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Effect of annealing temperature on the optical and electrical properties of Mg doped TiO_2 thin films

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In order to achieve high conductivity and transmittance of transparent conducting oxide (TCO), we attempted to fabricate Mg doped TiO_2 ($Mg_{0.01}Ti_{0.99}O_2$) thin films and characterized them for their structural and optical properties. The materials is prepared by modified sol-gel route. $Mg_{0.01}Ti_{0.99}O_2$ 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 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.

Key words: Modified sol-gel route; Optical properties; Electrical properties.
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1. Introduction

In this era of nanotechnology, nanomaterials 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 nanomaterials are one of the potential candidates for solar energy application due to TiO_2's unique optoelectronic and photochemical properties in general and especially, as a photovoltaic performer to convert solar radiations to efficient energy and thus receiving a great deal of attention for research. 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 [1-3], nano-size TiO_2 as anode of dye sensitized solar-cell [4] . The large band gap (≈3.2 eV) restrict most of the solar spectrum unutilized. Thus 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 TiO_2 to the visible region, various dopants have been added to the oxide to improve its solar efficiency [8-9]. To improve the quality 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]. In the process of doping if the metal does not incorporate into the TiO_2 frame work and remains on the surface it blocks the reaction site and thus it is the main demerit of metal doing into the TiO_2 matrix. 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 [14]. Mg is an alkaline earth metallic material which is used to dope into TiO_2 anatase to improve photo activities [15]. There were several studies on alkaline earth metal doped TiO_2, out of which Mg is the most suitable one for doping into TiO_2 due to its atomic radius. Mg doped TiO_2 thin films were used as the cathode for solar cell application by Wang et al. [16] have found to have higher short circuit current density in comparison to that of undoped TiO_2, which is mainly due to the reduction in elecron-hole recombination rate. According to K. Manseki etal.[17] it is found that use of Mg doped TiO_2 nano particles increases the open circuit voltage of perovskite solar cell. The study of Mg doped TiO_2 nano particles by Md. A. Behnajadi etal.[18] showed a decrease in band gap energy and it was also found to enhance photo catalytic activity for degradation of acid red (AR-27**).** Accoding to T. Siva Rao etal.[19] Mg doped TiO_2 is found to reduce its band gap and hence its photo catalytic activity in visible light region in comparison to undoped TiO_2 increases.

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 by creating a hole. But UV light only constitutes 5% of solar radiation so maximum part of solar radiation **remain** unused. Thus, 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 TiO_2 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 **observed** that there is almost no change in the particle size between pure TiO_2 and Mg doped TiO_2 thin films but, the strongest peak is oriented towards the a-axis corresponding to (300) plane. 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 (0.01 M :0.99 M).

2. Method of analysis

The crystal structure of the annealed film was investigated by X-ray diffraction (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 was measured by the Hall measurement.

3. Experimental procedure

Mg-doped TiO_2 ($Mg_xTi_{1-x}O_2$) thin film for x=0.01 have 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 solvent. Stoichiometric proportionate powders of MgO and TiO_2 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 at 500 rpm until a homogeneous transparent sol is formed. Further with the adition of 0.1M HNO_3 refluxing was done at 180°C for 6-7 hrs at 1200 rpm to get the gel. Mg-doped thin films were deposited on the glass slide by doctor blade technique [20-21] and the films were annealed at temperatures like 300, 350 and 400 °C. Subsequently the annealed films were subjected to different types of characterization like, XRD, SEM and UV-VIS spectro photometer.

4. Results and discussion

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. All the x-ray micrographs matched with the anatase phase of nanocrystalline TiO_2. All the film 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 when annealed at 300℃. But, for annealing temperature 350℃ and 400℃, the lattice parameters are, a=b=10.635Å, c=7.564 Å and a=b=10.632Å, c=7.562 Å, respectively**.** Here, it is seen that, magnesium modified titanium dioxide thin film is stretched more along the axis. But, with increasing annealing temperature the cell volume is decreasing slowly from 857.45 to 855.45 to 854.76 Å^3**.** This can be attributed to local lattice distortion induced by impurity site and shrinkage along the c--axis. 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 **[**22]. 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 [23-24]. The particle size also changes from 11.416nm to 11.419nm by addition of Mg. The different estimated parameters as obtained from xrd analysis are presented in table-1.

