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ABSTRACT

In this work, we have adopted a sol-gel spin-coating technique and prepared alternative TiO$_2$/Si$_3$N$_4$ multilayers on glass substrates. These alternating layers of TiO$_2$/Si$_3$N$_4$ thin film samples were calcinated at two different temperatures and studied for their optical performance. The optical properties of fabricated thin films were investigated by UV-Visible spectrophotometer, X-ray diffractometer (XRD), Fourier transform infrared (FTIR), and Raman spectroscopy. UV-visible spectra showed broader and higher optical reflectance in the visible spectral region. FTIR transmission spectra show Ti-O-Ti and Si-N stretching modes at around 600 and 881 cm$^{-1}$. XRD pattern confirmed the presence of anatase-TiO$_2$ and α-Si$_3$N$_4$ phases. Finally, Raman spectra revealed the presence of anatase-TiO$_2$ and N-Si vibration modes.

Keywords: Sol-gel, Multilayers, Thin film, Calcination, FTIR, Anatase

INTRODUCTION

Nowadays, metal and semiconductor compounds (oxides and nitrides) are plays a major role in various microelectronics and nanotechnology-based devices. Titanium dioxide (TiO$_2$) is recognized as a fascinating material in various applications, for example, dye-sensitized solar cells, self-cleaning, photocatalytic, etc. TiO$_2$ also known as Titania is a metal oxide, which is interesting due to its mechanical, thermal, optical (wider bandgap), and chemical properties. Sol-gel spin coating, dip-coating, hydrothermal, solvothermal, electron beam evaporation, chemical vapor deposition, and ion-sputtering methods are employed for obtaining TiO$_2$ nanostructures. TiO$_2$ depends on its crystalline phases like rutile, anatase, and Brookite. Similarly, silicon nitride has higher oxidation, corrosion resistance, thermal stability, and constant dielectric material. It has been prepared by different methods like plasma enhanced chemical vapor deposition (PECVD), RF sputtering, atomic layer deposition, sol-gel, magnetron sputtering etc. Among various methods, TiO$_2$/Si$_3$N$_4$ multilayers are fabricated by the sol-gel spin coating method. Pasternak and Paz (2018) investigated silicon nitride (Si$_3$N$_4$) deposition on glass by low-temperature plasma-assisted direct bonding. The bonding mechanism between glass and Si$_3$N$_4$ was studied using various measurement techniques such as X-ray photoelectron spectroscopy, attenuated total reflection Fourier transform infrared, contact angle (ᵒC), and high-resolution transmission electron microscopy. They have shown the high-quality activated surfaces between the air (based on humidity) and glass substrates. These obtained results revealed a better bonding with plasma nitrogen. Iwahashi et al. (2015) experimentally prepared Si$_3$N$_4$ thin film on a silicon substrate at 750, 800, and 800 ᵒC deposition temperatures by chemical vapor deposition (CVD) for photovoltaic (PV) applications. They demonstrate increased Si$_3$N$_4$ refractive index (n) and film thickness (t) concerning the deposition temperature. Fourier transform infrared (FTIR) spectra showed Si-N-Si stretching mode at 917 cm$^{-1}$ and optimal reflectance of silicon nitride film at 800°C confirmed its appropriateness as an anti-reflection coating (ARC) layer of solar cells. Ferre et al. (2016) investigated better optical and thermal properties of
SiO$_2$, Si$_3$N$_4$, and TiO$_2$ dielectric thin film using plasma-enhanced chemical vapor deposition and MATLAB software engine for quantum cascade laser used as passivation layer applications. The refractive indices ($n_1$ and $n_2$), extinction coefficient (k), thermal resistance, and modal losses of passivation layers were calculated by Mueller ellipsometry and optical simulations. The optical and thermal properties of SiO$_2$ and TiO$_2$ (or Si$_3$N$_4$) thin-film are shows their best performance at shorter and longer (8.3 or 8.5μm) wavelengths. They found the impact of dielectric, and thermal conductivities and showed their good laser performance.

Among these methods, the sol-gel spin-coating process is a suitable and conventional method for the formation of TiO$_2$/Si$_3$N$_4$ thin film, which involves initial hydrolysis, condensation, and rapid gel formation.

![Fig.-1: The Block Diagram of Synthesis and Deposition Procedural Steps of TiO$_2$/Si$_3$N$_4$ thin films](image)

**EXPERIMENTAL**

**Materials and Methods**

Hexamethyldisiloxane (HMDSO, C$_6$H$_{18}$OSi$_2$), ethanol (C$_2$H$_5$OH), acetic acid (C$_2$H$_4$O$_2$), nitric acid (HNO$_3$), ammonium persulphate ((NH$_4$)$_2$S$_2$O$_8$), acetone (C$_3$H$_6$O), hydrochloric acid (HCl), and titanium isopropoxide (TTIP, Ti(OCH(CH$_3$)$_2$)$_4$). All the chemicals were used without any purification.

