Transparent dielectric TiO_2/SiO_2 coatings for thermal shielding and self-cleaning applications

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Abstract

The economical fabrication of one-dimensional dielectric reflectors using the hybrid sol-gel spin coating process is significant compared to sophisticated chemical and physical vapor deposition techniques. In this work, we opted for alternate layers of TiO_2 and SiO_2 films to fabricate near-infrared dielectric reflectors owing to their high refractive index contrast and easy tunability of the reflection window in the desired spectral range. X-ray diffraction (XRD) studies of the monolayer TiO_2 and SiO_2 confirmed the existence of anatase-TiO_2 and amorphous-SiO_2 phases, respectively. Spectroscopic ellipsometry investigation of TiO_2 and SiO_2 films revealed the refractive indices of 2.6 and 1.5, respectively. The field-emission scanning electron microscopy (FESEM) analyses evidenced the fabrication of 2.5 stacks/bilayers of TiO_2/SiO_2 $(TiO_2/SiO_2)_{2.5S}$. The reflectance measurement demonstrated 100% reflection in the near-infrared region with its center wavelength of 833 nm. In addition, we have examined the water contact angle of various samples using the sessile drop technique, and 2.5 stacks-based reflector showed its lowest contact angle of 29.3^{o}, which suggests its anti-fogging and self-cleaning applications.

Keywords: Contact angle measurement; hydrophilic coating; near-infrared reflector; sol-gel spin coating; titania.

1. Introduction

Presently, nanoscale technology is growing swiftly with its novel applications in the science and technology sectors. Nanotechnology is nothing but inspiration from nature. For example, the lotus-leaf effect and butterfly wings are a few of them, which helped researchers to develop hydrophobic coatings and transparent dielectric reflectors. Inspired by lotus leaves ' characteristics, Yang *et al.,* (2015) demonstrated the superhydrophobic coating by using the strawberry-like Janus particles. The water contact angle of the coating investigation revealed its contact angle of 140^{o}, indicating the flushing off the water quickly from the surfaces. The potential applications of TiO_2 and SiO_2 based dielectric reflectors brought these materials demanding owing to their high refractive index contrast and hydrophilic nature. This aids researchers in developing an optical component that can be used for several purposes. In the automotive industry, alternating interfaces can be installed as a reflector for the required wavelength spectrum and as the self-cleaning and anti-fogging coatings.

Huang *et al.,* (2017) used the atomic layer deposition (ALD) technique to deposit TiO_2 thin film on a Co-Cr substrate and studied its wetting behaviour under the exposure of ultraviolet (UV) light. The static contact angle analysis of the TiO_2 films showed the contact angle of 37.3° and suggested for its use as an antifungal coating to treat denture stomatitis. Akbar & Ameneh**,** 2012 employed the dip-coating method for various kind of coatings (TiO_2, TiO_2-SiO_2 and TiO_2-SiO_2-In_2O_3) on the glass substrates and examined their hydrophilic nature. The coatings of TiO_2, TiO_2-SiO_2, TiO_2-SiO_2-In_2O_3 showed their contact angle of 10.3°, 4.3°, and 1.1°, respectively. Further, after storing the coated samples in the dark environment for 24 hours, they noticed an increased value of contact angles of about 17.1° for TiO_2, 6.7° for TiO_2-SiO_2, and 2.9° corresponding to the samples TiO_2, TiO_2-SiO_2 and TiO_2-SiO_2-In_2O_3. This increased hydrophilicity was attributed to the acidic surface, which caused the dissociative water adsorption by adsorbing the hydroxyl groups and H_3O^+ ions on the surface. Shokuhfar *et al.,* (2012) investigated the effect of sintering temperatures on the wetting behaviour of composite SiO_2-TiO_2 coatings on glass substrates. The variation of sintering temperature from 500°C to 700°C evidenced the increased hydrophilic nature. Further, they proposed its application in automobile windshielding for dispersing water across the surface and remove the dust particles from it. Damchan *et al.* (2008) spin-coated the composite TiO_2-SiO_2 layer while altering the precursor's molar concentrations and evaluated their wetting behaviour. Their findings showed improved hydrophilic characteristics with the increased molar concentration of SiO_2, which caused more hydroxyl groups.