Tables 1 Electronic parameters of TiO_2 and $Mg_{0.01}Ti_{0.99}O_2$ thin film**s** annealed at different temperatures.

Sample name	**Band-Gap in eV**	**Carrier Concentration in/cm3**	**Resistivity in Ohm.cm**	**Mobility in Cm^2/Vs**
TiO_2As is	2.82	3.9×10^{13}	1.59×10^{2}	1300
Mg-TiO_2As is	2.56	9.6×10^{13}	1.438×10^{3}	45.2

Mg-TiO_2@300°C	1.85	1.325x10^{13}	2.677x10^{4}	17.6
Mg-TiO_2 @350°C	1.64	2.714x10^{13}	4.63x10^{3}	57
Mg-TiO_2@400°C	2.69	1.47x10^{14}	1.32x10^{4}	32.3

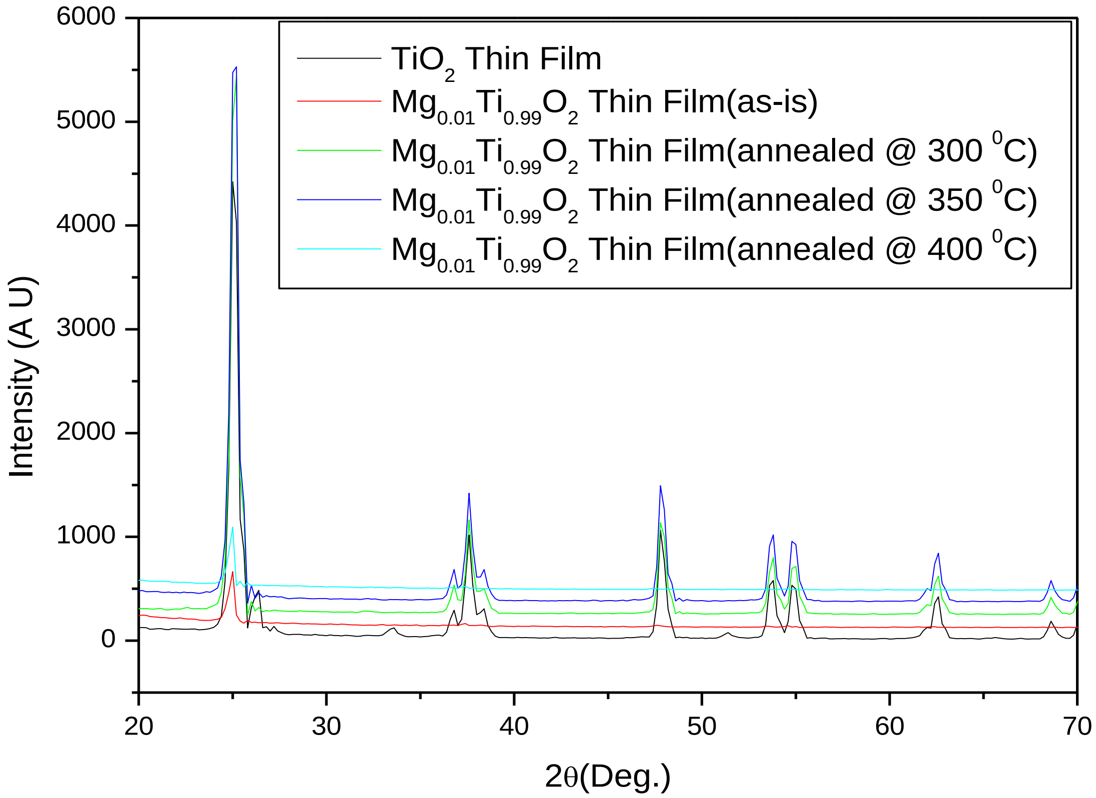

Figure 1 X-ray diffractogram of TiO_2 and $Mg_{0.01}Ti_{0.99}O_2$ thin film annealed at different temperatures.

