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# Deposition of silicon nitride films using chemical vapor deposition for photovoltaic applications

K. Jhansirani [a], R.S. Dubey [a,*], M.A. More [b], Shyam Singh [c]

[a] Advanced Research Laboratory for Nanomaterials and Devices, Department of Nanotechnology, Swarnandhra College of Engineering and Technology, Seetharampuram, Narsapur (A.P.), India

[b] Center for Advanced Studies in Materials Science and Condensed Matter Physics, Department of Physics, University of Pune, (M.S.), India

[c] Department of Physics, University of Namibia, Windhoek, Namibia

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ABSTRACT

Silicon nitride is a versatile material since many decades due to its compatibility with conventional fabrication technology. Other than its potential applications in microelectronics, this material has been regarded as an antireflection coating in solar cells. In this paper, we present the fabrication and characterization of silicon nitride ($Si_3N_4$) films deposited at 750, 800 and 850 °C using atmospheric chemical vapor deposition. We have investigated the effect of deposition temperature on the physical and optical properties of the prepared films. The refractive index and film thickness were found to be increased in accordance with an increase in the deposition temperature. Fourier transform infrared (FTIR) spectroscopy analysis showed the Si–N–Si stretching peak at 917 $cm^{-1}$ further, the full width at half maxima and Si–N–Si peak position showed their dependency on the deposition temperature. Finally, the optimal reflectance was observed through $Si_3N_4$ film deposited at temperature 800 °C which confirms its suitability as an antireflection coating.

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## Introduction

Thin dielectric films have been demanded for their potential applications in microelectronics and optoelectronics. Among dielectric films such as silicon dioxide, titanium dioxide etc., silicon nitride ($Si_3N_4$) is one of the significant materials and well recognized to its promising applications in integrated circuits and optical devices. For example, silicon nitride films have got wide applications as passivation insulating layer, interlayer dielectric, capacitor dielectric etc. The properties of silicon nitride films can be tuned by controlling the various process parameters such as deposition time, deposition temperature, pressure, reactants flow rate and substrate temperature during the fabrication. For the deposition of thin films, chemical vapor deposition method is a good choice and used since several years. During the growth of thin film, the preferred precursor in the form of vapors are needed to be transported into the reaction chamber where a substrate is kept to a desired temperature which enables the reactive gas molecules to decompose onto the substrate and yields film deposition. Depending upon the experimental procedures, the deposited film may be in amorphous or polycrystalline in nature.

Several workers have reported on the deposition and characterization of silicon nitride films. Scardera et al. have reported the Fourier transform infrared spectroscopy (FTIR) study of silicon-rich silicon nitride thin films. They have investigated the correlation between bonding changes at high-temperature and reported the formation of silicon nanocrystals. The post heated film showed a FTIR peak from 1000–1100 $cm^{-1}$ which has been attributed to the increased bonding with the formation of silicon nanocrystal precipitates. The enhanced FTIR peak intensity of Si–N symmetric stretching mode was found to be dependent on the large nitrogen bond formation [1]. Ding et al. have prepared the silicon nitride film deposited by plasma-enhanced chemical vapor deposition. The post heat treatment to the erbium doped silicon nitride film showed a strong visible and infrared photoluminescence peaks correspond to the silicon nanocluster and interface state [2]. Tijanic et al. have carried out the study of low temperature deposited silicon nitride films prepared by low pressure chemical vapor deposition technique. The thickness of the deposited films was found to be dependent on the various process parameters and showed a variation in the Si–N stretching peak intensity [3]. Khemasiri et al. investigated the composition, morphology, corrosion resistance and the hardness properties of the silicon nitride films as a function of gas timing ratio. The corrosion resistant was observed due to the formation of passivating oxide layer. However, hardness

* Corresponding author.
*E-mail address:* rag_pcw@yahoo.co.in (R.S. Dubey).