**Sol-gel Synthesis and Preparation**

The procedural steps of Si$_3$N$_4$ and TiO$_2$ thin film coated on glass substrates by sol-gel spin-coating deposition techniques as shown in Fig.-1. Initially, the homogeneous and transparent solutions were prepared by using ethanol, HMDSO, acetic acid, and nitric acid solutions mixed with a 2:2:1:1 ratio. During the sol-gel process, each step maintained 5 minutes interval under constant magnetic stirring. Next, 70 mg of ammonium persulphate was added and stirred for 90 minutes. Finally, the silicon nitride solution prepared and noticed a smaller amount of white colour precipitate powder was formed. Titanium isopropoxide (TTIP) was used as a titanium precursor. Next, TTIP (0.75 ml) was dissolved in solvent 10ml of ethanol with constant stirring at room temperature. Further, the chelating agent of acetic acid
(0.5ml) and catalyst hydrochloric acid (0.25ml) was added drop wise. After, one hour of stirring the homogeneous and transparent solution is obtained. Deionised (DI) water, acetone, and ethanol y focused for the cleaning glass substrate by ultra-sonicator. After the cleaning process, alternative TiO$_2$/Si$_3$N$_4$ thin film coating is made on glass substrates using the spin-coating process. The duration of the deposition process was 30 seconds at 3000 rpm and kept calcination temperatures were 100°C (named ‘Sample-A1’) and 500°C (named as ‘Sample-A7’). The two alternative layers of TiO$_2$ and Si$_3$N$_4$ thin films are known as a stack. Initially, sample 1 (A1) maintained the calcination temperature at 100°C (45 minutes) after every stack by the hot air oven. Overall, 5.5 stacks were deposited on glass and 500°C calcined at 20 minutes by a muffle furnace. Next, Sample 2 (A7) included 6.5 stacks, and each stack was calcined at 500°C at 20 minutes.

Characterization

After the deposition, the calcined thin film samples were tested for their optical properties by UV-Visible spectrophotometer (Shimadzu, Japan) used for the reflectance, Fourier transform infrared spectroscopy (Perkin Elmer, Spectrum 2, USA) used for the chemical composition, or molecular analysis carried out using ZnSe discs between the regions of 400-4000 cm$^{-1}$. X-ray diffractometer (X-Pert Pro, UK) recorded a diffraction pattern with CuK$_\alpha$ radiation ($\lambda$=1.54060). Finally, chemical and molecular structure analyses have been done through Raman spectroscopy (Micro, USA) techniques.

RESULTS AND DISCUSSION

The functional group, crystallite size, and reflectivity of fabricated TiO$_2$/Si$_3$N$_4$ thin films with different calcination temperatures were investigated. First, basic FTIR spectroscopy was used to demonstrate the presence of molecular or chemical bonding in alternative TiO$_2$ and Si$_3$N$_4$ nanostructures. Figure-2 represents the FTIR transmittance (%) spectra in the range from 400 to 4000 cm$^{-1}$.

![Fig. -2: FTIR Spectra of Alternative TiO$_2$/Si$_3$N$_4$ Multilayers](image)

The transmittance bands from 400 to 800 cm$^{-1}$ are attributed to the Ti-O or Ti-O-Ti bonds. The peaks at 625, 689, 794 (Sample A1), and 617 (Sample A7) are associated with Ti-O vibration modes in TiO$_2$ nanostructures. Both spectra showed the bending and stretching vibration modes of Si-N at 881 cm$^{-1}$. Also, a transmittance band of 1457(A1), 1635 (A1), 1377 (A7), and 1506 cm$^{-1}$ (A7) was assigned to an O-H bending vibration. The strong transmittance band appeared at 3065 (A1), and 3041 cm$^{-1}$ (A7) depicting TiO$_2$ nanostructures. Further, the broader bands have ascertained the wave number from 3200 to 4000 cm$^{-1}$.
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cm$^{-1}$ could be ascribed the absorbed to a water molecule in the TiO$_2$ surface.\textsuperscript{17,18} The crystalline nature and crystallographic orientation of prepared alternative layers of TiO$_2$/Si$_3$N$_4$ were characterized by the XRD technique using copper K$\alpha$ (1.54060 Å) radiation.