A dielectric reflector is a multilayer structure of thin films with high- and low-refractive-index materials. The alternate high and low refractive index films felicitate constructive interference at the interfaces, which yields enhanced reflection from the coated surface. Dubey & Ganesan, 2017 reported the fabrication of a multilayer structure on the glass substrates using the sol-gel spin coating process and presented its optical properties. The cross-section FESEM study of the multilayer structure evidenced the periodic arrangement of bright and dark layers indicating the formation of TiO_2 and SiO_2, respectively. Similarly, UV-Vis spectroscopy analysis demonstrated a maximum 90% reflectance at the center wavelength of 617 nm i.e., in the visible spectrum. Further, they suggested the application of a fabricated reflector for light trapping in the thin-film solar cell. Lin *et al.,* (2015) analyzed the reflector made-up of thin films of TiO_2/SiO_2 prepared by the e-beam evaporation approach. The reflectance analysis using UV-Vis spectroscopy endorsed a maximum of 100% reflectance in the wavelength region between 390 and 650 nm [12]. The reflector was integrated with the LED, and they observed enhanced brightness compared to the ordinary LED. Anaya *et al.,* (2016) investigated a dielectric reflector with porous and dense films of TiO_2 and SiO_2 using the spin coating technique. The appearance of the periodic bright and dark bands in the cross-section FESEM examination confirmed the fabrication of TiO_2 and SiO_2 layers, respectively. The optical study demonstrated a 90% reflectance in the 300-500 nm spectral range. Feng *et al.,* (2013) reported the fabrication of multilayer reflector of TiO_2/SiO_2 by e-beam evaporation process. The reflectance analysis revealed about 95 % reflectance in the wavelength from 1.1 to 1.6 μm, indicating that it can be used in various applications, such as optical amplifiers and infrared emitters. Nagayoshi & Murooka**,** 2015 investigated a dielectric reflector of composite TiO_2 and SiO_2 nanoparticles using the sol-gel spin coating technique. The morphological study using FESEM evidenced the alternate fabrication of TiO_2/SiO_2 films. Further, UV-Vis spectroscopy's reflectance analysis endorsed about 90% reflectance in the near-infrared region. The practical lifetime of the produced optical component was investigated and compared to that of TiO_2 nanoparticles coated with aluminum, evidenced a longer lifetime when combined with a thin SiO_2 passivation layer.

The above findings reported in the literature involved the high-cost fabrication using advanced equipment. Hence, to decrease the fabrication cost and increase the durability of the coating, we put forward the development of a straightforward methodology to fabricate such dielectric reflectors for their various applications. Section 2 explores the materials and methods involved in the proposed work, while Section 3 discusses the obtained results. Finally, the research work is concluded in Section IV.

2. Experimental

We have produced the coatings of titania (TiO_2) and silica (SiO_2) films on the glass substrates by the spin coating technique. The respective gels of TiO_2 and SiO_2 were synthesized by the sol-gel process, as shown in figure 1(a)-(c). For the synthesis of TiO_2 and SiO_2 gels, the solvent ethanol, chelating agents nitric acid (HNO_3, Sdfine), and acetic acid (AcAc, Sisco Research Laboratories) were taken along with the precursors i.e., titanium isopropoxide (TTIP, Sigma-Aldrich) and tetraethyl orthosilicate (TEOS, Sigma-Aldrich), in the following molar ratios ethanol:HNO_3:AcAc:TTIP: 1.2:0.05:0.3:0.3 and ethanol: HNO_3:AcAc: TEOS was1.2:0.05:0.3:0.3 respectively.