The sharp decrease in the transmittance with most of the radiation absorbed for incident photons in the wavelength range 400–600 nm is associated with the fundamental absorption. It is evident from the spectra that the fundamental absorption edge shows a positive shift in the wavelength with increasing grain size, which indicates a shift in the optical band gap to lower energy. Further, the shift in the fundamental absorption edge is associated with a slight decrease in the transmittance above and below the absorption edge. However, the relative high spectral transmission above the fundamental absorption edge (λ > 600 nm) reveals that these oxide films, in general, are weakly absorbing in the spectral range of investigation. An increase in the scattering coefficient would decrease the optical transmittance in the UV region [25]. This feature clearly observed in the transmittance curves as shown in Fig. 2 supports the idea of scattering losses due to random distribution of grains.

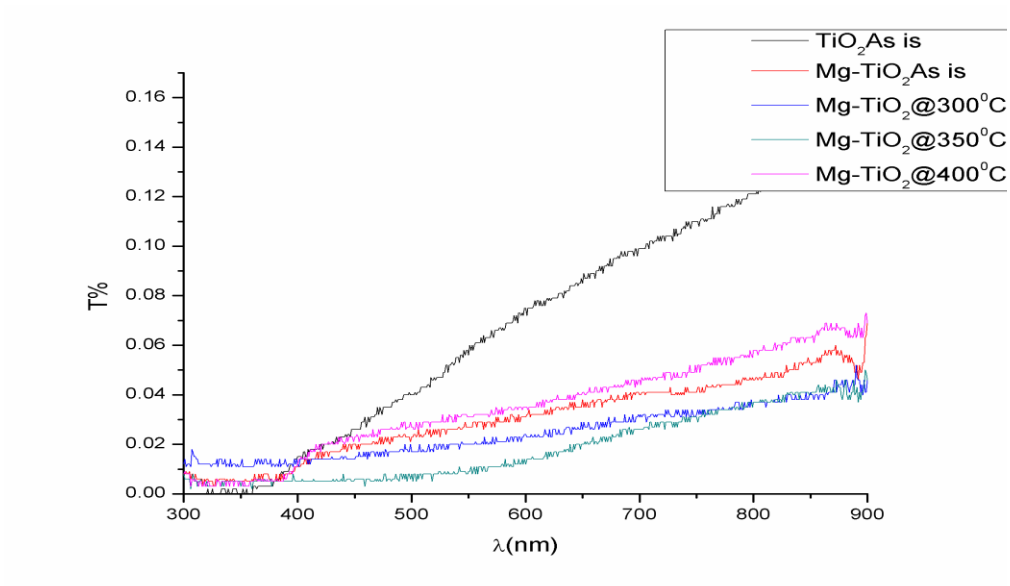

Figure 2 Transmitted spectra of TiO_2 and $Mg_{0.01}Ti_{0.99}O_2$ thin film annealed at different temperatures.

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_2 thin film. The comparative absorption spectra are represented in Figure-3. As seen in the fig.3, the absorption % suddenly falls in pure TiO_2 thin film, but in case of Mg doped TiO_2 thin films the absorption % is consistent and uniform in the visible light range and that it is temperature dependent. For the sample which is annealed at 350℃ it is maximum and uniform from 400 to 500 nm and there after the absorption % decreases slowly in the visible range. Whereas for all other samples it is almost the same in the visible range. However, in the wavelength range 300 to 400 nm, there is a lot of longitudinal vibration in the higher orbital and transfer of charge particles is ultrafast giving rise to an anomalous behaviour, which is very clearly seen in TiO_2 as-is and other samples too.

