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Effect of V_2O_5 content on the optical, structural and electrochromic properties of TiO_2 and ZrO_2 thin films

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Vanadium oxide (V_2O_5) mixed titanium oxide (TiO_2) and zirconium oxide (ZrO_2) thin films were fabricated on glass substrates (corning 2947) and on indium tin oxide (ITO) coated glass substrates by sol gel spin coating process. Their optical, structural and electrochromic properties were investigated. The results were compared with pure TiO_2 and ZrO_2 thin films. Mixture of V_2O_5 with both types of film reduces the transmittance at the higher wavelengths. The refractive index of the V_2O_5 mixed TiO_2 and ZrO_2 films increases when compared with pure TiO_2 and ZrO_2 films. AFM images demonstrate no significant topographical changes for V_2O_5 mixed TiO_2 whereas for V_2O_5 mixed ZrO_2 films a topographical change is observed. V_2O_5 mixed TiO_2 showed slight increase in their charge capacity.

1. Introduction

Metal oxides are important for the effective use of solar energy and solar energy materials [1]. Their use extends from solar cells, smart windows to anti-reflective coatings. Optical, structural and electrochromic properties of metal oxides are becoming increasingly important since these properties are changing with respect to the preparation method and some other parameters such as the mixture content and concentration. Many works have been made on TiO_2 [2–4], ZrO_2 [5–7] and V_2O_5 [8–10] and their mixtures [11–14]. These materials have already proved to be promising for the development of the solar energy devices such as counter electrodes for the electrochromic windows and thin film layers for the antireflective filters. We have worked on mixed oxide thin film systems TiO_2-V_2O_5 and ZrO_2-V_2O_5 to investigate their optical, structural and electrochromic properties.

Several techniques are available to prepare thin films. Some of these include sputtering, chemical vapor deposition (CVD), plasma enhanced CVD and sol-gel. Most of these methods allow the production of high quality thin films but the production costs are relatively high. Among these, sol-gel method has some advantages because of low production costs and control over thickness and index of refraction.

The thickness, refractive index and extinction coefficient of the films were calculated through transmission and reflection measurement. An atomic force microscope is used for the surface analysis. Electrochemical characterization was performed with a potentiostat.

2. Experimental

Preparations of V_2O_5, TiO_2, and ZrO_2 solutions are given in Fig. 1. Mixed solutions are prepared for (1:9)

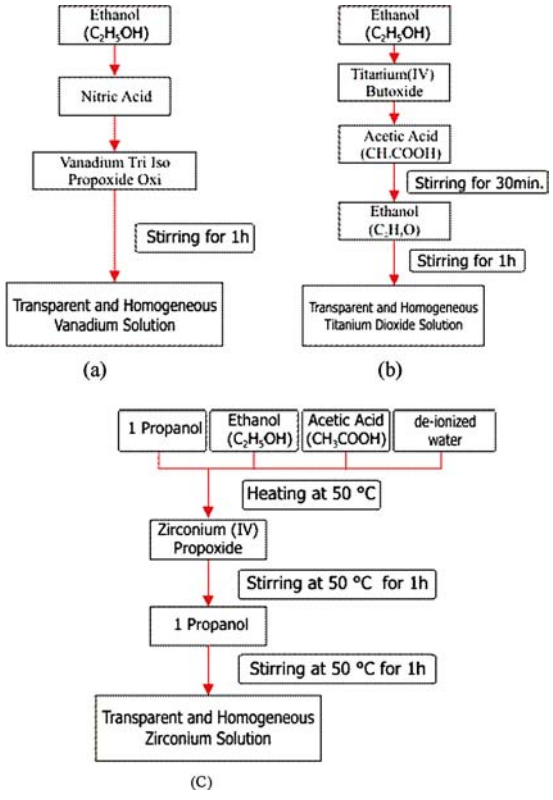


Figure 1 Preparation route for (a) V_2O_5, (b) TiO_2, and (c) ZrO_2 solutions.