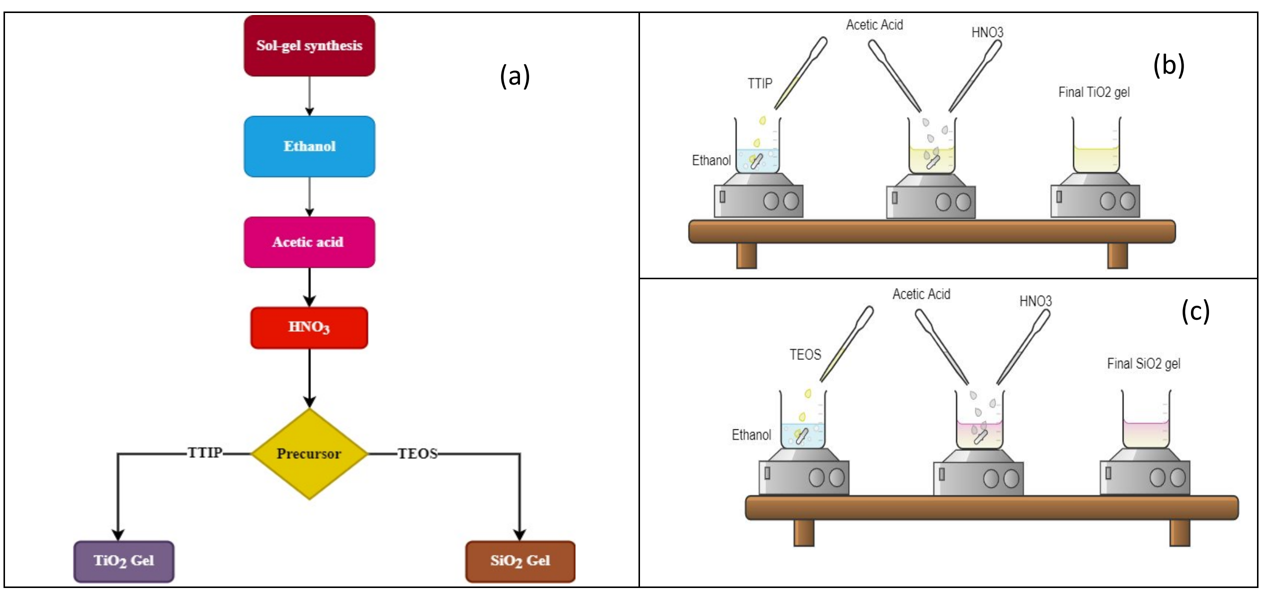

Fig. 1. Flow chart of the sol-gel process (a), sol-gel synthesis of TiO_2 (b), and SiO_2 gels (c).

Figures 1(a) and 1(b) represent the sol-gel process's flow chart and schematic. The glass substrates were thoroughly washed with the soap solution and ultrasonicated in ethanol for 30 minutes before being used. Finally, the substrates were washed with deionized water to remove any solvent residues from the surface. To fabricate the multilayer structures, titania (TiO_2) and silica (SiO_2) gels were layer by layer spin-coated on the cleaned glass substrates at a spin rate of 3000 RPM for 30 seconds. Then each layer was annealed for one hour at temperature 500 ^oC in a muffle furnace as shown in figure 2. The multilayer structures were fabricated following the above procedure on the glass substrates and named as $(TiO_2/SiO_2)_{1.5S}$ and $(TiO_2/SiO_2)_{2.5S}$, where "s" indicates the number of stacks or bilayers on the glass substrates.