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measurement showed similar results with the nitrogen gas flow time. The proposed gas flow timing technique could show the enhanced hardness of the film as comparison to the existing gas mixing techniques. With this approach, the controlled deposition of silicon nitride films for very large scale integration (VLSI) applications was explored [4]. Masuda et al. have investigated the coating, passivation and insulating properties of silicon nitride films and claimed the suitability of the deposited films for electronic applications. The deposited films showed dense and high barrier properties at the temperature below 100 °C [5]. Xiao et al. reported the plasma-enhanced deposition of silicon nitride coatings by using hexamethyldisiloxane and ammonia. The prepared films were found mechanically hard and optical transparent with corrosion-resistant. The growth rate was maintained to 0.5 μm/min and it was further increased in accordance with the applied microwave power and decreased with the large gas flow ratio of $NH_3$/HMDSO [6]. Molinari et al. have investigated the photoluminescence properties of a-$SiN_x$:H films with various precursor compositions. FTIR analysis showed the basic peaks whereas the hydrogen involvement could yield enhanced photoluminescence intensity from the a-$SiN_x$:H films. To prevent the non-radiative defects and the passivation of silicon dangling bonds, the incorporation of hydrogen was observed to be significant [7].

Worldwide the scarcity of power is one of the prime issues and therefore, the research on non-conventional energy sources has been intensively focused. Today also, silicon is the most demanding material used in the manufacturing of solar cells. However, mirror polished silicon is having ~36% optical losses due to the surface reflections [8,9]. To address this issue, surface texturing has been explored which could reduce this loss up to about 30% only. In this situation, antireflection coating at the top of the solar cell is a solution through which the molding of light is possible. The property of the antireflection coating can be tuned to have low surface reflection or high transmission through that surface. To possess the antireflection feature, the electromagnetic waves must be out of 180° to support the destructive interference of the incident light onto the antireflection film surface. This destructive inference can be assured if the optical thickness of the antireflection coating is one-quarter of the center wavelength. For silicon solar cells, silicon nitride film is a promising material for the antireflective coating as its refractive index can be tuned in-between 1.7 and 2.0. Among various fabrication techniques of silicon nitride films, chemical vapor deposition and sputtering are the most preferred methods for antireflective coating. For chemical vapor deposition of silicon-based thin films, organosilicon precursors such as hexamethyldisiloxane (HMDSO), hexamethyldisilazane (HMDSN) and diacetoxy-di-t-butoxysilane (DADBS) or tetraethoxysilane (TEOS) have been investigated. All these provide the controlled chemisorption of the precursors and yield quality film with good step coverage [5–7,10,11]. As these precursors are available in the liquid, so easily can be vaporized using a bubbler at ambient temperature. Iwahashi et al. have prepared the antireflection coating film of silicon nitride film at the top of solar cell and investigated the photovoltaic performance. They could reduce the reflectivity ~1.6% as a result the 2% gain in cell efficiency was achieved [12]. Kim et al. have studied the performance of the solar cell using silicon nitride film as an antireflection coating for the reduction of the surface reflections. The optimized deposition of silicon nitride film could yield 17% conversion efficiency [13]. Patil et al. have reported the deposition of silicon nitride films using e-beam evaporation and explored the feasibility as an antireflective coating. They could observe minimum reflectance at 547 nm wavelength which was validated with quarter wavelength theory [14].

In this work, we present the deposition and characterization of silicon nitride films prepared at different temperatures. The optimized deposition parameters could produce defect free films to be useful as an antireflection coating in solar cells. Section 'Experimental details' describes the materials and method used for the fabrication of the $Si_3N_4$ films. The characterized results have been discussed in Section 'Results & discussion' . Finally, Section 'Conclusions' presents the summary of the paper.

## Experimental details

### *Materials*

Silicon nitride ($Si_3N_4$) films were deposited onto the P-type silicon wafer of ⟨1 0 0⟩ orientation supplied by University wafers, USA. Hexamethyldisiloxane (HMDSO) supplied by Sigma-Aldrich was used as the source of silicon whereas ammonia gas with 99.999% purity was preferred as the source of nitrogen. The precursor HMDSO was filled in a stainless steel bubbler and ultra-pure argon gas was used as the carrier gas.

### *Method*

For the deposition of silicon nitride films, an indigenously developed atmospheric chemical vapor deposition (APCVD) system was used and described elsewhere [15]. Fig. 1 shows the schematic diagram of APCVD. The mass flow controllers (MFCs) are connected to the ammonia, oxygen and nitrogen/argon gas cylinders where V/NV represents the open/close valves/needle valves. A pressure gauge is connected to read the pressure inside the quartz tube during the process. However, in the present work the deposition was carried out at the atmospheric pressure. For the deposition, P-type silicon substrates were used after rinsing in de-ionized water followed by heating separately in trichloroethylene, methanol, and acetone for 10 min and then was dried in the presence of nitrogen gas flow. The flow rates of ammonia and HMDSO were maintained to 80 and 40 SSCM respectively. The deposition time 15 min was maintained for the silicon nitride films deposited at temperature 750, 800 and 850 °C.