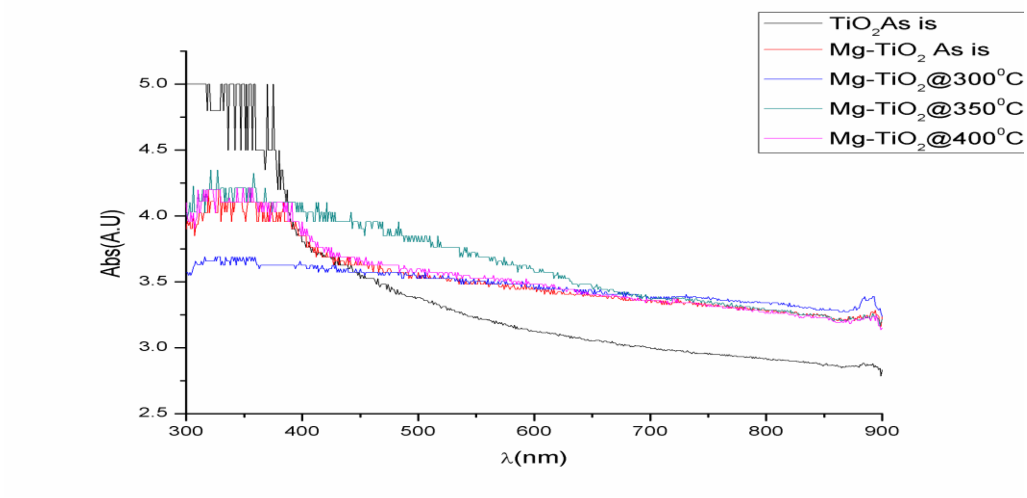

Figure 3 Absorption spectra of TiO_2 and $Mg_{0.01}Ti_{0.99}O_2$ thin film annealed at different temperatures.

The band-gap of all the films are calculated from Tauc plot that is a plot between $(\alpha h\nu)^n$ and hν, where hν is the incident photon energy [26-27]. 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 [28-29]. 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 favorable for anatase TiO_2 according to Reddy's paper [30]. The comparative band-gap calculation for both the films is shown in figure 4.

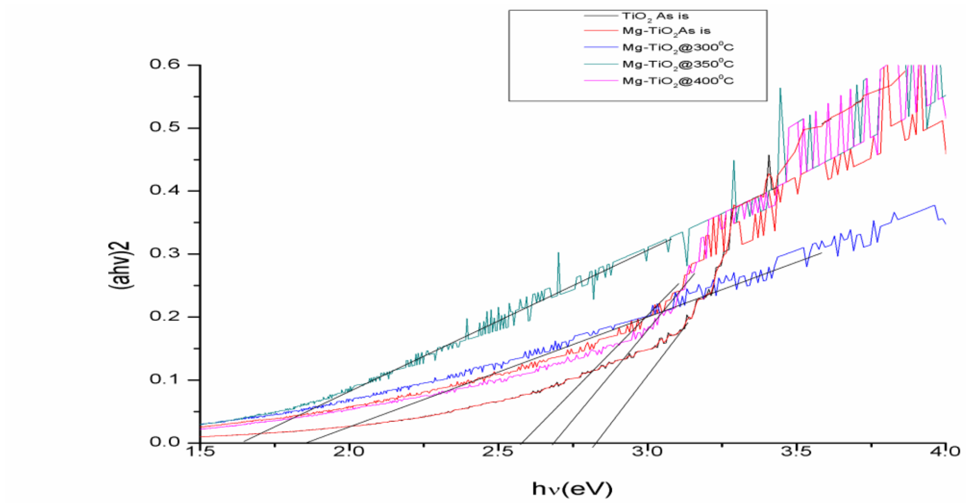

Figure 4 Band gaps of TiO_2 and $Mg_{0.01}Ti_{0.99}O_2$ thin film annealed at different temperatures.

The band-gap of TiO_2 thin film is found to reduce from 2.66 eV to 1.64 eV with Mg doping. This reduction in band-gap may be due to the four different interactions (i) the exchange interactions [31] (ii) carrier impurity interaction which affect the majority carrier band [32] (iii) carrier-carrier or electron–hole interaction [33] and (iv) Carrier impurity interaction which affect the minority carrier band [34-36]. Band gap values for different samples are presented in table-1. It is seen that though band gap decreases with Mg doping, from 2.82 to 2.56, it still further decreases when annealed with certain temperatures. In this case it is observed that at annealing temperature 350℃ the band gap value is minimize to 1.64 eV, but on further annealing to 400℃ the band gap value increases. In the studied range $Mg_{0.01}Ti_{0.99}O_2$ annealed at 350℃ is most suitable for photo voltaic applications.

The observed effects can be explained based on the electronic band structure of $Mg_{0.01}Ti_{0.99}O_2$. The band structure of $Mg_{0.01}Ti_{0.99}O_2$ has been studied several times. In general, the conduction band in $Mg_{0.01}Ti_{0.99}O_2$ is formed by magnesium modified titanium 3d bands and the valence band by 2p bands of oxygen [37–40]. In crystalline magnesium modified titanium, the fundamental absorption is mainly due to transitions from the oxygen p-type wave function to the 3d-type magnesium modified titanium wave functions. Therefore, the band gap corresponds to the energy gap between the top of the Oxygen 2p band and bottom of the magnesium modified titanium 3d band. The band gap widening in the films with relatively low grain size is mainly due to quantum size effects.