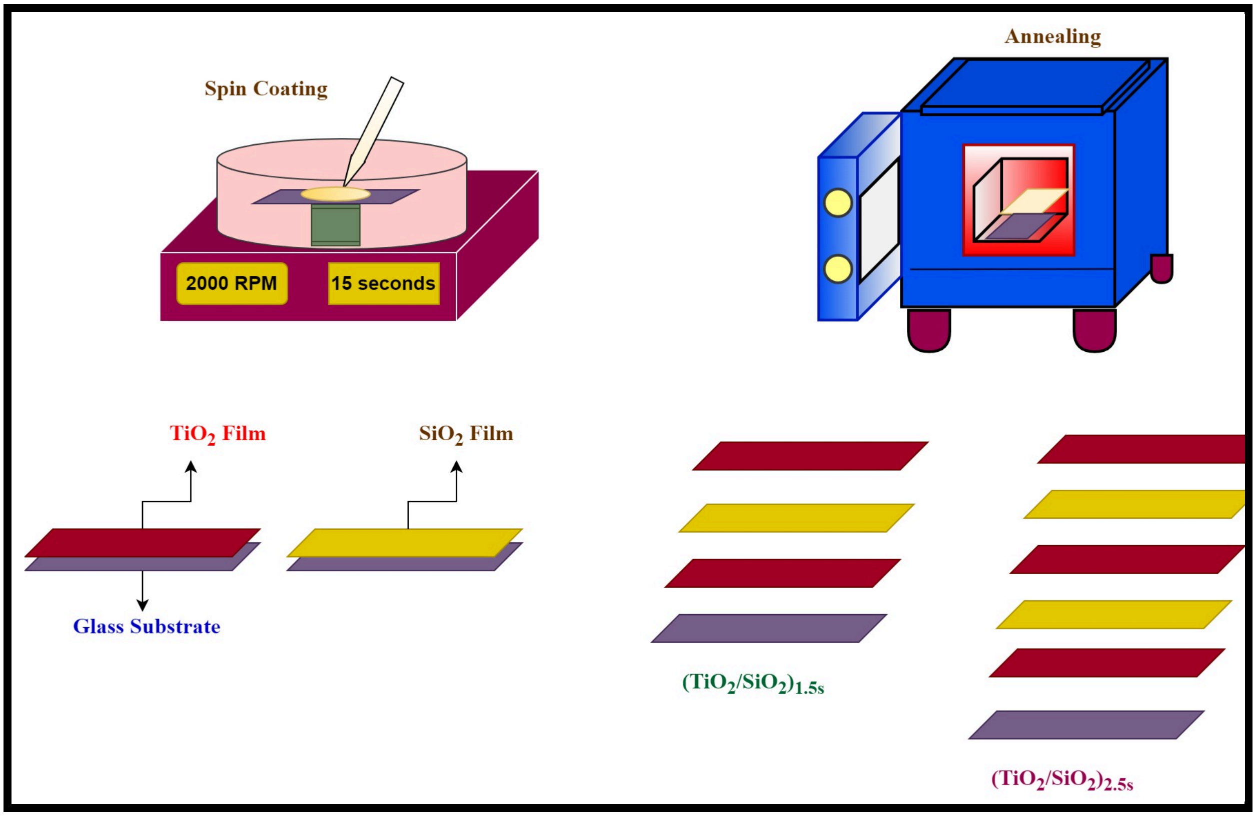

Fig. 2. Schematic illustration of the fabrication of multilayer structure.

The fabricated samples of monolayer and multilayer were characterized by using X-Ray diffractogram (Rigaku, smart lab, Japan) to know the crystallinity, ellipsometer (M-2000, J.A. Woollam Co., Inc.) to determine their optical constants, field-emission scanning electron microscopy (FESEM, MIRA3 TESCAN) to know the film thickness, ultraviolet-visible (UV-Vis, UV1800 Shimadzu, Japan) spectrophotometer having a specular reflectance attachment for reflectance analysis and contact angle meter (KYOWA DM501, Japan) to analyze the wetting behavior.

3. Results and Discussion

Figure 3 depicts X-ray diffraction (XRD) patterns of the individual of monolayer TiO_2 and SiO_2. The XRD pattern was recorded in the Bragg angle range from 10^O-80^O. Figure 3 (a) showed the anatase phase of TiO_2 coating, which is in good agreement with the JCPDS#21-1272. Furthermore, the diffraction peaks indexed at Bragg angles $2\theta=25^O$, 38^O, 48^O, 55^O, 62^O, and 75^O, were attributed to the crystal planes of (101), (004), (200), (211), (204), and (215), respectively and well-matched with the published literature by Permana *et al.,* (2017) and Khajeh *et al.,* (2021). The XRD pattern shown in figure 3(b) represents the characteristic peak of SiO_2 at Bragg angle $2\Theta=22^O$, which evidenced the amorphous nature of SiO_2. This result is found well-matched with the JCPDS#29-0085 and the reported work by Deshmukh *et al.,* (2011).

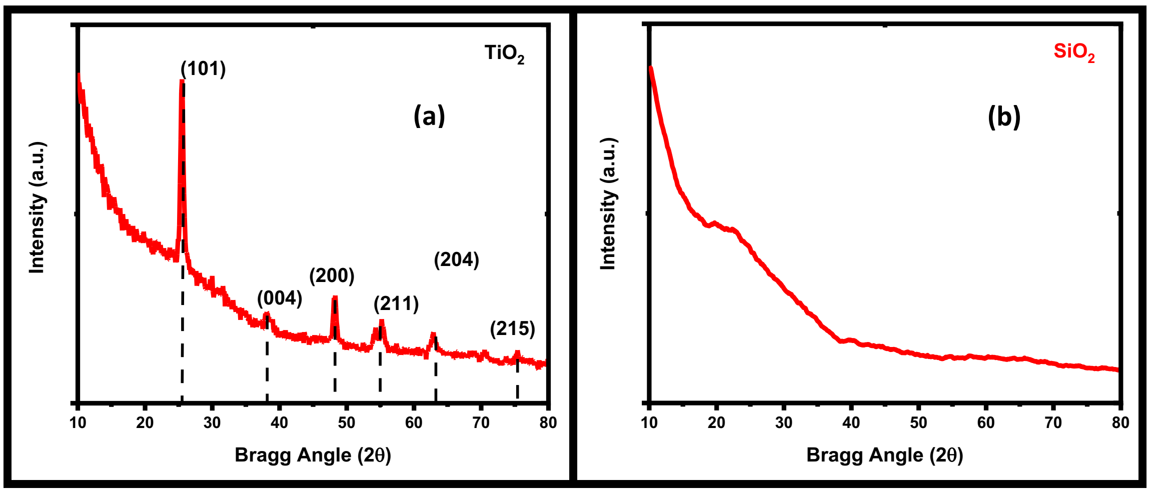

Fig. 3. XRD patterns of TiO_2 film (a) and SiO_2 film (b).

Figure 4 depicts the refractive index (a) and extinction coefficient (b) of the titania and silica films characterized by the spectroscopic ellipsometer.