After deposition, the prepared films were characterized for the refractive index and thickness measurements by Filmetric (F20), elemental quantitative analysis by Fourier transform infrared spectroscopy FTIR (8400-Shimadzu), surface morphology by Scanning electron microscopy (SEM-JSM-6360) and reflectance by UV–VIS spectrophotometer (UV-1800, Shimadzu).

## Results & discussion

There are three samples of $Si_3N_4$ films were grown at deposition temperature 750, 800 and 850 °C. Fig. 2 depicts the refractive index of the $Si_3N_4$ films which increases as the deposition temperature rises.

The deposition at high temperature variation yields densified growth of the film. Smith et al. have experimentally presented a mechanism of $SiN_xH_y$ deposition using NH-$SiH_4$ and concluded that the elemental composition of hydrogen and excess nitrogen was reduced at the high deposition temperature which could enhance the mass density of the film and hence, an increment in the refractive index of the $Si_3N_4$ film was noticed [16]. Bengi et al. have performed the low-temperature plasma deposition of silicon nitride film and found that the film composition was dependent on the active nitrogen flux released on the substrate and found responsible for the nitridation rate of Si–Si bonds. The nitrogen flux and nitridation rate were controlled by increasing power/decreasing the pressure as a result less SiH bonds were observed [17]. Rocheleau et al. have reported the densification of silicon nitride films by hydrogen dilution which has affected the silicon/nitrogen ratio. This has decreased the stoichiometric and relative