Fig.5 shows the variation of ln (resistivity) versus temperature of $Mg_{0.01}Ti_{0.99}O_2$ thin film annealed at different temperatures. Here, it is seen that, the resistivity jumps to a very high value when it is annealed at 300℃, but the resistivity drops when annealed with a further higher temperature at 350℃. On further annealing the sample the resistivity increases once again to half the value that decreases as we go from 300 to 350℃. Similar is the nature of Fig.6 which speaks about the variation of resistivity with annealing temperature. It is seen that, the sample annealed at 350 C has minimum resistivity and low band gap (≈1.64 eV). This is the beauty of this material at this particular temperature. Absorption % of this particular sample is almost linear in the wavelength range 350 to 500(nm) where as if one look into the transmitted spectra of all the annealed samples, it seen that for sample annealed at 350 C it has the minimum transmittance and linear within the wavelength range 350 to 500(nm). From Table-1 it is seen that at annealed temperature 350 C, the sample has minimum band gap (eV), maximum carrier conc. and mobility and minimum resistivity. Similarly, table-2 explain about the optical properties of the sample that, it has a thickness of 0.9018 um, maximum refractive index, and minimum coefficient of absorption ($\approx 3.74 \times 10^4$ cm^{-1}) with 99.21% GOF. Table-2 presented the optical properties of different samples in terms of thickness, refractive index, absorption co-efficient and goodness of fit.

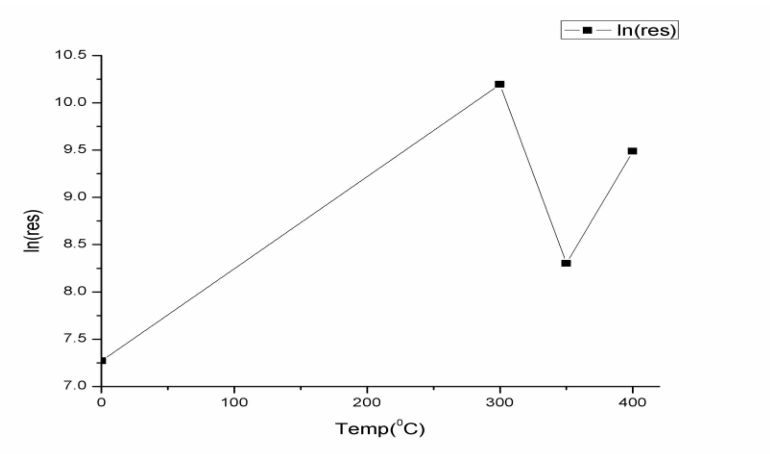

Figure 5 Tem. (℃) Vs. ln(Res.) of TiO_2 and $Mg_{0.01}Ti_{0.99}O_2$ thin film annealed at different temperatures.

