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Magnesium doped titania (TiO_2) thin films: deposition, structural, morphological and optical properties

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Pure and magnesium (Mg) doped titania (TiO_2) thin films were prepared on glass substrates by sol-gel method with dopant concentration varying up to 9.39 atomic % (metal base). The morphological, structural and optical properties were investigated by field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), X-ray diffraction (XRD) and ultraviolet–visible spectroscopy (UV–VIS). Results revealed that the films were highly crystalline and consist of brookite phase of titania, without any other phase such as magnesium oxide. Microstructures showed shrinkage cracking and decrease in root mean square resistance with increase in doping concentration. The optical transmittance has shown a decrease due to scattering of light through cracks and increases with increase in doping concentration. Moreover, the increase in band gap of titania has been observed from 1.81 eV to 2.52 eV.

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Keyword: Titania Thin films, Mg doping, Band gap, Sol gel spin coating

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1. Introduction

Currently TiO_2 thin films are considered as important for a number of applications such as dye sensitized solar cells, High Efficiency Perovskite Solar Cells [1], photovoltaic cells [2], self-cleaning, water-splitting, water and air purification and photocatalytic cells due to its low biological toxicity, unique photocatalytic activity, low cost and stability [3] Other potential applications for TiO_2 films are in filters [4], electrodes in photochemical solar cells [5], ETL in Provskite solar cell, dielectrics in thin film capacitors [6] and photoanode [7][8]. Titania is wide band gap n-type semiconductor, generally occurs in three phases with band gap ranging from 1.9 eV to 3.2 eV [9]. Rutile is usually the dominant phase in titanium dioxide thin films, while anatase rich films have also been synthesized [10]. Whereas, brookite is usually produced when the reaction is carried out in a highly acidic medium at low temperatures [11]. Anatase or brookite shows excellent results for photo-electrochemical activity as compared to rutile TiO_2 and are widely used in solar cells and photocatalysts.

Due to wide band gap, titania absorbs little portion of visible light (400-800 nm) [12]. Doping the material with cations and anions including Co [13], Zn [14], B [15], Fe [12], V [16], Cr [17], N [18], Cu [19], Mn [20], Sc [21], Ta [22] and Eu [23] is a very practical method to enhance its properties. TiO_2 is considered as poor semiconductor because of its bulk resistivity which is about 1×10^6 Ω.cm [24]. By introducing (aliovalent) cations, functional properties of titania can be modified. These cations form donors and acceptors and take part in changing oxygen sub-stoichiometry. Similarly Mg, as a dopant, is of interest owing to its ionic radius 0.086 nm, which is comparable to that of titanium (0.075 nm) [25]. Therefore doping of Mg does not change the crystal structure and it is possible to change the band gap by doping with suitable ratio of Mg, which can be useful in solar cell applications.

There are numerous approaches for the preparation of doped thin films including hydrothermal [16], metal organic chemical vapor deposition (MOCVD) [26], pulsed laser deposition (PLD) [27], sputtering [28], ultrasonic spray pyrolysis [29], electrohydrodynamic atomization [30], dip coating [31] and spin coating [32]. The film deposition using first three techniques are carried out in vacuum environment, referred to high infrastructural cost whereas later three are not well considered for large scale deposition [29]. However, the effectiveness, practicality and versatility of spin coating make it favorable over vacuum demanding methods in context to fabrication of titania thin films. Thin film properties mainly depend on three parameters; concentration of solution, spinning speed and annealing temperature. Thicker films of nearly 1-2 micron can be achieved at lower spinning speed and concentrated solution, whereas the higher spinning rate (≥ 5000 rev/min) will result in ultra-thin films (< 200 nm). Annealing temperature affects phase transformation and grain growth [33].

In the present work, we have focused on the deposition of Mg doped titania thin films by spin coating to study the role of doping concentration on optical, morphological and structural properties. Moreover, deposition was carried out in highly acidic medium along with drying at low temperature.