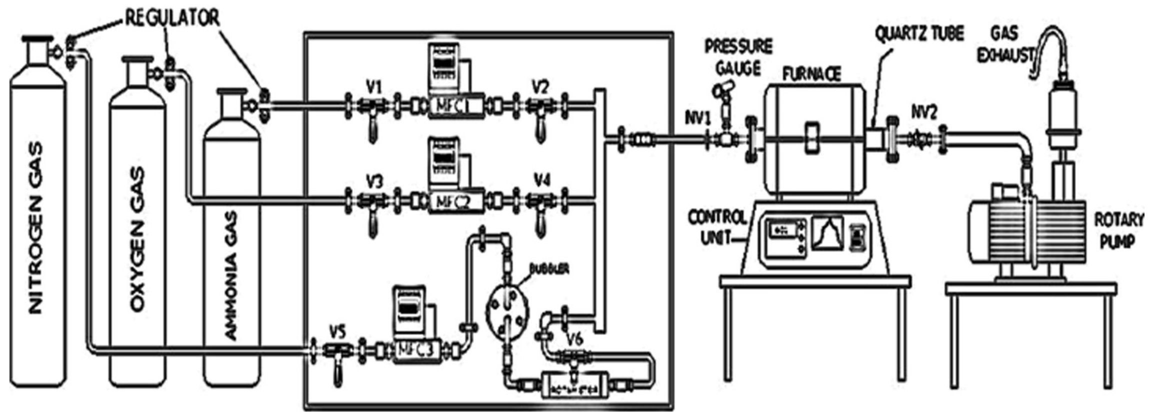


**Fig. 1.** Schematic diagram of the chemical vapor deposition system.

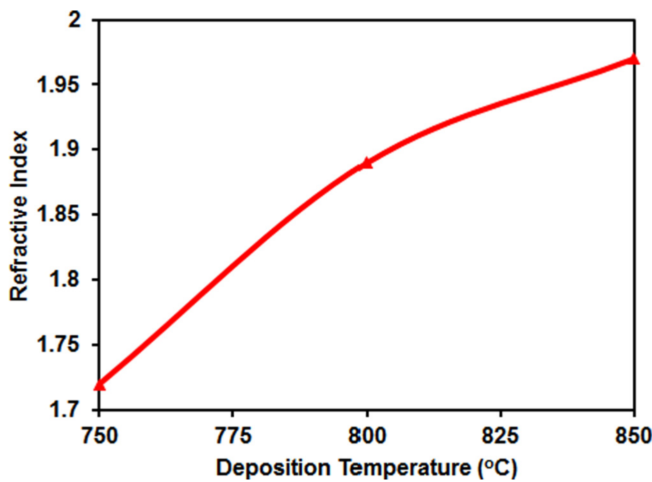


**Fig. 2.** Refractive index of $Si_3N_4$ films as a function of deposition temperature.

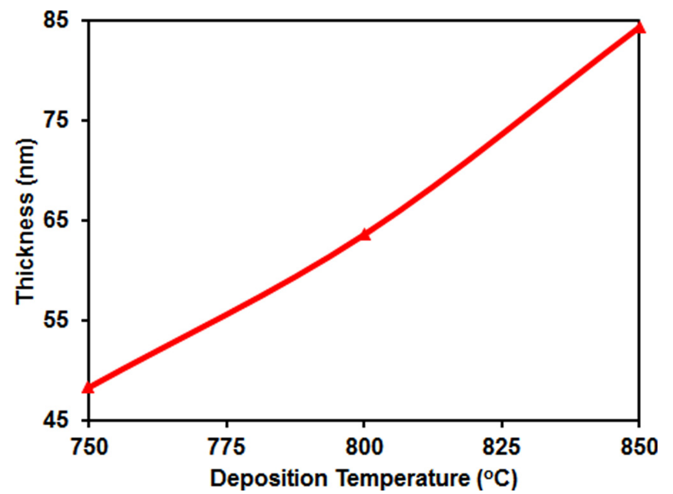


**Fig. 3.** Thickness of $Si_3N_4$ films as a function of deposition temperature.

variation in the hydrogen bonding mechanism. Such variations were related to the bulk film density and observed to be associated with Si–N bond density [18]. In similar work, Pandey et al. have presented the growth and characterization of silicon nitride films deposited by thermal chemical vapor deposition. They have observed a similar trend of hydrogen and excess nitrogen decrement for a range of deposition temperature and further found increased at high-temperature deposition. An increased H-content was responsible for the more N–H and less Si–H bond densities. The densified $Si_3N_4$ film was consistent with more Si–N bond density as a result of less H-bonding during the growth and therefore, enhanced refractive index has been attributed to the less Si–H bond density and more Si-content [19].

Fig. 3 shows the thickness variation of $Si_3N_4$ films in accordance with the deposition temperature. The thicknesses of the films were found to be increased with respect to the deposition temperature. In comparison to the other process parameters, the deposition temperature has its significant role as it affects the undergoing chemical reaction in the deposition chamber and ultimately the growth of the film. This happens due to H desorption after the reaction rate limit of the growth during the insertion of radicals which originated due to the thermal dissociation upon the deposition temperature and contributed to the growth rate of the film [18].

With 4 $cm^{-1}$ spectrum resolution, the Fourier transform infrared (FTIR) measurement of $Si_3N_4$ films deposited at various temperatures was performed. Fig. 4 depicts the FTIR absorption spectra of the $Si_3N_4$ film prepared at 800 °C. For the resolution, the spectral region was magnified from 400–1200 $cm^{-1}$ and there are four absorption peaks exhibit. The peak at 917 $cm^{-1}$ has been attributed to the Si–N–Si stretching mode. As reported, Si–N–Si stretching mode peak exists in between 900 and 922 $cm^{-1}$ [7,14,18,19]. A weak absorption peak at 450 $cm^{-1}$ corresponds to the Si–N stretching while a N–H bending peak is also observed at

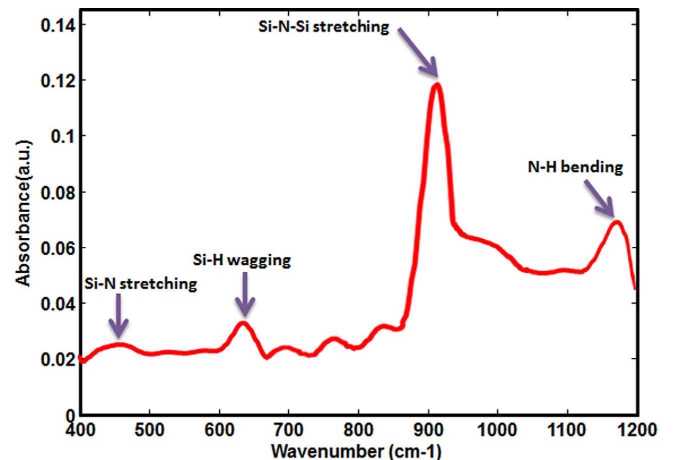


**Fig. 4.** FTIR absorption spectra of $Si_3N_4$ film at deposition temperature 800 °C.

1180 $cm^{-1}$ [20]. A wagging mode absorption peak has also been observed at 640 $cm^{-1}$ and the similar peak has also been reported [21].