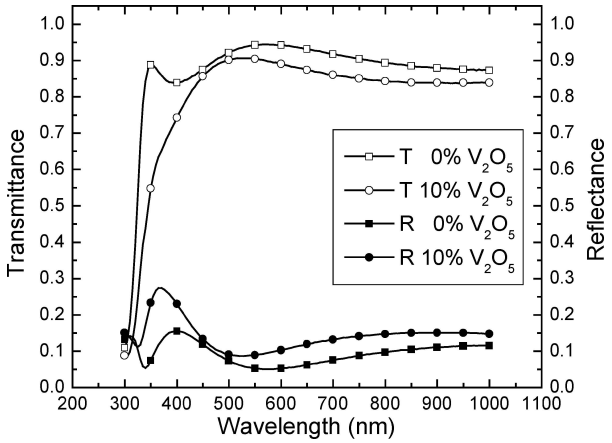


Figure 2 Transmittance and reflectance versus wavelength for TiO_2 and 10% V_2O_5-TiO_2 films.

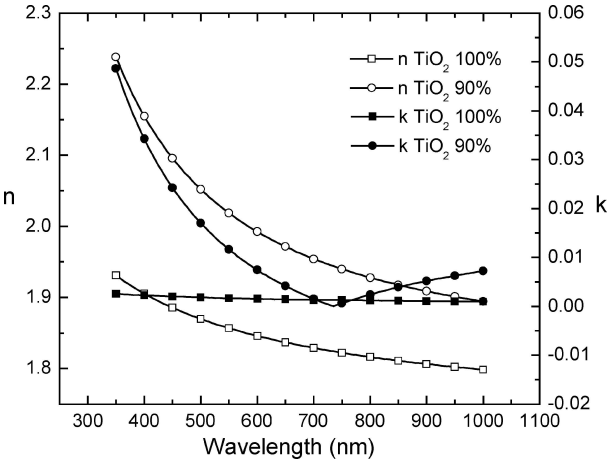


Figure 3 Refractive index (n) and extinction coefficient (k) versus wavelength for TiO_2 and 10% V_2O_5-TiO_2 films.

V_2O_5:TiO_2 and (1:9) V_2O_5:ZrO_2 volume percentages of these sols. Films are coated using the pure and mixed solutions by spin coating process on corning glass (2947) and ITO at 2000 rpm, spun for 30 s. After depositing each layer, films are dried at 100°C for 30 min.

NKD analyzer (Aquila Instrument, UK) is used to evaluate transmission and reflection intensity of the prepared films between the wavelength 300 and 1000 nm. Package software Pro-Optix in the NKD system is used to extract the optical parameters d (thickness), n (λ) (refractive index), and k (λ) (extinction coefficient) of these films from the measured transmittance and reflectance values.

The structural and surface analyses were made through Scanning Probe Microscopy (Shimadzu, SPM 9500-J3). Electrochemical analyses were carried out by EG&G Princeton Applied Research Potentiostat Model 273 using 1 M $LiClO_4$/PC (propylene carbonate) as the electrolyte. Saturated calomel electrode (SCE) as a reference electrode, and a platinum wire as a counter electrode were used.

3. Results and discussions

Fig. 2 shows transmittance and reflectance of TiO_2 and 10% V_2O_5-TiO_2 mixed films with respect to the wavelength. The pure TiO_2 film has about 5% higher transmittance than V_2O_5 mixed TiO_2 for the wavelength greater than 550 nm. The reflectance was lowered by the same amount at the same wavelength range.

Fig. 3 is a plot of n(λ) and k(λ) with respect to the wavelength. The values are obtained from the Pro-Optix software of the NKD analysis system. The graph shows that V_2O_5 mixed TiO_2 film has higher refractive index compared to the pure TiO_2 film even though TiO_2 film has a thickness of 160 nm compared to 124 nm of V_2O_5 mixed TiO_2 films. The AFM picture in Fig. 4 shows tighter structure for the V_2O_5mixed TiO_2 films when compared with the pure TiO_2. This also explains the increased refractive index for the mixed film. The surface roughness is about 4 nm.

Fig. 5 demonstrates a plot of transmittance and reflectance versus wavelength for pure and 10% V_2O_5mixed ZrO_2 films. The pure ZrO_2 film has about 3% higher transmittance than V_2O_5 mixed ZrO_2 for the spectral region between 300 and 1000 nm. The reflectance was lowered by the same amount at the same region.

