Fabrication and characterization of TiO$_2$/SiO$_2$ multilayers using sol-gel spin coating method

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The TiO$_2$/SiO$_2$ alternating multilayers of one-dimensional photonic crystals (1DPCs) was fabricated by the sol-gel process and a spin coating method. This study investigated the possibility of creating a better solar cell back reflector by introducing maximum and broader reflection towards longer wavelength spectral region with effect of optimal thin films. After the fabrication of 1DPCs, the optical properties were investigated by Raman spectroscopy, Fourier infrared spectroscopy (FTIR), UV-visible spectroscopy (UV-vis) and scanning electron microscopy (SEM). From the results, the Raman spectra exhibited notable peaks and indicates the presence of anatase TiO$_2$ and SiO$_2$ layered structures. Furthermore, the highest reflectance was observed in the visible region and shifting into the longer wavelength spectral region due to the increment of alternative layers (stacks). These structural and morphological results are encouraging for the realization of TiO$_2$ and SiO$_2$ materials for various applications, including LED and photovoltaics.

Keywords: multilayers, sol-gel, spin coating, back reflector, anatase.

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1. Introduction

Currently, TiO$_2$ has great attention due to its various applications and correlating research associated with nanomaterials that are environment-friendly. Y. Y. Liu et al. reported that the addition of SiO$_2$ onto TiO$_2$ films enhanced photon induction [1]. The fabrication of dielectric multilayers can be accomplished using various techniques such as ion-assisted-deposition (IAD), sol-gel, dip-coating, spin-coating, sputtering, etc [2–5]. Sol-gel is an appropriate method for the synthesis of TiO$_2$/SiO$_2$ thin films with enhanced electrical and optical performance in industrial applications because of large refractive index contrast. This is one of the significant features of one-dimensional photonic crystals (or multilayers) and existing photonic band gap (PBG) with high (n1) and low (n2) refractive index contrast. The alternative layers (stacks) of TiO$_2$/SiO$_2$ coatings mainly focusing on various applications such as antireflection coating, photocatalysis, light emitting diodes (LEDs), solar cells, optical filter, dental implants, sensor and thermal applications [6–12]. Dubey and Ganesan have studied the optical properties of SiO$_2$/TiO$_2$ multilayers by using sol-gel spin coating method. They have obtained maximum $\sim$78% reflection with the combination of six alternative low (SiO$_2$) and high (TiO$_2$) refractive indices of the films. For the corresponding fabricated multilayer structure, it was observed that when the number of stacks was increased, the reflectance was also enhanced. Furthermore, the film thickness (230 and 70 nm), refractive index (1.43 and 2.0) along with surface topography (AFM) were discussed [13]. Ding et al. have demonstrated the improvement of reflectance and efficiency of the light emitting diodes (LEDs) with the integration of aluminium film and double (16 stacks) distributed Bragg reflectors (TiO$_2$/SiO$_2$). They have also reported the light output power of LED with double distributed Bragg reflector (DBR) was $\sim$3.7% greater than single (8 stacks) DBR stacks [14]. Pana et al. have reported the design and fabrication of seven stacks TiO$_2$/SiO$_2$ multilayers by using optical modeling and RF magnetron sputtering. The RF magnetron sputtering used for the thermal solar collector consists of an optical filter comprising TiO$_2$/SiO$_2$ alternative layers. They have demonstrated colored glazing showing significant reflectivity $\sim$54% at 574 nm and integrated total transmittance was $\sim$80.3%. The yellow and green glaze had the best mechanical and thermal stability for thermal solar collectors [15]. Ilinykh and Matyushkin have fabricated 1DPCs using a sol-gel process and spin coating method. They have found minimum transmittance ($\sim$7%) between the photonic band gaps (450–600 nm). Also, the band gap varied with respect to the viscosity of the prepared solution and the thickness of the layers also changed [16]. Jena et al. have investigated design and fabrication of 1DPCs (TiO$_2$/SiO$_2$) using an asymmetric bipolar pulse DC magnetron sputtering technique. They have proved both theoretical and experimental works were congruent by measured photonic band gap (PBG) in the visible spectral region [17]. Hegmann et al. have prepared SiO$_2$-TiO$_2$ scattering layers using sol-gel process and a dip-coating method. They improved thin film solar cells with the addition of aluminium doped ZnO and a-Si:H/µc-Si:H by vapor phase deposition. Further, the electrical properties and performance have been studied by different
characterizations. They have implemented sol-gel based scattering thin films for light trapping mechanism with 
two different concepts for solar cell application [18]. In this present work, highly reflective TiO$_2$/SiO$_2$ multilayers 
were prepared using sol-gel spin coater techniques and characterized their optical performance. Section 2 explains 
the experimental works of sol-gel process and spin-coating techniques. After calcination, the thin films analysis 
results are discussed in section 3 and conclude the paper in section 4.