2. Methods and materials

Titania thin films were fabricated on soda lime glass microscope slides (25 mm×25 mm×1 mm) by sol-gel spin coating method. Titanium (IV) isopropoxide (TTIP, reagent grade, 97 wt%, Sigma Aldrich) and magnesium acetate 4-hydrate ($Mg(CH_3COOH)_2.4H_2O$, 98 wt%, PRS Panreac) were used as titanium and magnesium precursors respectively. 2.8 g of TTIP was diluted with Isopropanol (IPA) (reagent plus, ≥ 99 wt%, Sigma Aldrich) to 100 mL volume at titanium concentration of 0.1 M. 10 ml of 12 M HCl was mixed with TTIP solution on stirring for 30 min without heating. (Final solution has pH = 1). The Mg dopant concentration was varied in proportions of 1.95, 5.74 and 9.39 atomic % by adding magnesium acetate 4-hydrate in the solution. After that, the spin coating was carried out by dropping ~ 0.2 mL of solution on the substrate being spun in air at 2500 rev/min. After deposition, films were dried out by additional spinning for 20 sec, followed by heating for 5 minutes at 75℃. This procedure was repeated five times to achieve the thickness of deposited thin films ~ 400 nm. After that the annealing was performed in the tube furnace at 550℃ for 4 hours.

For identification of the crystal structural XRD (Bruker D8 Advance X-ray Diffractrometer with CuK_α source radiation, at 40 mA) was used. FESEM (field emission SEM, TESCAN, MIRA 3XMU 1.2 nm) was used for surface morphology with 230V operating voltage. Moreover, film thickness and EDX measurements were also recorded. Quantitative information about surface roughness and morphology were examined by AFM (Joel, JSPM-5200, software WinSPM scanning probe microscope) in non-contact mode. UV-Vis spectroscopy was used for transmittance study with Perkin Elmer, lambda 2.

3. Results and discussions

Doped titania thin films were fabricated on soda lime glass by using TTIP as precursor and isopropanol as solvent. Films were scratch resistant and quite adhesive as tested by scotch tape test. Moreover, doped and undoped films were highly transparent in visible portion of the spectrum (92-80 % @ 550 nm). Fig. 1 shows XRD spectrum of pure and Mg doped titania films. It is clear that XRD patterns exhibits strong diffraction peaks at 25.3°, 25.7^0, 30.8^0, 36.2^0 indicating TiO_2 in the brookite phase. All peaks are in good agreement with the standard spectrum (JCPDS no: 29-1360). The main brookite peak (210) at 25.3° is decreased in intensity with increasing Mg doping which indicates that crystallanity of thin films decreases with Mg doping. Also, peak shifts of the main peak (210) can be observed which is credited to the change in O-Ti-O bending vibration. These results are also consistent with the previous studies based on doping titania with W [34] and Nb [35]. It also indicates the fact that Mg doping caused lattice strain, accredited to the titanium (ionic radius = 0.075 nm) substituted with magnesium (ionic radius = 0.086 nm) [17]. This substitution arises charge balance that should be maintained by oxygen vacancies, which effects the band gap [12].

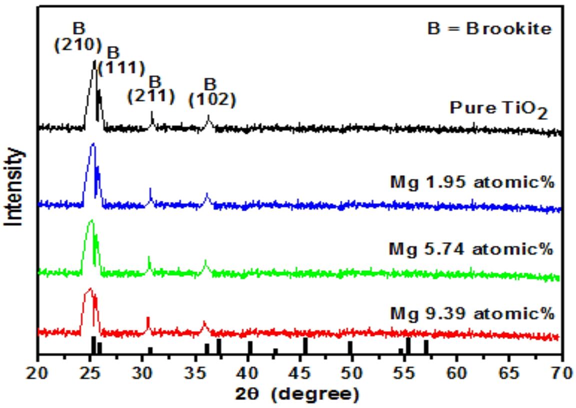

Fig. 1. XRD patterns of TiO_2 thin films at different atomic % Mg doping concentration

Fig. 2 displays 2-dimensional AFM micrographs (3.50 μm × 3.50 μm) of prepared pure and Mg doped titania films. Tightly packed grains having dissimilar grain sizes for different doping levels are clearly visible. Increase in doping level has decreased the densely packed grain size.

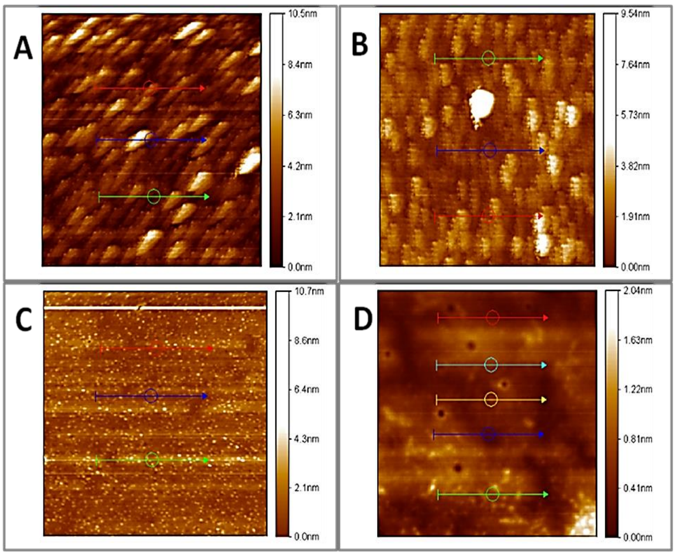

Fig. 2. AFM morphology of Mg doped TiO_2 thin films, (A) pure TiO_2 (B) 1.95 atomic% Mg doped (C) 5.74 atomic% Mg doped TiO_2 (D) 9.39 atomic% Mg doped TiO_2

