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Deposition and characterization of silicon nitride films using HMDS for photonics applications

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The silicon nitride (SiN_x) films were deposited using thermal CVD system with organic precursor hexamethyldisilazane (HMDS) and ammonia (NH_3) gas as a source of silicon and nitrogen respectively. The optical and physical properties of the deposited silicon nitride films have been investigated with the variation in deposition temperature in the range of 775 to 850 ^{0}C. The deposited SiN_x films were characterized using Ellipsometry, Fourier Transform Infrared (FTIR) Spectroscopy and Scanning Electron Microscopy (SEM-JSM-6360). The refractive index of the deposited films increases while stress found to be decrease with corresponding increase in deposition temperature. The peak position of Si–N-Si stretching vibration move towards lower wave number while FWHM increases with increase in the deposition temperature. The peak intensity of Si-H and N-H stretching peaks found to be reduced with increase in deposition temperature. The total H and Si-H concentration rapidly decreases with increase in deposition temperature. It signifies an improvement in the quality of the deposited films. These deposited silicon nitride films exhibit a very well controlled refractive index in the range of 1.76 –2.1, which is very attractive for the application of silicon nitride films in photonic wave-guides devices.

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1. Introduction

Silicon microphotonics became the major thrust in the field of design and development of silicon-based photonics devices [1-2]. They provide efficient data transfer with minimum loss at low cost as compare to conventional optoelectronics devices. The term microphotonics is optical equivalent to microelectronics, where light is communicated and manipulated at the sub-micrometer length scale. In recent years, all the silicon processing materials and tools are used to develop various kinds of photonic components. The optical wave-guides are one of the important components in silicon microphotonics, which used to channel the light signal in the system. The major obstacle in conventional materials wave-guide is the optical absorption losses, which occur in visible and infrared wavelength region. These losses can be minimized using the materials, which should have high refractive index and compatible with the conventional silicon technology.

The silicon nitride (SiN_x) material has found more suitable due to its high refractive index and minimum losses in interested wavelength region for the fabrication of photonics wave-guides. It has been extensively investigated because of its inherent advantages in the chemical, mechanical and optical properties. Silicon nitride has important applications in photonics devices such as optical wave-guides [3-4], optical microcavity [5-6], air-bridged photonic crystal slabs [7], antireflection (AR) coatings in solar cells [8] and in microelectronics as a gate insulator in thin film transistors. It is also used in nonvolatile memory devices because of its trapping ability. Accordingly, a considerable number of detailed investigations have been carried out on the deposition and characterization of silicon nitride films by employing a variety of techniques for over two decades.

Stoichiometric silicon nitride has prepared by direct nitridation of silicon [9], nitrogen ion implantation into silicon [10] or sputtering of silicon in a nitrogen ambient [11]. However, these methods produce a damaged silicon/silicon nitride interface. Chemical vapor deposition (CVD) processes such as APCVD, LPCVD and PECVD are the most common methods used in the semiconductor industry today. APCVD involves the reaction of silane and ammonia at atmospheric pressure and temperatures in the range 700–900 ^{0}C. LPCVD involves the reaction of dichlorosilane and ammonia at reduced pressure (0.01–1 Torr) and temperatures below 500 ^{0}C. The last process i.e. PECVD has great significance due to its low temperature processing which reduces the problems such as the minority carrier lifetime degradation, dopant redistribution and degradation of metallization schemes. However, PECVD grown silicon nitride films often contain large amount of hydrogen approximately 10-30 at.% [12], which alters the properties of silicon nitride films and causes the optical absorption losses in photonics wave-guides. Therefore, it's a major challenge to deposit silicon nitride films with optimized refractive index and reducing hydrogen contents.

In our previous work [13], we have demonstrated the deposition of silicon nitride films by using Thermal CVD system with DMDS (Dimethyl dichloro silane) and ammonia (NH_3). The deposited films were characterized by using Ellipsometry, Fourier Transform Spectroscopy, Scanning Electron Microscopy (SEM) and Energy Dispersive Analysis of X-rays (EDAX). The quality of the films was found to be very good. The silane (SiH_4) and ammonia (NH_3) gas mixture as the most common gas sources for the deposition of silicon nitride films using plasma enhanced CVD [14-15]**.** Silane gas is explosive and toxic in nature, which generate the problems in handling. However, Kohshi Taguchi et al [16] has deposited the silicon nitride films with HMDS and nitrogen using radical-beam deposition technique. They have reported the deposition of high quality of silicon nitride films with very less amount of carbon without using hazardous silane.