2. Experimental approach

An experimental technique for the synthesis of the TiO$_2$/SiO$_2$ multilayer structure was a spin coating of SiO$_2$ 
sol and TiO$_2$ sol on a glass substrate in which the prepared solution was used in a sol-gel technique at room 
temperature. Fig. 1 shows the schematic diagram of the preparation of TiO$_2$/SiO$_2$ thin films.

![Schematic diagram of the preparation steps of TiO$_2$/SiO$_2$ thin films](image)

Prior to coating, the glass substrates were cleaned using ultra sonication process in distilled water, acetone, 
ethanol respectively. First, SiO$_2$ and TiO$_2$ solutions were prepared independently. The TiO$_2$ solution was prepared 
by adding 1.7 mL CH$_3$COOH (acetic acid) in 20 mL CH$_3$OH (methanol) and to this mixture 1.2 mL of C$_{16}$H$_{36}$O$_4$Ti 
(TBOT) was added dropwise and stirred for 30 minutes. After magnetic stirring, the TiO$_2$ solution was deposited on 
the glass substrate with the rotation speed of 3000 rpm for the 30s. Then, the coated glass substrates were annealed 
at 500°C for 1 hour. Next, a solution of SiC$_8$H$_{20}$O$_4$ (TEOS-1.5ml), C$_2$H$_6$O (ethanol-20ml) and CH$_3$COOH (Acetic 
Acid-2.3ml) was first prepared and stirred for 90 minutes at room temperature. Then, SiO$_2$ solution coated on a 
TiO$_2$ coated glass substrate by the spin-coater technique with the 3000 rpm for the 30s. The coated glass substrates 
were dried at room temperature and then heat-treatment (300°C) for 1 hour. Both the final stirred solution was 
aged in a closed glass container at room temperature for one day and then used for coating. Simultaneously, we 
prepared the 5, 7, 9 and 11 stacks of alternating TiO$_2$ and SiO$_2$ layers. Fig. 2 shows the schematic diagram of 
final multilayer stacks of TiO$_2$/SiO$_2$.

3. Results and discussion

The Raman spectroscopic technique was employed to study the presence of different frequency modes. Fig. 3 
shows the comparison of Raman scattering spectra at various TiO$_2$/SiO$_2$ stacks. The relevant positions of the bands 
are also indicated and calculated band range from 300 to 2300 cm$^{-1}$. 

![Schematic diagram of the final multilayer stacks of TiO$_2$/SiO$_2$](image)
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First, the anatase phase TiO$_2$ thin films were successfully observed on glass substrates using Raman spectroscopy. The Raman bands of the anatase phase noticed on 5, 7, 9 and 11 stacks at 393 and 640 cm$^{-1}$, which can be indicated B1g and Eg modes. These broader and low-intensity peaks the presence of a poorly-defined anatase phase [19,20]. The characteristics recorded in our studies were similar to those obtained in previous studies. Further, the deposition conditions such as solution viscosity, the deposition period and calcination temperature are significant for obtaining a better anatase TiO$_2$ phase. For SiO$_2$ deposited on TiO$_2$, we characterized and observed broad peak at higher frequencies such as 600 cm$^{-1}$ and 1369 cm$^{-1}$. Here, the first peak was assigned to breathing modes of oxygen atoms [21,22]. The SiO$_2$ grown layers on TiO$_2$ has higher peaks at 1369 cm$^{-1}$ as seen in Fig. 3. Compared to the TiO$_2$ spectrum, the SiO$_2$ is so broad and strong spectral curve. Fig. 4 shows typical infrared transmittance spectrum of various stacks (5S, 7S, 9S & 11S) of TiO$_2$/SiO$_2$ layers. The strong peaks at 3400 cm$^{-1}$ and 1644 cm$^{-1}$ are attributed to OH stretching bands due to water adsorbed by TiO$_2$ layers. The absorption band at 1089 cm$^{-1}$ confirmed the presence of Si–O–Si stretching vibration [23]. The characteristic of Ti–O vibration bending mode shows the presence of metal oxide at 686–742 cm$^{-1}$ [24]. We have observe that the peak intensity increasing at lower wavelength range for the case of 5S and 7S while it is decreases for the 9S and 11S samples.