Both XRD patterns of thin films were shown nearly the same intensities with the sharp and strong peaks depicting well the crystalline nature of the thin film (Fig.-3). The peaks at 2$\theta$=23.7, 38.55, and 48.7$^\circ$ are $\alpha$-Si$_3$N$_4$ and have consistent with the standard JCPDS No. 09-0250.\textsuperscript{11,19} The crystallite sizes (D) are 16.65 (A1), and 19.98 nm (A7) calculated Using Debye-Scherrer’s formula,

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

Where ‘D’ is the crystalline size, ‘$\lambda$’ is the incident wavelength, ‘0.9’ is the characteristic of an object, $\beta$ is full-width half-maximum (FWHM), and the diffraction angle ($\theta^\circ$).\textsuperscript{1,20,21} Table-1 shows the intense peak position, FWHM, and crystallite size (nm). The reduced crystalline nature was noticed from the A1 sample with 5.5 stacks of TiO$_2$/Si$_3$N$_4$. This indicates the crystallite size of thin films was increased at higher calcination temperatures due to the aggregation of crystallites leading to size and less surface area as reported by Phromma \textit{et al.} (2020).\textsuperscript{22} This improved crystalline was attributed to the thermally promoted crystalline growth. The reflectance spectra of the TiO$_2$/Si$_3$N$_4$ alternative layers (A1- 5.5 stacks and A7- 6.5 stacks) are shown in Fig.-4. With the effect of reduced alternative layers (or temperatures) the highest reflectance was achieved and shifted towards a longer wavelength (650 to 980 nm) region. But the broader band gap exhibits the highest number of multilayers (A7), and intensity decreased concerning the calcination temperature. Furthermore, the study of micro-Raman microscopic operating at 785 nm incident wavelength (source) and Raman scattering was noticed. The Raman spectra of the prepared materials are shown in Fig.-5.

| Sample       | 2$\theta$ (Degree) | FWHM  | D (nm) |
|--------------|--------------------|-------|--------|
| A1 (5.5 stacks) | 25.8742$^\circ$ | 0.4896$^\circ$ | 16.65 |
| A7 (6.5 stacks)  | 25.8362$^\circ$ | 0.4080$^\circ$ | 19.98 |

It indicates the Raman peaks of four different points (394, 571, 669, and 1364 cm$^{-1}$) noticed and intensities are nearly changed. The peaks of silicon nitride (Si$_3$N$_4$) positioned at 392 cm$^{-1}$ were reported by \textit{Fu et al.} (2014).\textsuperscript{23} In Raman spectra, the peaks below 400 cm$^{-1}$ are attributed to the vibration modes of the N(SiN)$_3$. The intermediate frequency peaks among 400-700 cm$^{-1}$ ascribed NSi$_3$ with the D$_{3h}$ symmetry from N(SiN)$_3$. Raman peaks at 700 cm$^{-1}$ correspond to the NSi$_3$ vibration.\textsuperscript{23} From the reported
works, the peak at 669 cm\(^{-1}\) vibration mode shifted towards a higher wave number which is corresponding to the anatase-TiO\(_2\) phase (Eg). These changes could be the presence of N\(^3\)-ions and modified the vibration modes of anatase-TiO\(_2\).\(^{24}\)

![UV-Visible Spectra of Alternative TiO\(_2\)/Si\(_3\)N\(_4\) Stacks](image)

**Fig.-4: UV-Visible Spectra of Alternative TiO\(_2\)/Si\(_3\)N\(_4\) Stacks**

The highest and broader peak noticed from 1000 to 2000 cm\(^{-1}\) may be assigned as the Si-N phase. Similarly, Si-N bond vibration presented a range between 700-100 cm\(^{-1}\) as demonstrated by Bandet et al. (1999).\(^{25}\) The Raman spectra intensity shows enhanced Si-N bond length due to the calcination temperature.

**CONCLUSION**

This experimental work demonstrated the synthesis and fabrication of alternative TiO\(_2\)/Si\(_3\)N\(_4\) thin film multilayer using sol-gel spin-coating techniques. The UV-visible spectrum showed a higher reflectance in the visible and near-infrared spectral range, and the FTIR transmittance spectra confirmed the vibration modes of Ti-O (400-800 cm\(^{-1}\)) and Si-N (881 cm\(^{-1}\)). Further, the XRD results revealed the presence of anatase-TiO\(_2\) and α-Si\(_3\)N\(_4\) crystalline phases and calculated the crystallite sizes are 16.65 (5.5 stacks), and 19.98 (6.5 stacks). In Raman spectra, the stretching (or vibration) modes of the Si-N bond length increased concerning the calcination temperature. Further, the optimization process will be carried out for better optical properties.

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