Further, we have extended the analysis of Si–N–Si peak position with respect to the $Si_3N_4$ films deposited at 750, 800 and 850 °C and plotted in Fig. 5. The Si–N–Si peak position was found to be shifted from 942 to 881 $cm^{-1}$ as a function of deposition temperature. According to the literature, the Si–N–Si peak was found to be shifted from the higher value of wavenumber to a lower which is as a result of Si–N bonds formation in case of higher-temperature deposition [22]. In simple words, large numbers of Si–N bonds led to stoichiometric $Si_3N_4$ film composition.

The full width at half maximum (FWHM) is an essential factor to understand the structural order and existing chemicals distribution in the deposited films [23–25]. Fig. 6 depicts the full width at half maxima (FWHM) of Si-N-Si stretching peaks of various $Si_3N_4$ films prepared at 750, 800 and 850 °C. The FWHM increases as the deposition temperature is raised and this behavior confirms the quality of the deposited films. It is important to note that during the $Si_3N_4$ film growth hydrogen adds in as N–H and Si–H however, the elimination of hydrogen is possible by the dissociation of nitrogen and silicon bonds at high deposition temperature or annealing [26,27].

Fig. 7 depicts the scanning electron microscopy image of the $Si_3N_4$ film deposited at 800 °C with the magnification of 30 K. The SEM image represents the uniform deposition of the film with no pinhole or defect into the deposited $Si_3N_4$ film.

Fig. 8 shows the typical reflectance of the $Si_3N_4$ film prepared at 800 °C. The minimum reflection ~16% was observed at wavelength 482 nm. As the thumb of rule, the optical thickness and refractive index of an antireflection coating must satisfy: $d = \lambda_c/4n_{arc}$ and $n_{arc} = \sqrt{n_m n_{Si}}$ where $\lambda_c$, $n_{arc}$, $n_m$ and $n_{Si}$ are the center wavelength, refractive index of the antireflection layer, surrounding medium and silicon respectively. If we assume $n_{Si} = 3.5$ and $n_m = 1$ then we can calculate $n_{arc} = 1.87$ and this value is matched with our filmetric measured value i.e. 1.87 [28]. Let us consider that the center wavelength is 482 nm as shown in above figure then we can an calculate the thickness as $d = 482/4 \times 1.91 = 64.4$ nm and this value nearly coincides with our measured value i.e. 63.6 nm. The deposited layer of $Si_3N_4$ film satisfies the quarter wavelength theory due to its low reflectance at the center wavelength and would be useful for antireflective coating of the solar cell.