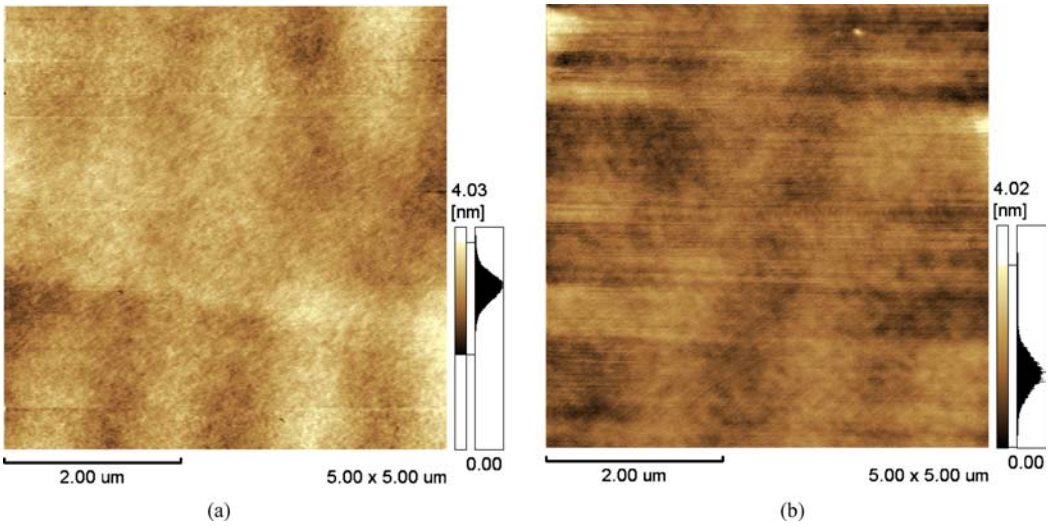


Figure 4 AFM images of (a) TiO_2, (b) 90% TiO_2:10% V_2O_5-TiO_2 thin films heat treated at 100°C for 1 h.

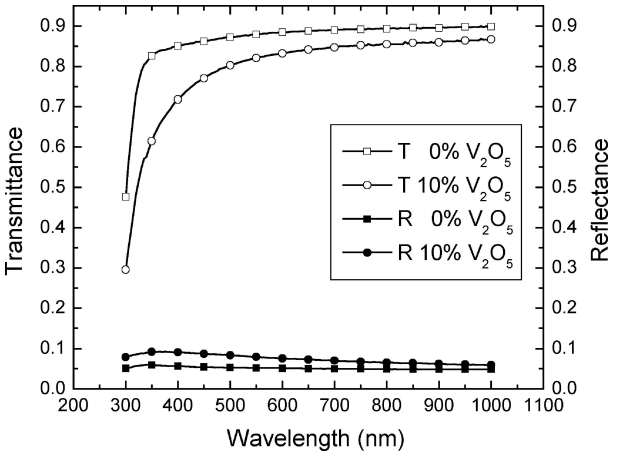


Figure 5 Transmittance and reflectance versus wavelength for ZrO_2 and 10% V_2O_5-ZrO_2 films.

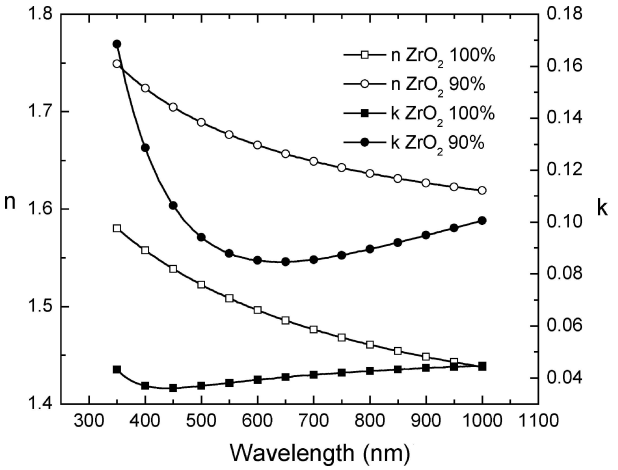


Figure 6 Refractive index (n) and extinction coefficient (k) versus wavelength for ZrO_2 and 10% V_2O_5-ZrO_2 films.