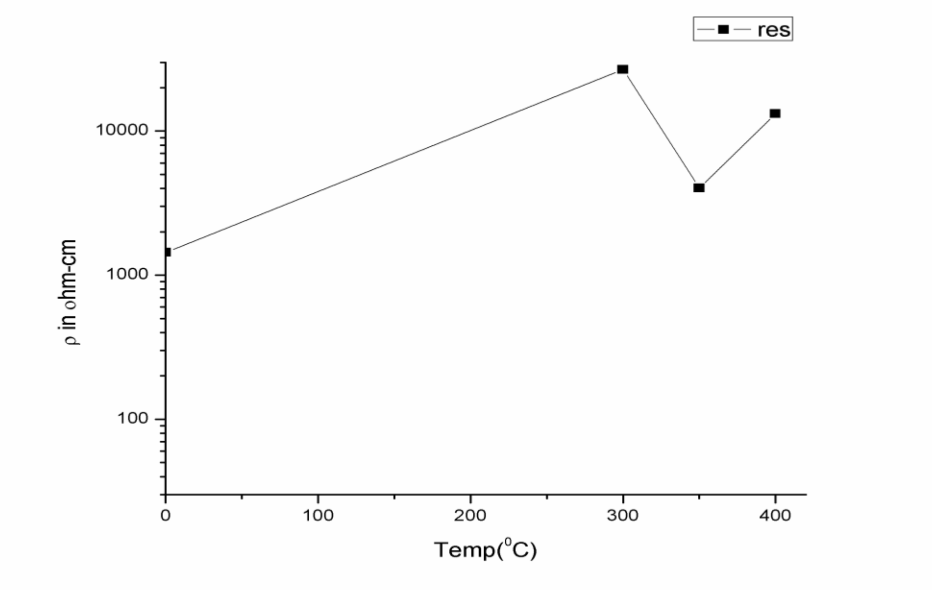

Figure 6 Tem. (℃) Vs. Resistivity of TiO_2 and $Mg_{0.01}Ti_{0.99}O_2$ thin film annealed at different temperatures.

Tables 2 Optical parameters of TiO_2 and $Mg_{0.01}Ti_{0.99}O_2$ thin film annealed at different temperatures.

Sample name	**Thickness in μm**	**n**	**α x(10^4) cm^{-1}**	**GOF**
TiO_2As is	0.9899	1.36	3.81	0.9888
Mg-TiO_2As is	0.9018	1.1765	4.18	0.9817
Mg-TiO_2@300°C	0.9018	1.2988	3.93	0.9954
Mg-TiO_2 @350°C	0.9018	1.3422	3.74	0.9921
Mg-TiO_2@400°C	0.9018	1.1752	4.18	0.9848

Fig.7 gives the very dense, uniform and euhedral micrographs of TiO_2 and Mg doped TiO_2 annealed at different temperatures in the studied range. It is seen that, the grain size is almost same and without much porosity. But, Mg doped TiO_2 annealed at 400 ^{o}C the grain size appears to be little bigger and may attributed to the fact that, the coalesce of nano size particle at a higher temperature.

