NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2019, 10 (1), P. 63–69

Fabrication and characterization of TiO_2/SiO_2 multilayers using sol-gel spin coating method

S. Saravanan, R. S. Dubey

Department of Nanotechnology, Swarnandhra College of Engineering and Technology, Seetharampuram, Narsapur-534280, (A.P), India

shasa86@gmail.com

DOI 10.17586/2220-8054-2019-10-1-63-69

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.

Received: 25 January 2019

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.

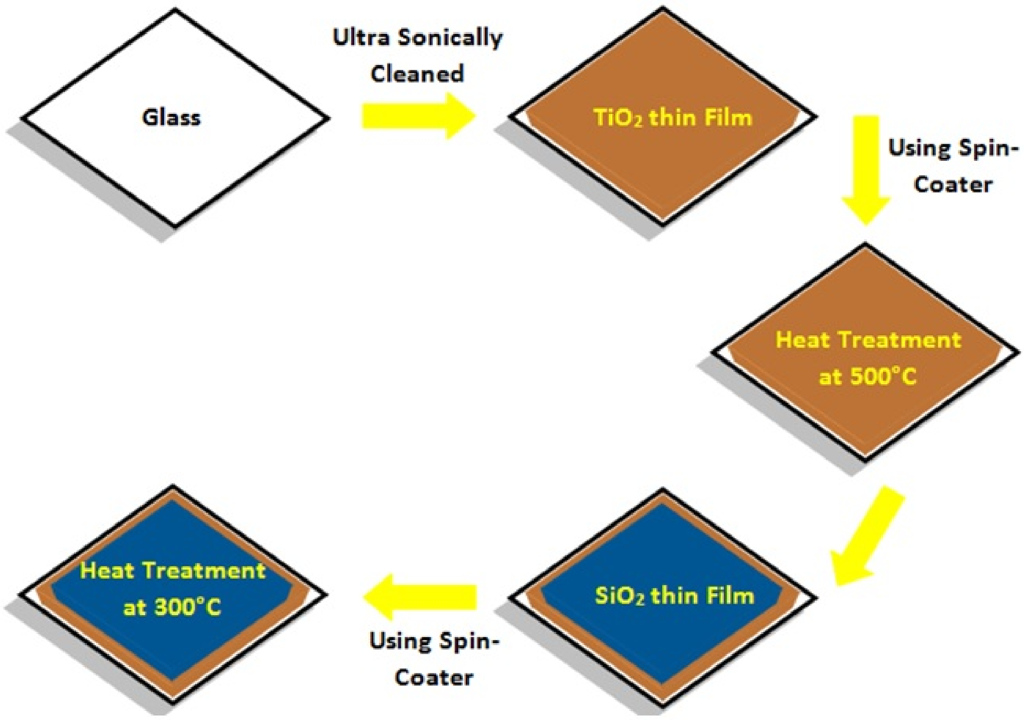

FIG. 1. The schematic diagram of the preparation steps of TiO_2/SiO_2 thin films

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_3COOH (acetic acid) in 20 mL CH_3OH (methanol) and to this mixture 1.2 mL of $C_{16}H_{36}O_4Ti$ (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 $SiC_8H_{20}O_4$ (TEOS-1.5ml), C_2H_6O (ethanol-20ml) and CH_3COOH (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}.