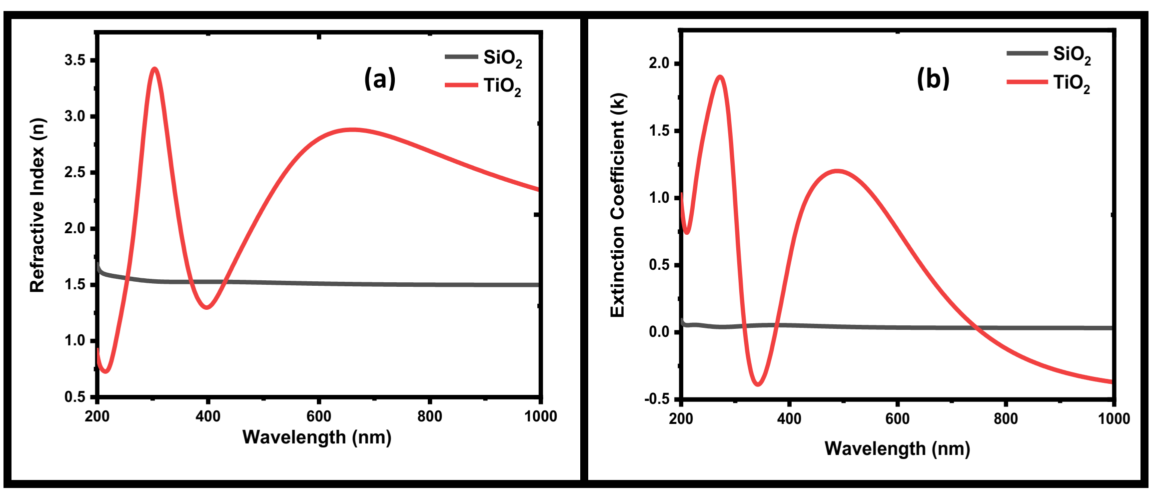

Fig. 4. Refractive index (a) and (b) extinction coefficient of TiO_2 and SiO_2 films.

The refractive index values of the titania film (red curve) are substantially higher (3.6) in the ultraviolet wavelength region and 2.6 in the near-infrared region compared to 2.2 in the visible range, as shown in figure 4(a). A similar trend can be observed for the case of extinction coefficient (red curve), as shown in figure 4(b). Furthermore, the silica film demonstrates a similar variation in the refractive index (black curve) and extinction coefficient (black curve) with respect to increased wavelength depicted in figure 4(a) and 4(b), respectively. The obtained refractive was found in good agreement with the reported work by Julia *et al.,* (2020). With the study of the refractive index and the extinction coefficient, we notice the refractive index contrast (refractive index of TiO_2/refractive index of SiO_2) with the redshift, which is desirable to achieve the reflection band in near-infrared reflector

The spin-coated monolayers of TiO_2 and SiO_2, and multilayers of TiO_2/SiO_2 composed of 1.5 stacks/bilayers $(TiO_2/SiO_2)_{1.5S}$, and 2.5 stacks/bilayers $(TiO_2/SiO_2)_{2.5S}$ were investigated using the field-emission scanning electron microscopy to know their thicknesses and visualize. Figure 5 demonstrates the cross-section view of various prepared samples.