The plot of $n(\lambda)$ and $k(\lambda$ versus wavelength for pure and 10% V_2O_5 mixed ZrO_2 films is shown in Fig. 6. The result shows that the incorporation of V_2O_5 leads to an increase in the refractive index. Table I summarizes the indices of all the films at the wavelength of 550 nm and their corresponding thickness. Fig. 7 shows the AFM surface images of ZrO_2 and V_2O_5 mixed ZrO_2 thin films. The mixed film shows clustered structures of the grains. Surface roughness is about 100 nm for these films. This value is higher when compared with TiO_2 films.

TABLE I Thickness, refractive index and extinction coefficient values at the wavelength of 550 nm for pure and V_2O_5 mixed TiO_2 and ZrO_2 thin films

	d (nm)	n	k
TiO_2	160	1.86	0.0017
10% V_2O_5-TIO_2	125	2.02	0.0116
ZrO_2	90	1.51	0.0381
10% V_2O_5-ZrO_2	55	1.68	0.0879

The coloration is achieved by inserting ions M^+ ($Li^+ + H^+$) from a liquid solution, where M^+ can be any ion from group 1 element of the periodic table. Molar $LiClO_4$/PC solution is used for our electrochromic measurements.

A 20% V_2O_5 added TiO_2 films have an increased electrochromic properties compared to the pure TiO_2 as they are shown in Fig. 8. The intercalated charge capacity of TiO_2, 20% V_2O_5-TiO_2 and V_2O_5 were 0.68, 1.33 and 18.11 $mCcm^{-2}$ respectively. The intercalated charge capacity is found by dividing total intercalated charge per unit area to the sweep rate. It is also known that charge capacity of TiO_2 depends on the deposition and post annealing process [15].

In our previous work we demonstrated that 10 and 20% ZrO_2-V_2O_5 films can be used for electrochromic devices due to improvement in their optical transmittance [16]. Films prepared using low volume percentage of Vanadium content in Zirconium Oxide solution were not investigated for the electrochromic properties, since ZrO_2 exhibits no electrochromic properties.