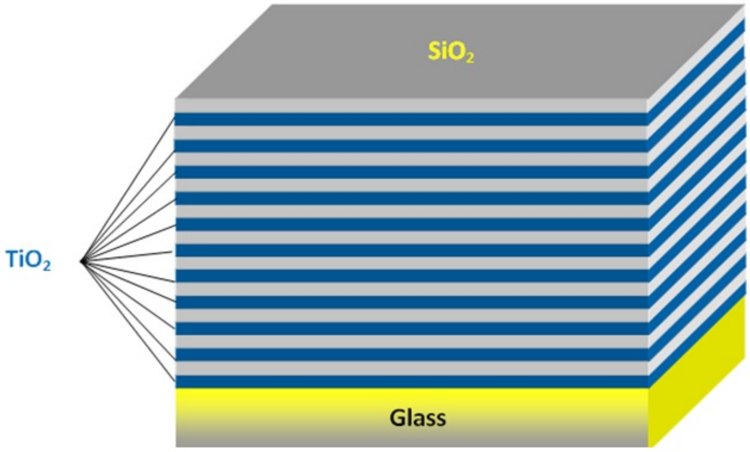

FIG. 2. The schematic diagram of the fabricated TiO_2/SiO_2

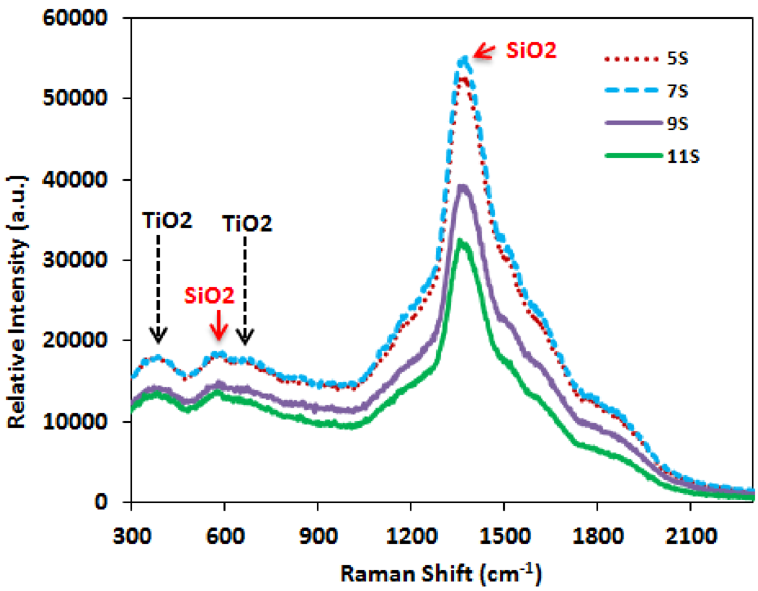

FIG. 3. Raman spectra of anatase TiO_2/SiO_2 multilayer thin films grown on a glass substrate

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 similarto 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