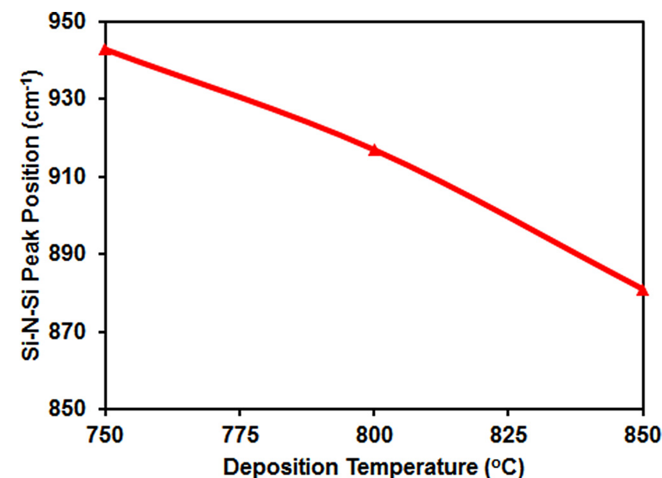


**Fig. 5.** Si–N–Si stretching peak position of $Si_3N_4$ films as a function of deposition temperature.

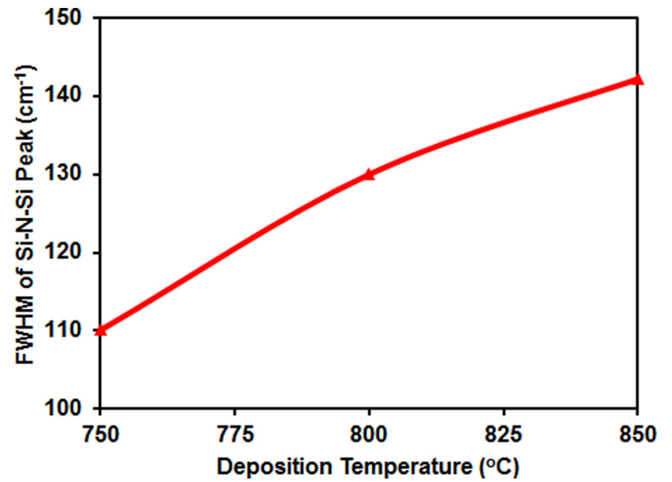


**Fig. 6.** FWHM of Si–N–Si stretching peak of $Si_3N_4$ films as a function of deposition temperature.

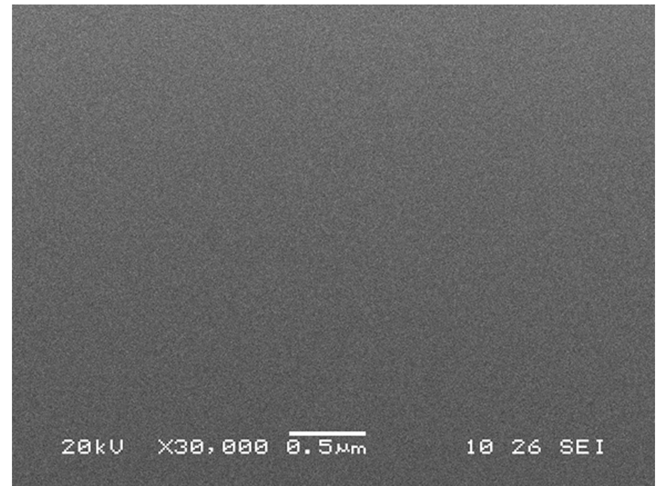


**Fig. 7.** Scanning electron microscopy image of $Si_3N_4$ film deposited at temperature 800 °C.

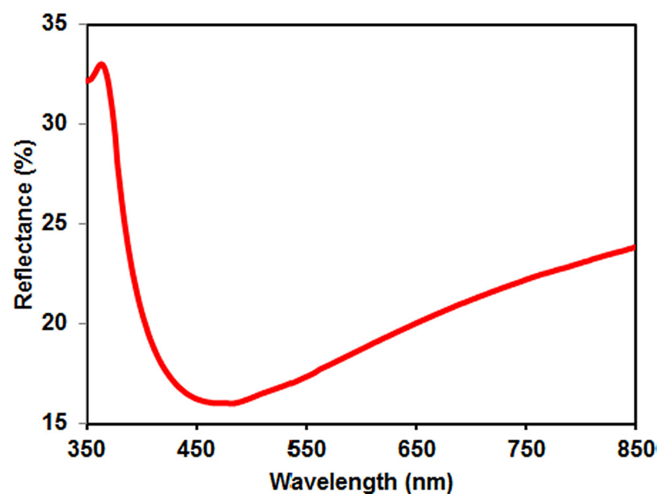


**Fig. 8.** Reflectance of silicon nitride film deposited at temperature 800 °C.

## Conclusions

Using APCVD, silicon nitride films were grown at three different temperatures 750, 800 and 850 °C. The filmetric study showed an increase in refractive index and film thickness as the deposition temperature is increased. At high deposition temperature, the mass density of the film was enhanced due to the possible reduction of the elemental composition of hydrogen and excess nitrogen which resulted in an enhancement of refractive index of the $Si_3N_4$ films. FTIR measurement exhibited various absorption peaks corresponding to the N–H bending at 1180 $cm^{-1}$, Si–N–Si stretching at 917 $cm^{-1}$, Si–N stretching at 450 $cm^{-1}$, and wagging peak at 640 $cm^{-1}$. The shift in the Si–N–Si stretching mode from 942 to 881 $cm^{-1}$ was observed as a function of deposition temperature. An exponential shifting of Si–N–Si peak from higher to lower value of wavenumber represents the Si–N bonds formation. The full width at half maxima of Si–N–Si was found to be increased with respect to an increase in the deposition temperature which ultimately yields the quality film. The experimental and calculated optical thickness of the silicon nitride film prepared at 800 °C was validated according to the quarter wavelength theory. The reflectance study of silicon nitride film deposited at 800 °C showed low reflection at wavelength 482 nm which indicates its potential application as an antireflection coating in solar cells.

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