To the best of our knowledge, an attempt has been made for the first time to deposit silicon nitride films using indigenously developed thermal CVD system [17] with organic precursor hexamethyldisilazane (HMDS) and ammonia (NH_3) gas to study and analyzed their optical and physical properties with variation in deposition temperature. HMDS makes the deposition process easier by eliminating need of toxic silane gas. HMDS has suitable vapor pressure for applications in CVD and widely used in semiconductor industry to improve photoresist adhesion to oxide layers.

The main emphasis has been given to optimize the refractive index as well as thickness with reduced H concentration, which are the most prominent for the fabrication of photonics wave-guides. Several series of growth experiments were performed for the different values of one parameter while controlling that the other parameters were kept constant. Deposited films were characterized using Ellipsometry, Fourier transform infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM).

Section 2 of the paper describes the experimental procedure used to deposit the silicon nitride films. The obtained results have been discussed in section 3. Finally, conclusions are highlighted in section 4 of the paper.

2. Experimental procedure

Silicon nitride films were deposited on a silicon monocrystal wafer <100>. Silicon substrates were cleaned before deposition by using hydrogen peroxide and sulphuric acid mixture, rinsed in deionized water and spin dried in nitrogen atmosphere. The organic precursor hexamethyldisilazane (HMDS) and the ammonia (NH_3) gas were used as source of silicon and nitrogen respectively. These gases were supplied to the CVD reactor in a controlled manner. The inert nitrogen gas has been used as a carrier to carry the HMDS in to the reactor chamber. A stainless steel bubbler is filled with HMDS chemical as a source of silicon. Usually, the incorporation of H contents in silicon nitride films depends on the deposition temperature. David E. Kotecki [18] et al has reported that the total hydrogen contents in remote electron-cyclotron-resonance CVD grown silicon nitride films decreases from 2×10^{22} to 6×10^{21} cm^{-3} linearly with increasing deposition temperature. Thus, the deposition temperature is one of the important parameter, which prominently affects the hydrogen contents and tailor the optical and physical properties of silicon nitride films. We have performed the numbers of experiments at different deposition temperature. The optimized values of different process parameters for the deposition of silicon nitride films are listed in Table 1.

Table 1. Optimized values of the process parameters used for the deposition of the silicon nitride films.

Process parameter	Physical value
Ammonia (NH_3) flow rate	3 Lit/min
Hexamethyldisilazane (HMDS)	0.5 Lit/min
Deposition time	5 min
Deposition temperatures	775-850 ^{0}C
Pressure	760 torr

The deposited silicon nitride films were characterized for its refractive index, film thickness and stress by using a PHILIPS (SD-1000) Ellipsometer at 632 nm wavelength. The absorption spectra were taken in the range of 400–4000 cm^{-1} using a FTIR (8400-Shimadzu) with 4 cm^{-1} resolutions at room temperature. The detailed analysis of various bonds present in FTIR spectra has been carried out. The morphological analysis of the deposited silicon nitride films has been performed using Scanning Electron Microscopy (SEM- JSM-6360).

3. Results and discussion

The variation in refractive index of the deposited silicon nitride films with increase in deposition temperature has been illustrated in Fig. 1. It is apparent that the refractive index (R.I.) of the deposited films increases nonlinearly from 1.76 to 2.1 in accordance with the corresponding increase in deposition temperature. It is attributed to the densification of the deposited films, which cause decrease in hydrogen and excess nitrogen contents with increase in deposition temperature. It results an increase in mass density, which may cause an increase in refractive index of the deposited silicon nitride films [19]. However, we kept the constant relative flow ratios of reactant ingredients 1:6. of $NH3/C_6H_{19}NSi_2$. Therefore, the increase in refractive index of the silicon nitride films is only due to the increase in deposition temperature.