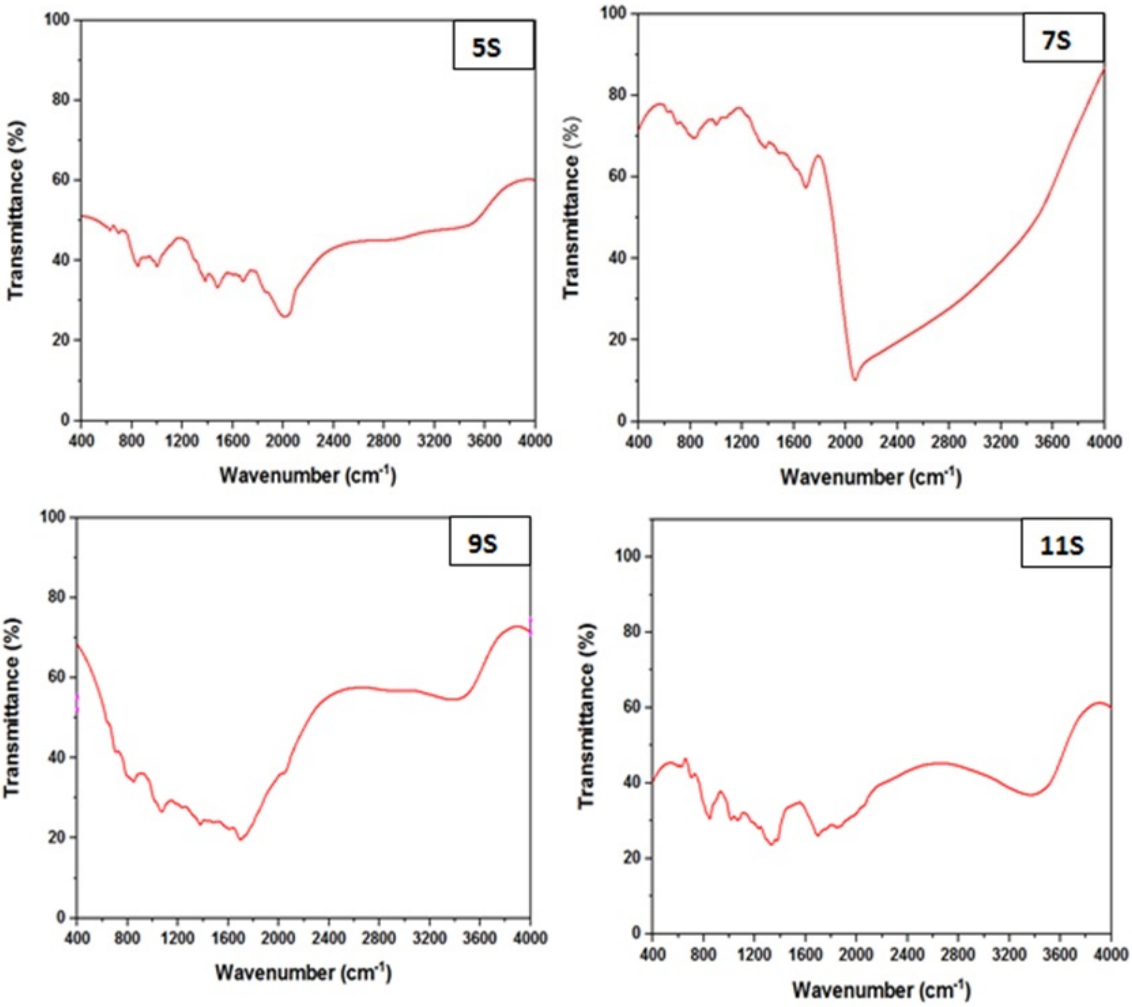

FIG. 4. FTIR spectrum of TiO_2/SiO_2 multilayer films deposited on glass with 3000 rpm at room temperature

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]:

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

here, $\omega_{max} = 2\pi c/\lambda_{max}$, 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:

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

where λ_{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].