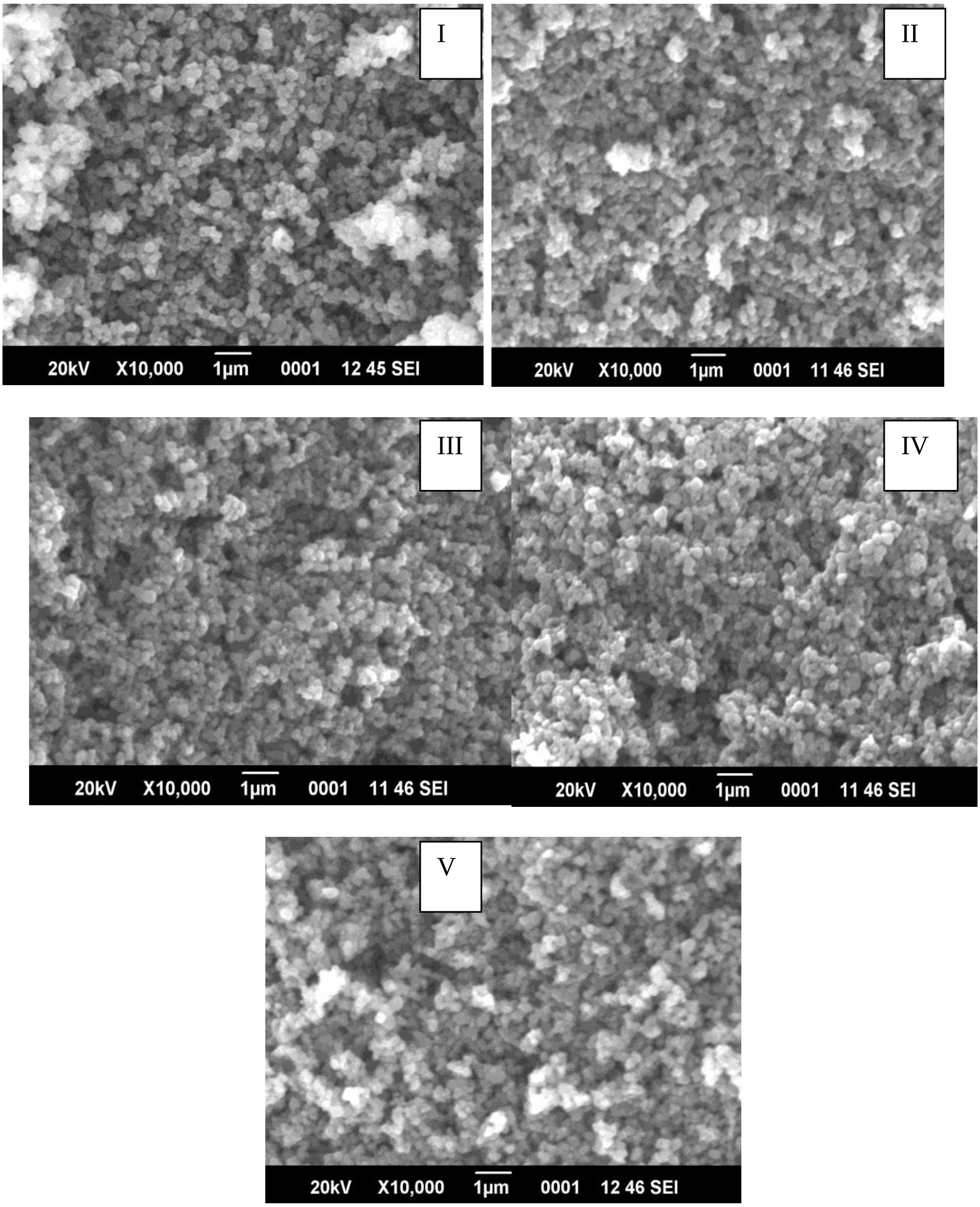

Figure 7 SEM micrographs of (I) TiO_2 As-Is,(II) Mg doped TiO_2 As-Is,(III) Mg doped TiO_2 annealed at 300 ℃, (IV) Mg doped TiO_2 annealed at 350 ℃, and (V) Mg doped TiO_2 annealed at 400 ℃.

5. Conclusion

Mg doped TiO2 thin films were synthesized by sol gel technique from powder reagent and annealed at different temperatures at 300 to 400℃. Structural, electrical and optical properties of these thin films were analysed. In this study it is observed that, Mg drops the band gap in $Mg_{0.01}Ti_{0.99}O_2$ from 2.82 to 1.62 eV in Mg doped TiO_2 thin film annealed at 350 ℃. Band gap of all the Mg doped TiO_2 thin films reduces in comparison to pure TiO_2 thin film. However, $Mg_{0.01}Ti_{0.99}O_2$ thin film annealed at 350℃ shows low band gap, high absorption %age, high mobility, low resistivity and large carrier conc. and hence may be suitable for different photovoltaic applications. The random distribution of the grains makes the film surface rough and results in the increased light scattering losses at the interface. Further, an increase in the scattering coefficient would decrease the optical transmittance in the UV region. This feature clearly observed in the transmittance curves as shown in Fig. 2 supports the idea of scattering losses due to random distribution of grains. The decrease in the band gap and changes in the spectral characteristics are attributed to random grain distribution, and structural modification of the material in the films. These observations could be useful while considering the $Mg_{0.01}Ti_{0.99}O_2$ thin films for electronic and optical applications.