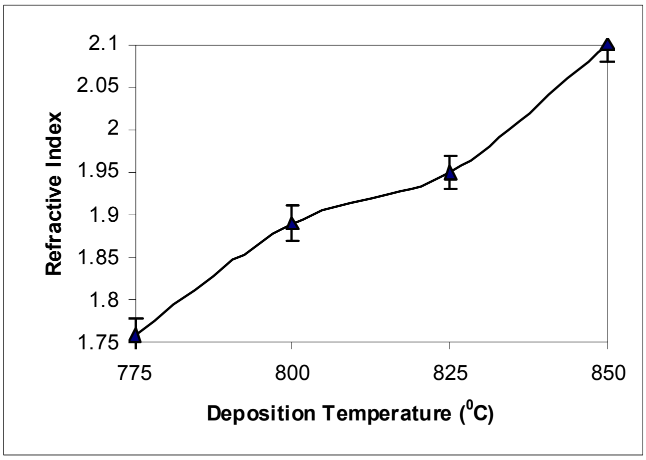

Fig. 1. Effect of deposition temperature on the refractive index of the deposited silicon nitride films.

The stress is one of the important mechanical properties, which can extensively affect the performance of the deposited silicon nitride films. Fig. 2 shows the variation in stress of the deposited silicon nitride films with corresponding increase in deposition temperature in the range of 775 to 850 ^{0}C. The film stress was observed to be compressive in nature and decreases with corresponding increase in deposition temperature. A decrease in stress of the deposited silicon nitride films may be due to the dissociation of more Si-H and N-H bonds and rearrangement of the dangling bonds to form stable Si-N bonds with corresponding increase in deposition temperature [20].

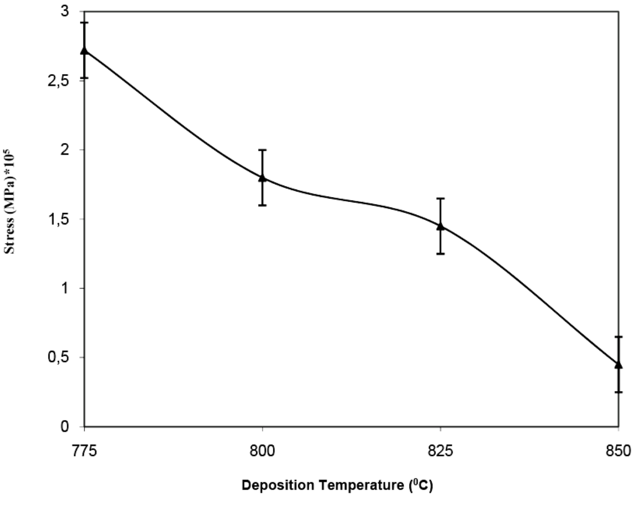

Fig. 2. Stress of the deposited silicon nitride films as a function of deposition temperature.

The variation in thickness of deposited silicon nitride films with corresponding increase in deposition temperature is illustrated in Fig. 3. It was observed that the thickness of the films increases with corresponding increase in deposition temperature. Generally, the variation in thickness depends on gas phase composition. It is evident from our analysis that the hydrogen desorption takes place after the rate limiting step for deposition being the insertion of radicals in to Si-H and N-H bonds. Radicals can be formed via thermal dissociation of parent molecules, which reaction is highly dependent on deposition temperature leading to a deposition rate, which strongly depends on temperature [21].

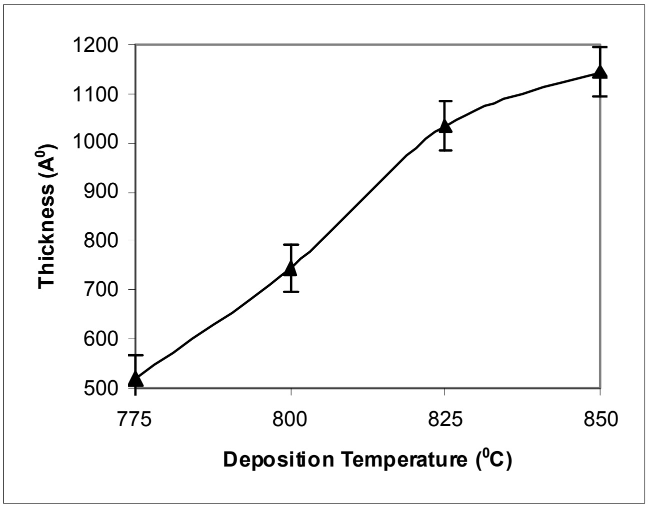

Fig. 3. Effect of deposition temperature on thickness of deposited silicon nitride films.