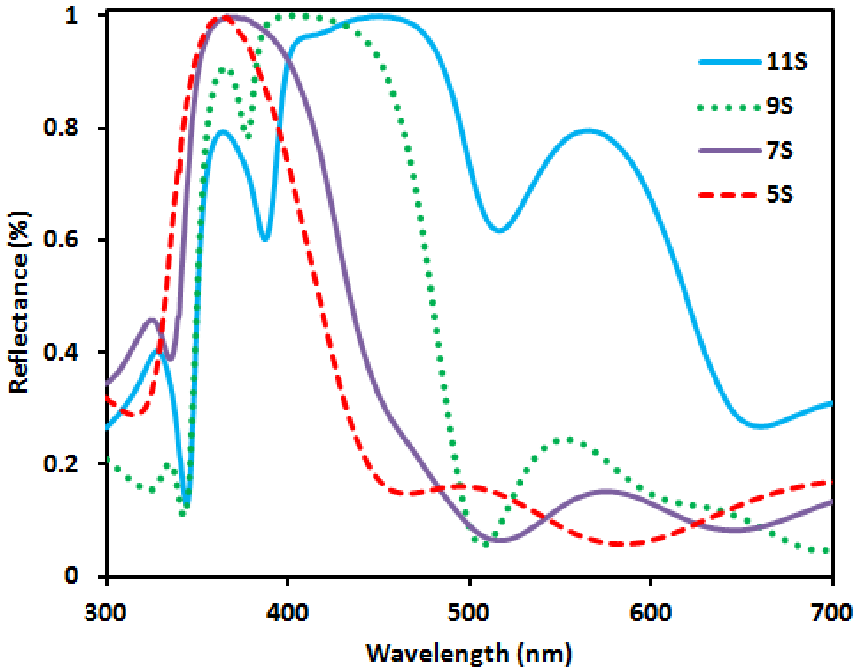

FIG. 5. The reflectance spectra of different stacks of TiO_2/SiO_2 layers

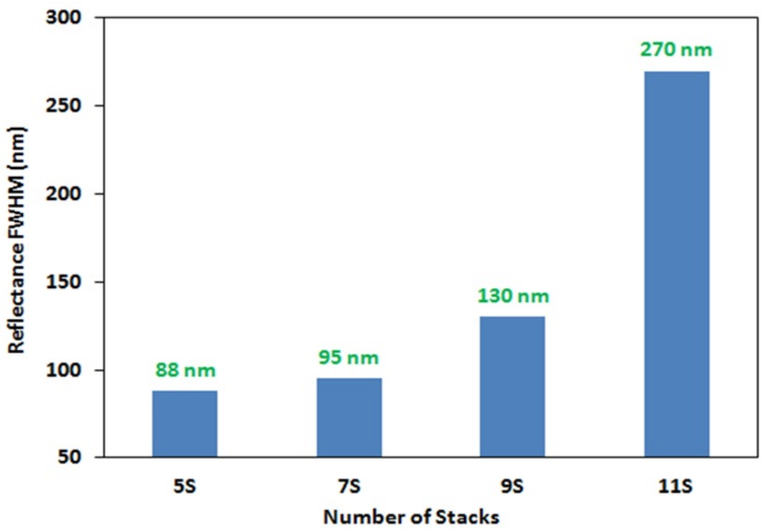

FIG. 6. The bar diagram of the reflectance of FWHM vs a number of stacks

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 μm 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

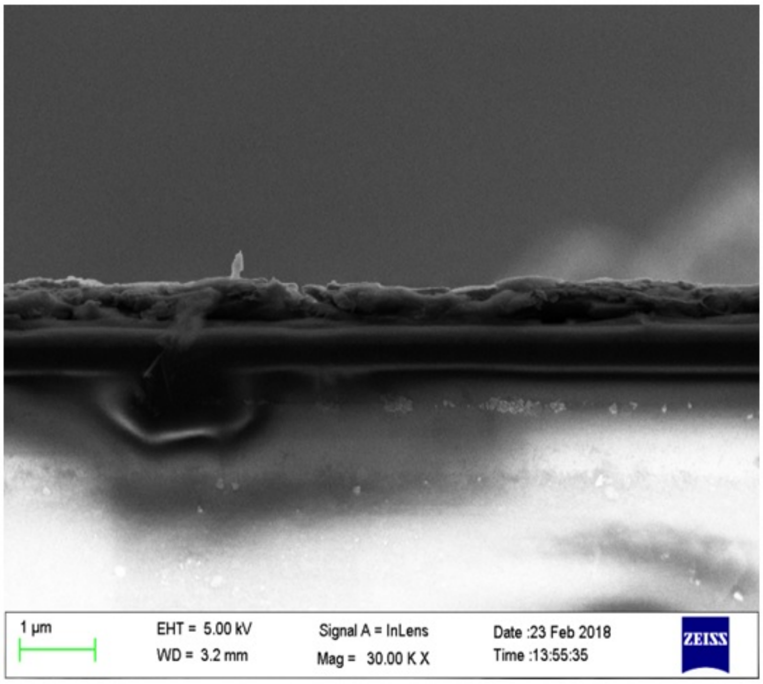

FIG. 7. The cross-sectional image of FESEM representative TiO_2/SiO_2 multilayers

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

[1] Liu Y.Y., Qian L.Q., Guo C., Jia X., Wang J.W., Tang, W.H. Natural superhydrophilic TiO_2/SiO_2 composite thin films deposited by radio frequency magnetron sputtering. *J Alloys Compd*, 2009, **479**(1-2), P. 532–535.