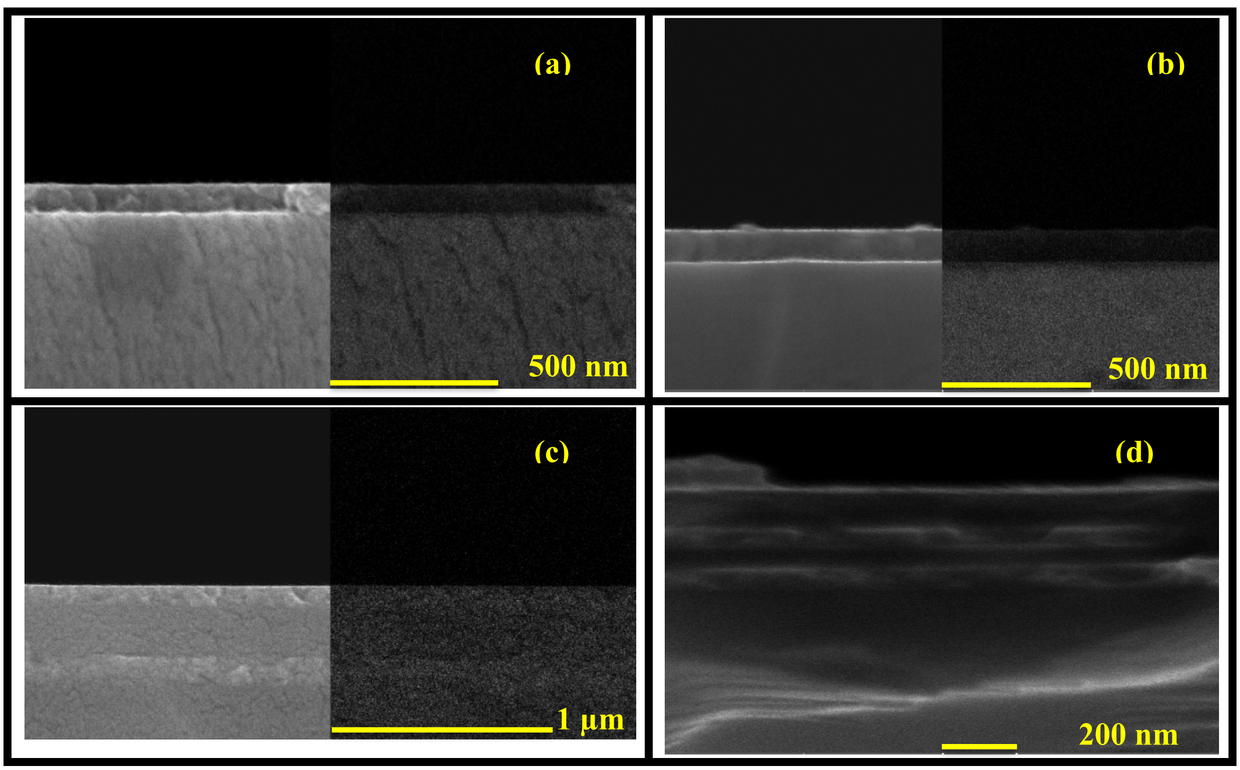

Fig. 5. FESEM cross-section images of TiO_2 (a), SiO_2 (b) and multilayer $(TiO_2/SiO_2)_{1.5}$ (c) and $(TiO_2/SiO_2)_{2.5}$ (d).

The bright and dark layers shown in figure 5 corresponds to the formation of TiO_2 and SiO_2 thin films. The thicknesses of the monolayers of TiO_2 and SiO_2 films were estimated to be 62.5 nm and 78.4 nm as shown in figure 5 (a) and (b), respectively. Similarly, as depicted in figures 5(c) and

5(d), the multilayer structures of 1.5 stacks $(TiO_2/SiO_2)_{1.5}$ and 2.5 stacks $(TiO_2/SiO_2)_{2.5}$ demonstrates their thicknesses of 86.3, 229.7, 78.39 and 92.06, 86.50, 75.69, 11.53, and 64.8 nm corresponding to the TiO_2 and SiO_2 layers. This arrangement of alternate layers of TiO_2 and SiO_2 is promising for the occurrence of constructive interference to produce high reflection in the specified spectral region, Dubey & Venkatesh**,** 2021.

The reflection of the individual TiO_2, SiO_2, and $(TiO_2/SiO_2)_{1.5S}$ and $(TiO_2/SiO_2)_{2.5S}$ were examined using UV-Visible spectroscopy, and the obtained results are shown in figure 6. The alternate arrangement of the multilayer structure endorsed a reflection window in the near-infrared region. According to reflectance studies, the monolayer of TiO_2 itself shows the opening of the reflection window in the near-infrared region, and further increases reflection with the increased number of stacks i.e. $(TiO_2/SiO_2)_{1.5s}$ and $(TiO_2/SiO_2)_{2.5s}$. The stacks of 1.5 and 2.5 demonstrated about 65 % and 100 % reflection in the near-infrared (NIR) spectrum with their centre wavelengths of 865 and 833 nm respectively. These kinds of coatings are useful for windows in the houses/offices and windshields in automotives as the thermal shields.