We have characterized the deposited silicon nitride films using Fourier transform infrared spectroscopy (FTIR) in reflection-absorption mode. Fig. 4 shows the infrared absorption spectra of the deposited silicon nitride film at the 800 ^{0}C temperature in the range of 400 cm^{-1} to 4000 cm^{-1} wave numbers. The spectral region has been magnified two fold to identify the presence of chemical bonds in deposited silicon nitride films. The absorption peaks appeared in the spectrum has been attributed to various vibration modes. A significant band assigned at 916.1 cm^{-1} is associated with the Si-N-Si stretching mode [11,13]. There is a weaker Si–N feature, associated with a Si-N atom breathing motion at about 449.4 cm^{-1} [22-23]. A peak in the absorption spectra appeared at 613.3 cm^{-1} due to a two phonon Si lattice absorption [24]. The peak at 2366.5 cm^{-1} indicates the presence of Si–H stretching vibrations [13]. Despite of these, absorption stretch bond of Si-OH was found at 3650 cm^{-1} [12]. The presence of nitrogen was identified in the form of a peak, which lies at 3350 cm^{-1} and associated to N-H stretching mode [14-15]. A very small peak of NH_2 appears at 1550 cm^{-1} in absorption spectra [7, 25], which can be neglected due to very less integrated area as compared to N-H integrated absorption. Smith et al. [19] has reported that NH_2 bonding group appears in the deposited films primarily as fragmentation products of the dissociation of the NH_3 source gas. A slight shift in the position of Si-H stretching peak towards lower wavenumber has been observed with corresponding increase in deposition temperature. It is attributed to decrease in electronegativity of the atoms backbonded to the Si [26]. It is interesting to note that, the peak intensity of both Si-H and N-H absorption peaks decreases with increase in deposition temperature. It may be due to the decrease of total bonded hydrogen concentration in the deposited films. The reduction in concentration of hydrogen in deposited films may be due to breaking of weak hydrogen bonds with increase in deposition temperature, which further signifies an improvement in the quality of the deposited SiN_x films [27].

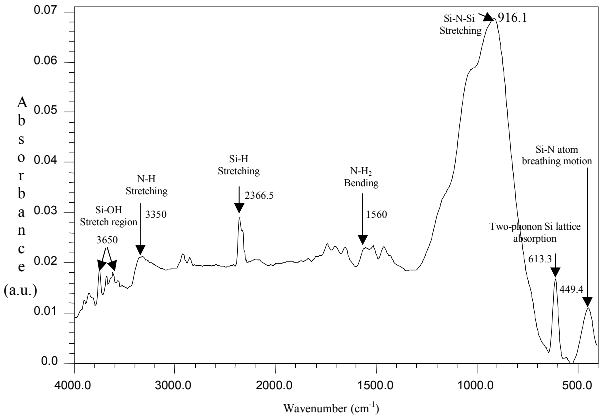

Fig. 4. Absorption spectra of silicon nitride films deposited at 800 ^0C.

It is interesting to study the behavior of shift in peak position of Si–N-Si stretching bond as a function of deposition temperature as depicted in Fig. 5. It was observed that with increase in deposition temperature, the position of Si–N-Si stretching peak moves toward lower wave number from 945.3 to 848.6 cm^{-1}. D .V. Tsu et al [28] has reported a similar nature of the Si-N stretching mode frequency as a function of deposition temperature. The variation in FWHM of Si–N-Si stretching peak with deposition temperature of SiN_x films, has been illustrated in Fig 6. It was observed that FWHM of Si–N-Si stretching peak increases from 190 to 245 cm^{-1} with corresponding increase in deposition temperature.