[2] Bin Fan, Masahiro Suzuki and Ken Tang. Ion-assisted deposition of TiO_2/SiO_2 multilayers for mass production. *Appl Opt.*, 2006, **45**(7), P. 1461–1463.

[3] Li D., Wan D., Zhu X., Wang Y., Han Z., Han S., Shan Y., Huang F. Broadband antireflection TiO_2-SiO_2 stack coatings with refractive-index-grade structure and their applications to Cu(In,Ga)Se_2 solar cells. *Sol. Energy Mater Sol. Cells*, 2014, **130**, P. 505–512.

[4] Dubey R.S., Ganesan V. Fabrication and characterization of TiO_2/SiO_2 based Bragg reflectors for light trapping applications. *Results Phys*, 2017, **7**, P. 2271–2276.

[5] Yamaguchi T., Tamura H., Taga S., Tsuchiya S. Interfacial optical absorption in TiO_2-SiO_2 multilayer coatings prepared by RF magnetron sputtering. *Appl Opt.*, 1986, **25**(16), P. 2703–2706.

[6] Liu Z., Zhang X., Murakami T., Fujishima A. Sol-Gel SiO_2/TiO_2 bilayer films with self-cleaning and antireflection properties. *Sol. Energy Mater Sol. Cells*, 2008, **92**(11), P. 1434–1438.

[7] Liu C., Yang D., Jiao Y., Tian Y., Wang Y., Jiang Z. Biomimetic synthesis of TiO_2-SiO_2-Ag nanocomposites with enhanced visible-light photocatalytic activity. *ACS Appl. Mater. Interfaces*, 2013, **5**(9), P. 3824–3832.

[8] Lin C.H., Lai C.F., Ko T.S., Huang H.W., Kuo H.C., Hung Y.Y., Leung K.M., Yu C.C., Tsai R.J., Lee C.K., Lu T.C., Wang S.C. Enhancement of InGaN-GaN indium-tin-oxide flip-chip light-emitting diodes with TiO_2-SiO_2 multilayer stack omnidirectional reflector. *IEEE Photonics Technol.*, 2006, **18**(19), P. 2050–2052.

[9] Mbakop F.K., Djongyang N., Raidandi D. One-dimensional TiO_2/SiO_2 photonic crystal filter for thermophotovoltaic applications. *Journal of the European Optical Society-Rapid Publications*, 2016, **12**(23), P. 1–9.

[10] C.M. Pecnik, D. Muff and R. Sailer. Color evaluation of a dielectric mirror coating using porcine tissue and prosthetic gingival material: a comparison of two models. *Clin Oral Implan Res.*, 2015, **27**(2), P. 139–148.

[11] Hopman W.C.L., Pottier P., Yudistira D., Van Lith J., Lambeck P.V., De La Rue R.M., Driessen A., Hoekstra H.J.W.M,. de Ridder R.M. Quasi-one-dimensional photonic crystal as a compact building-block for refractometric optical sensors. *IEEE J. Sel. Top. Quantum Electron.*, 2005, **11**(1), P. 11–16.

[12] Pavlichenko I., Exner A.T., Lugli P., Scarpa G., Lotsch B.V. Tunable thermoresponsive TiO_2/SiO_2 Bragg stacks based on sol-gel fabrication methods. *J. Intell. Material Syst. Struct.*, 2012, **24**(18), P. 2204–2214.

[13] Dubey R.S., Ganesan V. Reflectance modulation using SiO_2/TiO_2 multilayer structures prepared by sol-gel spin coating process for optical applications. *Superlattices and Microstruct*, 2017, **111**, P. 1099–1103.