Figure 5 shows the reflectance spectrum of 5S, 7S, 9S and 11S stacks of TiO$_2$/SiO$_2$ prepared by spin coating process. The partial reflection wave of each layer produces maximum reflections and the many reflected waves.
creating high-quality back reflectors. This reflected wavelength range is called distributed Bragg reflector (DBR) and referred as photonic band gap (PBG). The band gaps (full width at half maximum-FWHM) of DBR changing with respect to refractive index contrast between the layered structures. This can be expressed in the terms of frequency by using the following equation [25, 26]:

$$\Delta \omega = \frac{4\omega_{\text{max}}}{\pi} \sin^{-1} \left( \frac{|n_h - n_l|}{n_h + n_l} \right),$$

here, $\omega_{\text{max}} = \frac{2\pi c}{\lambda_{\text{max}}}$, $n_h$ and $n_l$ are the high and low refractive index. Overall, the reflectance peaks achieved maximum (> 99 %) level and shift can be verified. When increasing the number (N) of alternating layers from 5 to 11 stacks, the enhanced reflection shifts significantly and broadening towards higher wavelength region which will be optimized.

Figure 6 shows the enhanced reflectance FWHM with increased number of stacks, it is dominant for the case of 11S sample with its reflectance FWHM 270 nm. Particularly, the reflectance is mainly dependent on the optical thickness and surface structure of the layers also called first-order center wavelength:

$$\lambda_{\text{max}} = 2(n_h d_h + n_l d_l)$$

where $\lambda_{\text{max}}$ is the reflected wavelength, $d$ is the thickness of the layers. The bright and dark color (interference) shows the illuminated light yields a good reflectance band at desired wavelength region. These films exhibit bright colors when the stop band fell in the visible spectral region. By controlling the optical thickness, thin film color can be varied across both the visible and infrared spectral region [27, 28].
Cross-sectional TiO$_2$/SiO$_2$ multilayer (11 stacks) thin films were characterized by the field emission scanning electron microscopy (FESEM) as depicted in Fig. 7. From the cross-sectional image of the alternating dielectric layers, we can find some of the borders and remaining are merged with each other. The structural defect was achieved by multiplying the layers of TiO$_2$ and SiO$_2$ embedded in which the light bands correspond to titanium dioxide and dark bands are silicon dioxide layers. The cross-sectional image indicates that the film thickness is 1 $\mu$m TiO$_2$/SiO$_2$ multilayer film and confirms the heterogeneous structure.

4. Conclusion

In this paper, TiO$_2$/SiO$_2$ multilayers were fabricated and studied. TiO$_2$ nantase phase and amorphous SiO$_2$ were confirmed by the Raman Study. The back-side light reflecting structures of alternating high-index and low-index multilayers of 11 stacks had shown maximum reflection in the visible spectral region. The reflectance center
wavelength noticed at 362, 365, 404 and 450 nm corresponding to the sample 5S, 7S, 9S and 11S upon increasing the number of stacks the reflection bands were found shifted towards the longer wavelength with enhanced reflectivity. The FESEM showed the formation of alternative layers of light (TiO$_2$) and dark (SiO$_2$) strips with their one-dimensional periodicity. The morphological and optical measurement confirmed the changes in thin films and surface roughness are attributed to the better backside reflector for the photovoltaic device. Further, the work optimization is required to enhance optical behavior.

References