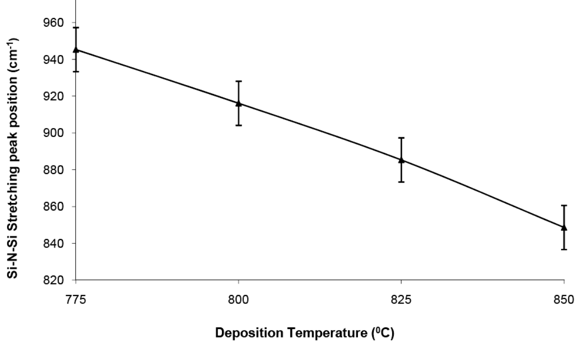

Fig. 5. Variation in Si-N stretching frequency of silicon nitride films with corresponding deposition temperature.

The amount of hydrogen incorporation and its bonding configuration of the deposited SiN_x films have been deduced from infrared (IR) spectroscopy. The measurements have been performed by using Fourier transforms infrared (FTIR) spectrometer in the mid infrared region (i.e. 400 cm^{-1} to 4000 cm^{-1}). During the deposition of SiN_x films hydrogen mainly incorporated in the form of Si-H and N-H bonds. The loss in hydrogen content is mainly determined by dissociation of N-H and Si-H bonds by trap-limited diffusion during high temperature growth processing or post deposition processing [29,30]. Stain et al [31] have reported the silicon nitride films deposited by APCVD and LPCVD show small initial instabilities between N-H and Si-H as the band is observed at a slightly higher annealing temperature than that for loss of Si-H. This difference may be a consequence of slightly higher bond dissociation energy for N-H than for Si-H bond. In order to quantify the hydrogen absorption in the silicon nitride films we have calculated the integrated area of the FTIR Si-H and N-H absorption bands and following the procedure reported by Lanford and Rand [32].

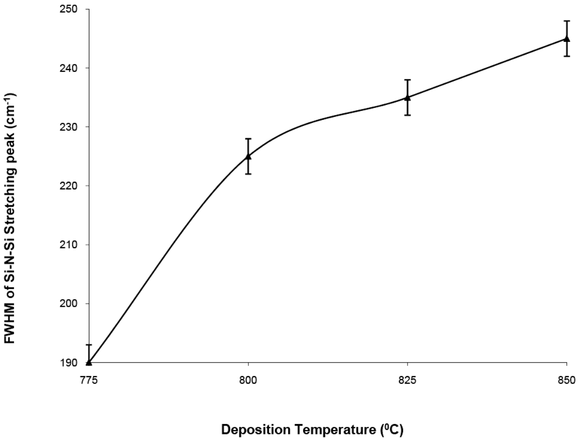

Fig. 6. Effect of deposition temperature on FWHM of Si-N stretching frequency of silicon nitride films.

Fig. 7 shows the total hydrogen concentration and the concentration of hydrogen as Si-H and N-H bond in the film at different deposition temperatures. The total H and Si-H concentration rapidly decreases with increasing deposition temperature. This decrease in H concentration is mainly due to a reduction in Si-H incorporation in the deposited silicon nitride films. Kotecki et al [18] have reported that the Si-H and N-H bonds are broken, on the surface of the depositing film, by a combination of collisional and thermal excitations. Hydrogen is liberated from the growing surface, and the rate of hydrogen evolution is greater in films deposited at higher temperatures. However, the N-H concentration initially, found to be decrease up to a certain value of deposition temperature and further it increases with corresponding increase in deposition temperature.

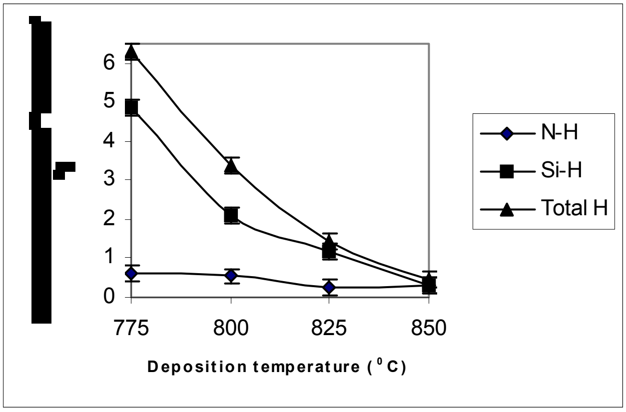

Fig. 7. Total H atomic concentration and the concentration of H as Si-H and N-H as a function Of deposition temperature.