[14] Ding X., Gui C., Hu H., Liu M., Liu, X., Lv J., Zhou S. Reflectance bandwidth and efficiency improvement of light emitting diodes with double distributed Bragg reflectors. *Applied Physics*, 2017, **56**(15), P. 4375–43810.

[15] Pana I., Vitelaru C., Kiss A., Zoita N.C., Dinu M. Design, fabrication and characterization of TiO_2-SiO_2 multilayer with tailored color glazing for thermal solar collectors. *Mater. Des.*, 2017, **130**, P. 275–284.

[16] Ilinykh V.A., Matyushkin B. Fabrication of One-Dimensional Photonic Crystals by Sol-Gel Method. *IEEE*, 2016, P. 47–50.

[17] Jena S., Tokas R.B., Sarkar P., Haque S.M., Misal J.S., Rao K.D., Thakur S., Sahoo N.K. achieving omnidirectional photonic band gap in sputter deposited tio_2/sio_2 one dimensional photonic crystal. *AIP Conf. Proc.*, 2015, **1665**, P. 060018-1-3.

[18] Hegmann J., Jahn R., Schonau S., Sommer N., Lobmann P. SiO_2-TiO_2 scattering layers prepared by sol-gel processing for light management in thin film solar cells. *J. Sol gel Sci Technol.*, 2015, P. 1–9.

[19] Vernardou D., Spanakis E., Vlachou K., Kalogerrakis G., Costello J., Koudoumas E., Katsarakis N. , Pemble M.E. A Comparative study of the photoinduced of TiO_2/SiO_2 and $TiO_2/ZnO/SiO_2$ layers prepared by chemical routes. *ECS Trans.*, 2009, **25**(8), P. 73–80.

[20] Vijayalakshmy S., Subramanian B. Enhanced Performance of dye-sensitized solar cells with TiO_2 blocking layers and Pt counter electrodes prepared by physical vapor deposition (PVD). *Electrochim. Acta*, 2014, **116**, P. 334–342.

[21] Narasimha Rao Mavilla, Chetan Singh Solanki and Juzer Vasi. Raman spectroscopy of silicon-nanocrystals fabricated by inductively coupled plasma chemical vapor deposition. *Physica E*, 2013, **52**, P. 59–64.

[22] Galeener F. Planar rings in glasses. *Solid State Communications*, 1982, **44**(7), P. 1037–1040.

[23] Hecht E. *Optics*, 4th edn, Pearson Inc. San Francisco, California, USA, 2002.

[24] Puzzo D.P., Bonifacio L.D., Oreopoulos J., Yip C.M., Manners I., Ozin G.A. Color from colorless nanomaterials: Bragg reflectors made of nanoparticles *J. Mater. Chem.*, 2009, **19**, P. 3500–3506.

[25] Joannopoulos J.D., Johnson S.G., Winn J.N., Meade R.D. Photonic Crystals: Molding the Flow of Light, 2008, 2-nd edn, Princeton University Press, Princeton, New Jersey, USA, 2008.

[26] Wu Z., Lee D., Rubner M.F., Cohen R.E. Structural color in porous, superhydrophilic, and self-cleaning SiO_2/TiO_2 Bragg stacks. *Small*, 2007, **3**(8), P. 1445–1451.

[27] Madani M., Omri K., Fattah N., Ghorbal A., Portier X. Influence of silica ratio on structural and optical properties of SiO_2/TiO_2 nanocomposites prepared by simple solid phase reaction. *J. Mater. Sci. Mater. Electron.*, 2017, P. 5–7.

[28] Suwarnkar M.B., Dhabbe R.S., Kadam A.N., Garadkar K.M. Enhanced photocatalytic activity of Ag doped TiO_2 nanoparticles synthesized by a microwave assisted method, *Ceram Int.*, 2014, **40**, P. 5489–5496.