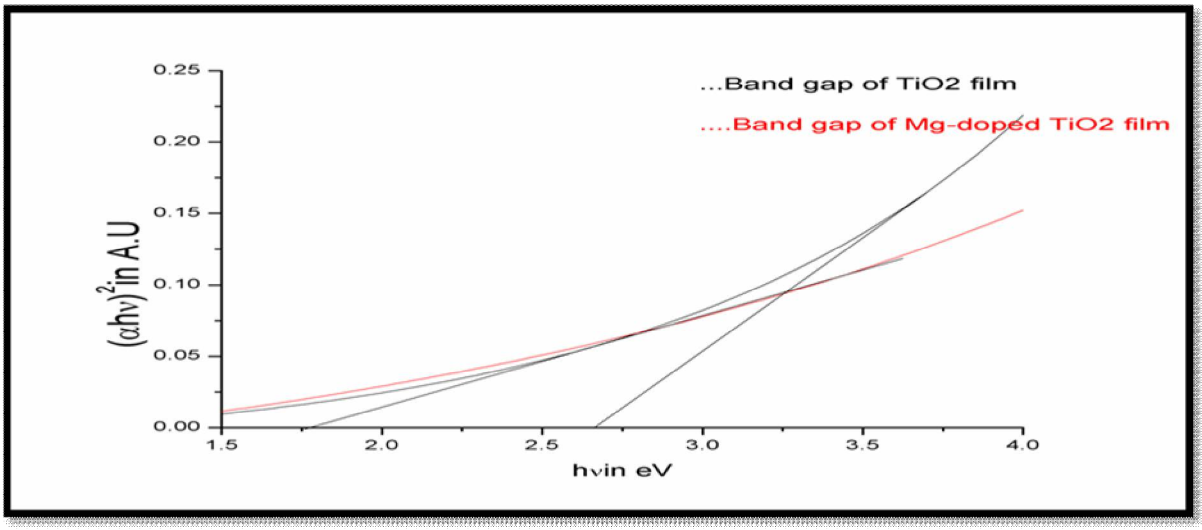


Figure3: Estimation of band gap of TiO_2 and $Mg_{0.01}Ti_{0.99}O_2$ Thin film

The band-gap of TiO_2 thin film is found to reduce from 2.66eV to 1.79eV with Mg doping . This reduction in band-gap may be due to the four different interactions (i) the exchange interactions (ii) carrier impurity interaction which affect the majority carrier band (iii) carrier-carrier or electron–hole interaction and (iv) Carrier impurity interaction which affect the minority carrier band [19-21].

Table-2: The optical parameters of pure & Mg-doped TiO_2 thin films

Sample	Thickness in µm	Goodness of fit	Band gap in eV
Plain TiO_2	0.9818	0.9991	2.66
Mg-doped TiO_2	0.9018	0.9954	1.79

4.Conclusion

Here, in this paper it is tried to prepare magnesium modified titanium dioxide ($Mg_{0.01}Ti_{0.99}O_2$) thin film by sol-gel route. The crystal structure of the modified film is same as that of the unmodified film and is tetragonal. In $Mg_{0.01}Ti_{0.99}O_2$ thin film, Mg doping enhances the absorbance of TiO_2 thin film in the visible light range. Thus, $Mg_{0.01}Ti_{0.99}O_2$ thin film can be said as visible light active TiO_2 nano thin film and may be suitable for solar cell applications. Also the band gap of the $Mg_{0.1}Ti_{0.99}O_2$ film is much lower than that of pure TiO_2 thin film. So, the transition of energy is much faster and the conversion is more. Thus, the study shows that doping a small amount of Mg can enhance the visible light absorption in the epitaxial thin film of TiO2 to trap the solar-radiation and hence can be a suitable material for solar cell. Usually recombination is facilitated by impurity or defect. Prevention of recombination is usually done by doping with ions or hetrojunction coupling. This is yet another reason to fabricate $Mg_{0.01}Ti_{0.99}O_2$ thin film.

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