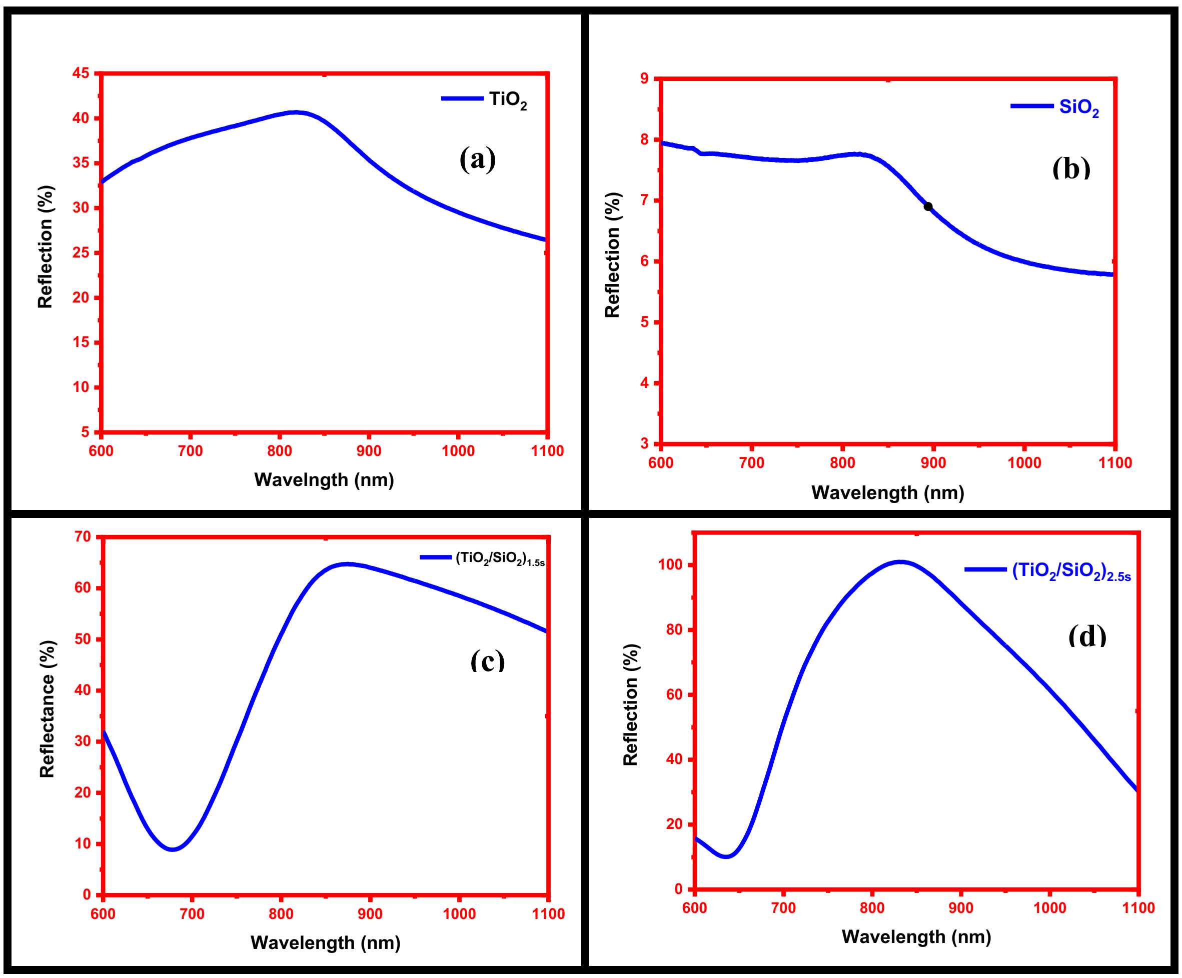

Fig. 6. Reflectance Spectra of TiO_2 (a), SiO_2 (b), multilayer $(TiO_2/SiO_2)_{1.5}$ (c) and $(TiO_2/SiO_2)_{2.5}$ (d).

Monolayers of TiO_2, SiO_2, and their multilayer structures based on 1.5 and 2.5 stacks of TiO_2/SiO_2 were examined for the contact angle to analyze the wetting behavior and presented in figure 7. Figure 7(a) of thin-film TiO_2 demonstrates the water contact angle of 16.6^o and found in good agreement with the work reported by Golobostanfard *et al.,* (2013). Similarly, the contact angle of single-layer SiO_2 and multilayers $(TiO_2/SiO_2)_{1.5s}$ and $(TiO_2/SiO_2)_{2.5s}$ were found to be 30.9^o, 23.4^{o,} and 29.3^o and shown in figure 7 (b), (c), and (d) respectively. The bar diagram shown in figure 8 represents the variation of contact angle with respect to various prepared samples. All these samples endorsed hydrophilic behavior and coincides with the reported works of Lee *et al.,* (2000) and Marcin *et al.,* (2006).

The multilayer structure $(TiO_2/SiO_2)_{1.5}$ has a top layer thickness of about 78.9 nm which resulted in the contact angle of 23.4^O, whereas the multilayer structure $(TiO_2/SiO_2)_{2.5}$ having the top layer thickness of about 64.8 nm endorsed the contact angle of 29.3^O, this conveys that the thicker TiO_2 films have a lower water contact angle and this result was found in goo-matching with the reported work of Zhang *et al.,* (2006). The increase in the contact angle value of the multilayer structure $(TiO_2/SiO_2)_{2.5}$ can also be noticed and can be attributed to the cracks on the TiO_2 surface as reported by Han *et al.,* (2012).