This can lower the crystallanity of doped films correlating with XRD patterns which also signify the decrease in peak height with increasing doping level. Root mean square value of surface roughness (Rq) observed from AFM is greater for pure titania film and decreases with increasing doping concentration, as given in Table 1.

The morphology of the surface was further confirmed by using high resolution FESEM scans as shown in Fig. 3.

From Fig. 3 B, C and D it is clear that doped films have cracks. These cracks have decreasing trend with increasing doping concentration. The area near the cracks is smoother than undoped crack free film. The roughness measured from AFM data is more likely due to shrinkage and cracks in doped films. Furthermore, the presence of Mg dopant in titania is confirmed by EDX spectrum shown in Fig. 3E. Fig. 4A shows UV-VIS spectrum of the pure and doped titania thin films. Transmittance through doped titania thin films is less than undoped titania films. The free carrier absorption of photons may have a part in observed reduction in the transmittance. Moreover, this decrease is attributed to the cracks present in the films that can cause increase in photon scattering from the crystal defects [36]. While considering doping, increasing doping concentration causes increase in transmittance and shift of the absorption edge towards shorter wavelength with increasing Mg doping level.

Table 1. Observed AFM parameters for present pure and doped TiO_2 thin films

Sample	Rq (nm) Root-mean-square roughness	Ra (nm) Average-amplitude roughness
Undoped	1.49	1.14
1.95 atomic%Mg	0.999	0.721
5.74 atomic%Mg	0.804	0.55
9.39 atomic%Mg	0.135	0.106

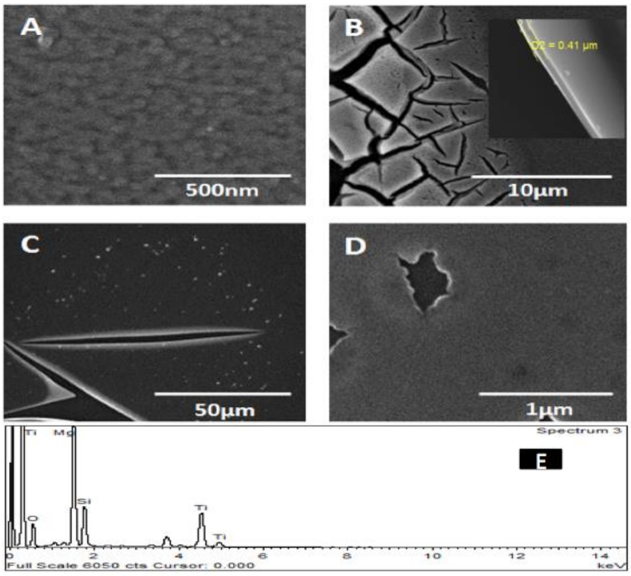

Fig. 3. SEM images of TiO_2 thin films, (A) pure TiO_2 (B) 1.95 atomic % Mg doped (C) 5.74 atomic% Mg doped (D) 9.39 atomic % Mg doped TiO_2 thin films (E) EDX spectrum at 9.39 atomic % Mg doping

The optical indirect band gap was calculated using UV-Vis spectroscopy data with the help of Kubelka munk function shown in Fig. 4B and optical indirect band gap was evaluated by plotting graph between energy and absorption-coefficient$^{1/2}$. Graph indicates the increase in indirect optical band gap from 1.81 to 2.52 eV with increasing doping concentration. Also, the change in indirect band gap can be attributed by two other significant factors, namely thermal contraction stresses and silicon contamination. Ti^{4+} (0.075 nm) has larger ionic radius than Si^{4+} (0.054 nm), which may cause lattice contractions and this would counteract the expansion of Mg^{2+} (0.086 nm).