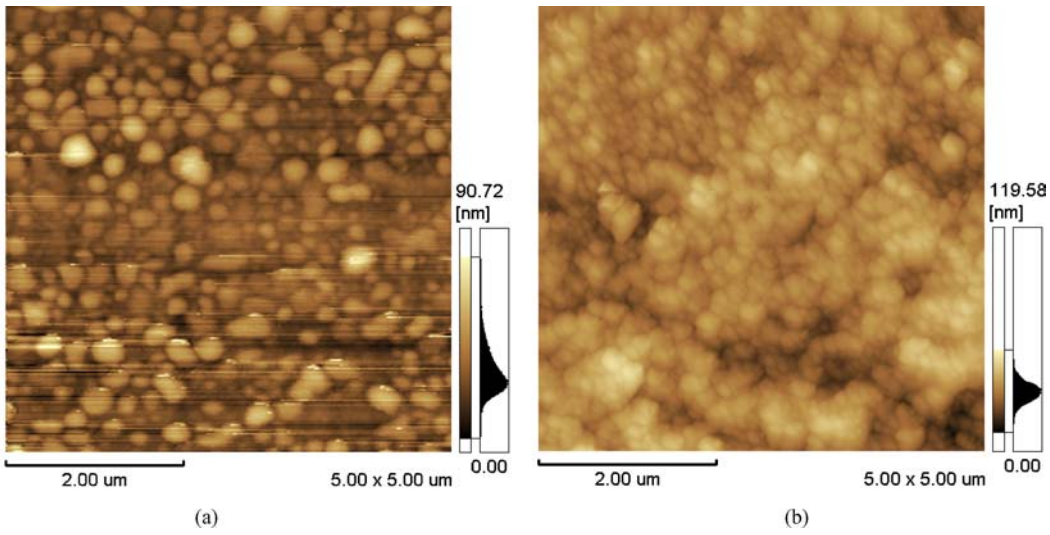
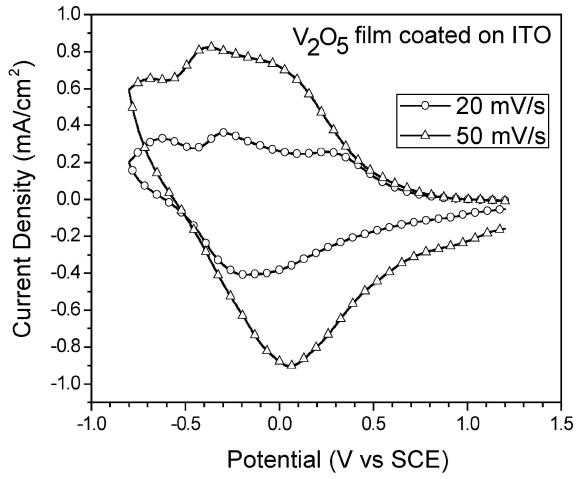
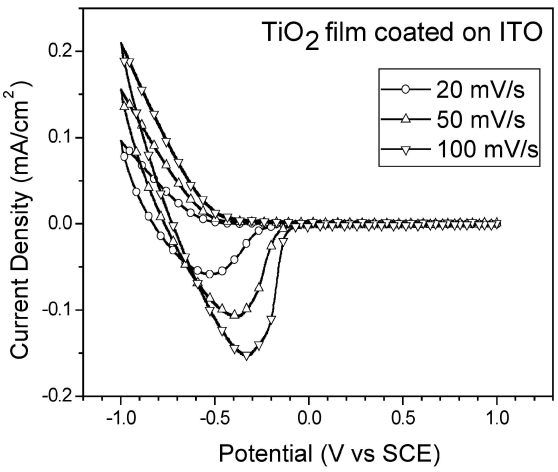


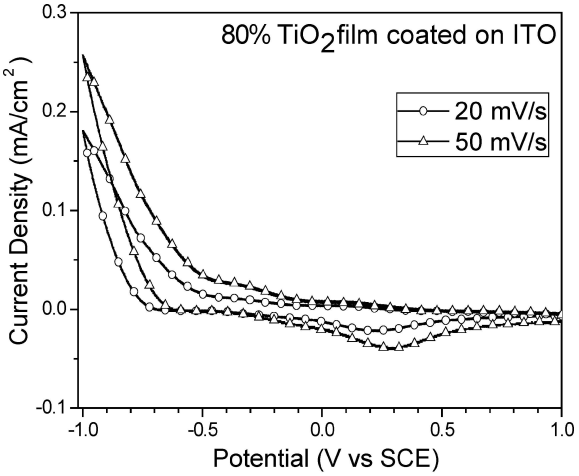
Figure 7 AFM images of (a) ZrO_2, (b) 10% V_2O_5-ZrO_2 thin films heat treated at 100°C for 1 h.



(a)



(b)



(c)

Figure 8 Cyclic voltammograms for (a) V_2O_5, (b) TiO_2, and (c) 20% TiO_2-V_2O_5 thin films.

4. Conclusions

V_2O_5-TiO_2 and V_2O_5-ZrO_2 films are prepared using sol gel spin coating process. For both TiO_2 and ZrO_2 films, addition of V_2O_5 reduces the transmittance slightly which results an increase of reflectance for TiO_2 and ZrO_2 films above 550 nm region. The refractive index increases either for mixed TiO_2 and ZrO_2 films. Refractive index value at $\lambda = 550$ nm increases from 1.86 to 2.02 for TiO_2 and from 1.51 to 1.68 for ZrO_2 when 10% of V_2O_5 is added. Varying refractive index value of the transparent materials with the mixture content allow us to construct antireflective, reflective, narrow band and broad band filters etc.

Slight increase of the high kinetic and reversibility by addition of V_2O_5 to TiO_2 films, can still be preferable in electrochromic application for its high contrast between colored and bleached state.

Acknowledgments

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