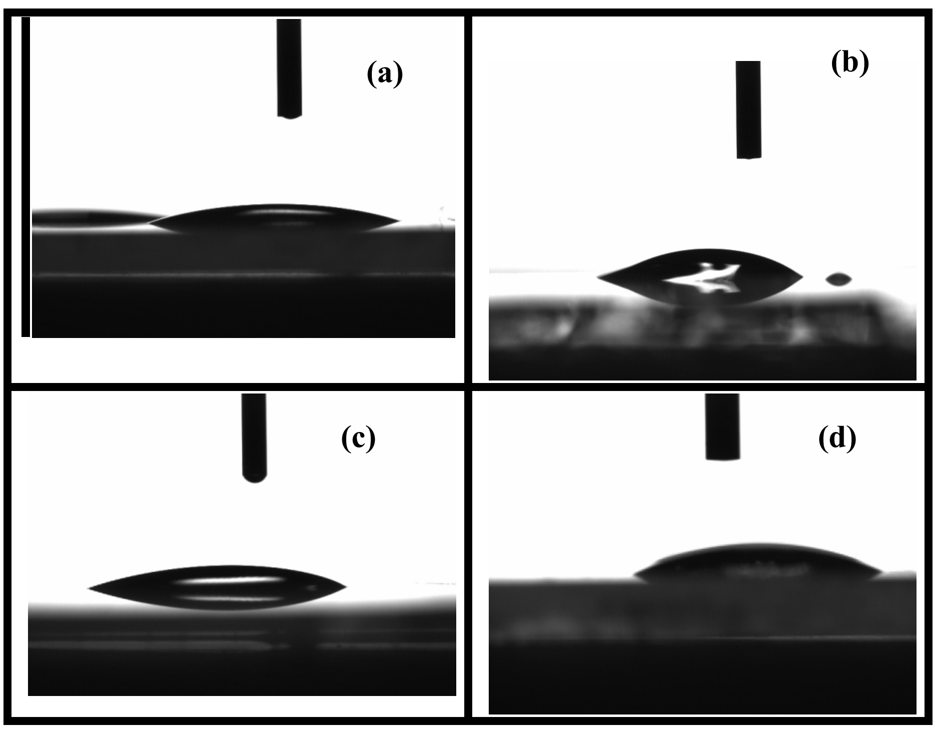

Fig. 7. Contact angle analysis of the monolayers of TiO_2 (a), SiO_2 (b), multilayer structures $(TiO_2/SiO_2)_{1.5}$ (c) and $(TiO_2/SiO_2)_{2.5}$ (d).

Further, the amorphous nature of the SiO_2 also induces more nucleation sites on the strongest anatase peak of TiO_2, for which the crystallite size tends to decrease and forth more, resulting in the effective change in contact angle. Thus, the hydrophilic nature obtained for these films suggest their application in windshields for their self-cleaning and anti-fogging ability. Due to the low contact angle, the water droplets tend to spread quickly on the surface, making the surface anti-fogging and self-cleaning.

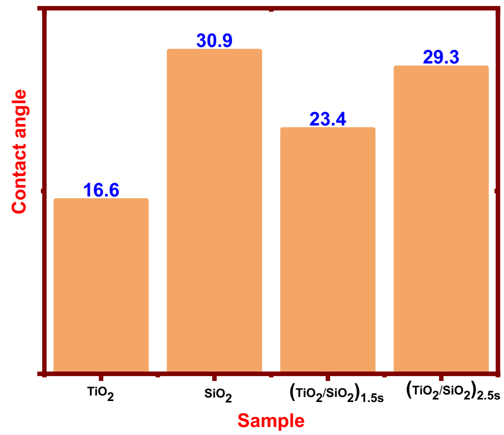

Fig. 8. Bar diagram of contact angle variation of monolayers of TiO_2, (a), SiO_2 (b), multilayer structures $(TiO_2/SiO_2)_{1.5s}$ (c) and $(TiO_2/SiO_2)_{2.5s}$ (d).

4. Conclusions

Monolayer and multilayer structures of TiO_2 and SiO_2 were spin-coated with their respective sol-gel synthesized solutions on the plain glass substrates. XRD investigations endorsed the anatase and amorphous phases of titania and silica films, respectively. The refractive index values were 2.66 and 1.5, corresponding to the of titania and silica films, as confirmed by the ellipsometry measurement. The FESEM investigations endorsed the formation of a multilayer structure consisting of bright and dark bands corresponding to the TiO_2 and SiO_2 films. The near-infrared reflectance of the multilayer structure was observed at its center wavelength of 833 nm. The prepared mono and multilayer structures of TiO_2 and SiO_2 were tested for the wetting behavior, which evidenced their hydrophilic activity. Finally, these reflectors exhibited the reflectance window in the near-infrared region, suggesting potential applications in houses/offices/hospitals and wind shielding in automotive for self-cleaning.

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