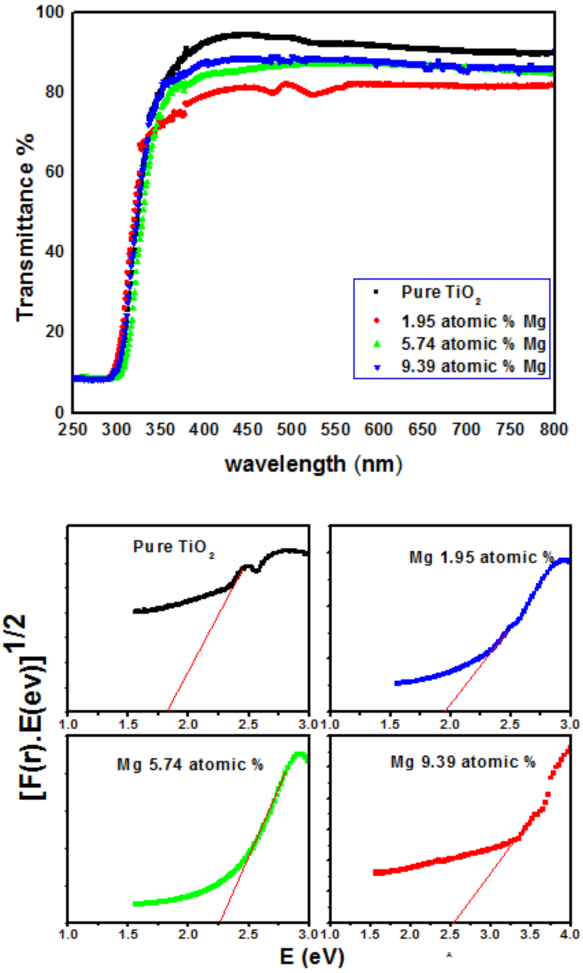

Fig. 4. (A) Transmission spectrum of TiO_2 thin films at different atomic % Mg doping concentrations (B) indirect band gap calculation of titania thin films with different atomic % Mg doping

Alternatively, the interstitial entry of silicon contamination into titania lattice could result in expansion of lattice. This effect has been reported previously on titania films by soda lime silica glass [33] and fused SiO_2 [29] substrates. Both Ti^{4+} and Si^{4+} are isovalent. Band gap reduction and lattice expansion are in agreement with the interstitial solid solution formation of silicon in titanium, that results in a measured value of 1.81 eV, lower than the published value of 1.9 eV for brookite titania. The existence of interstitial silicon can produce good organization of electrons and rise in conduction band, causing increased band gap.

Considering thermal expansion cracking, for titania on soda lime silica glass at 500℃ the typical thermal expansions are ~ 8 E 10^{-6} ℃$^{-1}$ and ~ 5E10^{-6} ℃$^{-1}$ [12]. The residual tensile stresses on films are the result of lattice expansion of TiO_2 caused by expansion of films from the greater cooling contraction. Conversely, titania films on fused silica (at 500℃ thermal expansion of only ~ 0.3 E 10^{-6} ℃$^{-1}$) have been published showing increase in indirect band gap owing to possibly residual compressive stresses [12]. Such results show the probability of direct relationship between band gap and residual stress, as intrinsic stress results in a raised energy configuration [37]. The increase in the band gap may also be due to defects produced by magnesium doping in titania thin films because of the difference in electronegativity and ionic radius of Mg and Ti [38]. More over, Mg doping increases electron concentration which introduces Burstein-Moss effect in TiO_2 could cause band gap expansion.

4. Conclusions

Mg doped titania thin films have been prepared by sol gel spin coating. Doped titania films have shown single brookite phase. Doping and thermal expansion coefficient mismatch between thin films and substrate caused cracking due to surface shrinkage, observed only in doped films. Therefore, both drying and doping played a role in cracking mechanism. The film roughness is decreased by increasing magnesium doping concentration. Cracking affects the transmittance, while increase in the doping levels have shown increasing trend in transmittance due to reduction of cracking. The optical indirect band gap was influenced possibly due to doping, residual thermal stresses and silicon contamination. Since the crack formation is strongly related to experimental techniques used, further work is in process to look into this side. It is suggested that the reasonable increase in band gap and structural properties of Mg doped TiO_2 thin films, along with easy deposition technique make it suitable for optoelectronic applications As the transmittance is increased, by controlling Mg content it is expected that Mg doped TiO_2 films can be optimized as the buffer layer of the CIGS solar cells. Mg as an effective ion dopant can possibly enhance the carrier transport ability of the compact ETL for planar Perovskite solar cells. It is recommended that this doping can shift the Fermi energy level of the ETL upward, increasing the free electron density or decreasing the density of deep trap states. The resistivity of the TiO_2 film is decreased, will lead to a decrease in the series resistance of the cell.

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