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References

[1] M.R. Hoffmann, S.T. Martin, W. Choi, D. W. Bahnemanns, Chem. Rev **95** (1995) 69
[2] M. A. Fox and M. T. Dulay, Chem. Rev **93** (1993) 341
[3] A. J. Maira, K. L. Yeung, C. Y. Lee, P. L. Yue, C. K. Chan, Catalysts J. Catal **192** (2000) 185
[4] B. O' Regan and M. Gratzel, Nature, **353** (1991) 737
[5] A.V. Emeline, V. N. Kuznetsov, V. K. Rybchuk, N. Serpone, International Journal of Photo energy **258394** (2008) 258394
[6] T. Umebayashi, T. Yamaki, H. Itoh, K. Asai, Appl. Phys. Lett **81** (2002) 454
[7] E. Borgarello, J. Kiwi, M. Gratzel, E. Pelizzetti, V. M. Visca, J. Am. Chem. Soc **2996** (1982) 14104
[8] K. L. Choy, Prog. Mater. Sci. **48** (2003) 164
[9] A. Goossens, J. Schoonman, J. Electrochem. Soc. **144** (1997) 1723
[10] R. W. Seigel, E. H. Hu and M. C. Roco, WTEC panel Report on R & D Status and Trend in nanoparticales Nanostructured Material, Nanodevices, Workshop, (1997).
[11] D. Szezuko, J. Werner, S. Oswald, G. Behr K. Wetzing, Appl. Surf Sci **179** (2001) 301
[12] Y. Cao, W .Yang, W. Zhang, G. Liub, New. J. Chem **2** (2004) 218
[13] W. Choi, A. Termin, M. R. Hoffmann, J. Phys. Chem. B **98** (1994) 13669
[14] A. J. Gjazai, H. A. Hassan, Z. Hassan and A. SH. Hussein, Int. J. Nanoelectronics and Materials **6** (2013) 113
[15] T. Nikolay, L. Larina, O. Shevaleevskiyb, B. Tae Ahn, Energy Environ. Sci **4** (2011) 1480
[16] J. Wang, M. Qin, H. Tao, W. Ke, Z. Chen, J. Wan, P. Qin, L. Xiong, H. Lei, H. Yu and G. Fang, Applied Physics Letters **106** (2015) 121104
[17] K.Manseki, I.Ikeya, A.Tamura, T.Ban, T.Suqiura and T.Yoshida, RSC Advances **4** (2014) 9652
[18] M. A. Behnajady, B.Alizade and N. Modirshahla, Photochemistry and Photobiology 87 (2011) 1308
[19] T. Siva Rao, T. Abdo Segne, T. Susmitha, A. BalaramKiran, and C. Subrahmanyam, Advances in Materials Science and Engineering **168780** (2012) 168780
[20] G. Ruani, C. Ancora, F. Corticeilli and C. Dionigi, Solar Energy Materials and Solar Cells **92** (2008) 537
[21] A. S. Kontos, A. G. Kontos, D. S. Tsoukleris etal., J. Mater. Process. and Tech. **196** (2008) 243

[22] S. Chen, J. H. Yang, X. G. Gong, Y. Yan, S. H. Wei, Appl. Phys. Lett **96** (2010) 221901
[23] T. Van Nam, N. T. Trang and B. T. Cong, VNU Journal of Science, Mathematics - Physics **28** (2012) 84
[24] J. G. Ma, Cai-Rong Zhang , Ji-Jun Gong and You-Zhi Wu etal., Materials, **8** (2015) 5508
[25]L. Zhang, D. Ouyang, and C. Mo, Nanostr. Mat. **8** (1997) 1991
[26] M. F. Alias, E. M. N. Al-Fawade and S. K. J. Ali-Ani, Int. J. Nanoelectronics and Materials **4** (2011) 101
[27] S. Kausar, S. Joshi and A. Srivastava, Int. J. Nanoelectronics and Materials **7** (2014) 77
[28] M. Sreemany, A. Bose, S. Sen, Physica B **405** (2010) 85
[29] H. Yang, X. Zhang, Q. Tao, A. Tang, J. Optoelectr. Advanc. Mater. **9** (2007) 2493
[30] K. Reddy, S. Manorama, A. Reddy, Mater. Chem. Phys **78** (2002) 239
[31] C. H. Kwon, H. Shin, J. H. Kim, W. Schoi and K. H. Moon, Mater. Chem. Phys. **84** (2004) 78
[32] C. S. Kim, B. K. Moon, J. H. Park and S. T. Chung, J. Cryst. Growth **254** (2003) 405
[33] Y. U. Kolenko, A. A. Burukhin and B. R. Cheraglove, Mater. Lett. **57** (2003) 1124
[34] S. C. Jain, D. J. Roulston, Solid-State Electron **34** (1991) 453
[35] G. Mahan, J. Appl. Phys. 51 (1980) 2634
[36] M. Devi, M. R. Panigrahi, U.P.Singh, J. Mater Sci: Mater Electron **26** (2015) 1186
[37] C. G. Granqvist, Handbook of Inorganic Electrochromic Materials, Elsevier (1995)
[38] C. V. Ramana, O. M. Hussain, B. S. Naidu, and P. J. Reddy, Thin Solid Films **219** (1997) 305
[39] A. Talledo and C. G. Granqvist, J. Appl. Phys. **77** (1995) 4655
[40] C.V. Ramana, R.J. Smith, O.M. Hussian, Phys. Stat. Sol. (A) **1** (2003) 199