Fig. 8 shows the variation in stress of deposited silicon nitride films with corresponding increase in film thickness. It was observed from figure that the film stress decreases slightly with corresponding increase in the film thickness and decreases rapidly beyond a particular value of film thickness. The shift in the Si-N-Si stretching frequency with film thickness, measured by FTIR absorption may be associated with the angle of the Si-N-Si bridge, as well as with the material stoichiometry, which means that either the composition or the structure of the silicon nitride films is thickness dependent. The results agree with our earlier work on the deposition of Si_3N_4 films using DMDS [13].

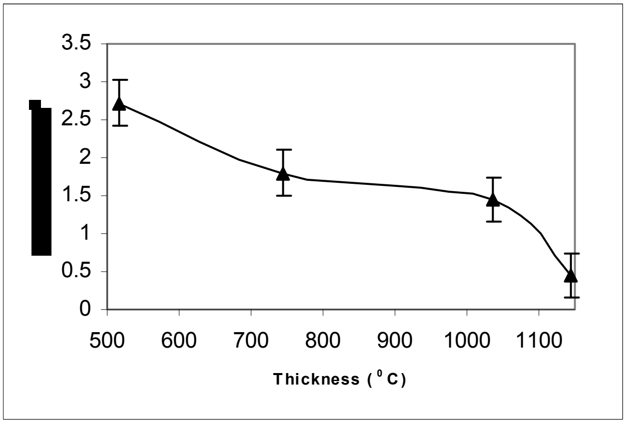

Fig. 8. Variation in films stress with corresponding increase in thickness of deposited films.

The surface morphology of the deposited silicon nitride films has been depicted in Figure 9 with magnification of 10000 using scanning electron microphotograph (SEM) operating at accelerating voltage of 20 KV. It shows almost uniform deposition of silicon nitride films. However, some white clusters of silicon nitride have been observed on the black surface of the films. These white clusters reveal the dense deposition of silicon nitride material in comparison with black surface.

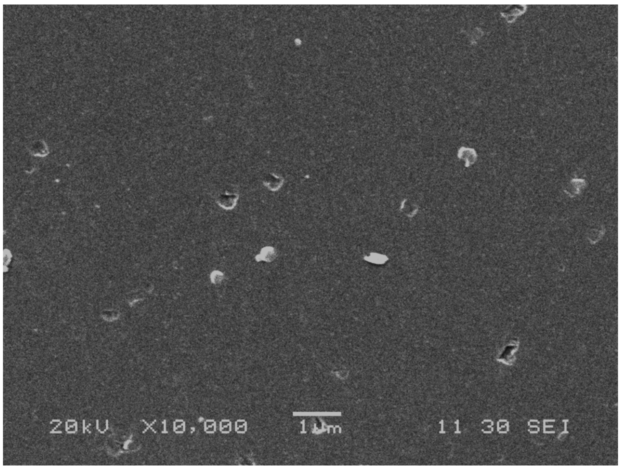

Fig. 9. SEM of the deposited silicon nitride film deposited at temperature 800 ^{0}C. (Magnification 10000 times, Accelerating Voltage = 20 V, Micron marker 1μm).

4. Conclusion

The silicon nitride films have been deposited on Si substrate using organic precursor HMDS, and NH_3 gas by thermal CVD process. The deposited silicon nitride films show good uniformity and reproducibility. The effect of deposition temperature has been investigated on the optical and physical properties of the deposited silicon nitride films. The refractive index of the films increases while stress found to be decrease with corresponding increase in deposition temperature. The peak of position of Si-N-Si stretching and Si-H stretching bonds shift toward lower wave number with corresponding increase in deposition temperature. The total hydrogen concentration has been estimated from FTIR absorption spectra, which found to be decrease with corresponding increase in deposition temperature. It reveals an improvement in the quality of deposited silicon nitride films. The SEM analysis shows the uniform deposition with some clusters of silicon nitride material on the surface of the deposited silicon nitride films. The obtained values of refractive index i.e. 1.76 - 2.1 will be found their best use in the fabrication of photonics wave-guides.

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