Conference Paper

Raman and FTIR Studies on PECVD Grown Ammonia-Free Amorphous Silicon Nitride Thin Films for Solar Cell Applications

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Ammonia- (NH_3 -) free, hydrogenated amorphous silicon nitride ($\text{a-SiN}_x\text{:H}$) thin films have been deposited using silane (SiH_4) and nitrogen (N_2) as source gases by plasma-enhanced chemical vapour deposition (PECVD). During the experiment, SiH_4 flow rate has been kept constant at 5 sccm, whereas N_2 flow rate has been varied from 2000 to 1600 sccm. The effect of nitrogen flow on $\text{SiN}_x\text{:H}$ films has been verified using Raman analysis studies. Fourier transform Infrared spectroscopy analysis has been carried out to identify all the possible modes of vibrations such as Si-N, Si-H, and N-H present in the films, and the effect of nitrogen flow on these parameters is correlated. The refractive index of the above-mentioned films has been calculated using UV-VIS spectroscopy measurements by Swanepoel's method.

1. Introduction

Amorphous silicon nitride (a-SiN_x) thin films deposited by PECVD are considered to be one of the most promising materials in semiconductor industry as gate dielectrics, isolation materials, diffusion barriers, and acoustic wave devices on semiconductor substrates [1, 2]. Also a-SiN_x layers are widely used as antireflection coatings, bulk, and surface passivation layers in solar cells applications [3, 4]. The main advantage of a-SiN_x thin films grown by PECVD is the low process temperature and high deposition rate. Low process temperature is a crucial parameter in the fabrication of multicrystalline silicon solar cells, where high-temperature thermal processing may cause degradation of the bulk life time of the charge carriers and thereby decreasing the efficiency of the solar cell [5]. Also the amorphous silicon nitride films grown by PECVD are nonstoichiometric in nature, that is, SiN_x with $x \neq 4/3$ [6]. Adjusting the deposition process parameters can vary the actual composition of the

films. Many researchers investigated the structural, optical, and electrical properties of silicon nitride films deposited using silane (SiH_4) and ammonia (NH_3) as source gases [7–9]. Fewer works have been reported on the deposition of a-SiN_x using SiH_4 and N_2 as the source gases [10, 11]. The major advantages of using N_2 over NH_3 are the abundant availability at a cheaper cost than NH_3 and nontoxic in nature. So in our present investigations, a-SiN_x thin films are deposited by PECVD using SiH_4 and N_2 as source gases. Structural properties are investigated using FTIR and Raman spectroscopy analysis and optical properties by UV-VIS spectroscopy analysis.

2. Experimental

Amorphous silicon nitride films have been deposited on corning (Eagle XG) glass using plasma-enhanced chemical vapour deposition technique (Plasmlab System 100, Oxford,

TABLE 1: Process Parameters of deposition of a-SiN_x:H films.

Sample number	SiH ₄ (sccm)	N ₂ (sccm)	Deposition time (min.)
SiN A	5	2000	12
SiN B	5	1900	12
SiN C	5	1800	12
SiN D	5	1700	12
SiN E	5	1600	12

TABLE 2: Modes of vibration of a-SiN_x:H films.

S. no	Modes of vibration			
	Si-H _n stretching	Si-N stretching	N-H wagging	Si-H _n wagging
SiN A	2046	783	1148	705
SiN B	2035	785	1151	688
SiN C	2029	788	1145	670
SiN D	2031	794	1148	684
SiN E	2033	800	1160	699

FIGURE 1: FTIR spectra of a-SiN_x films in ATR mode.

UK) at 13.56 MHz. During deposition, process gases such as silane (SiH₄), nitrogen (N₂), and argon (Ar) have been used. The process parameters are tabulated in Table 1. During the deposition process, SiH₄ flow has been kept constant at 5 sccm and N₂ flow has been varied from 1600 sccm to 2000 sccm. During deposition, plasma power and substrate temperature have been kept constant at 10 W and 600 mTorr, respectively.

Fourier transform Infrared (FTIR; Bruker Alpha T) spectroscopy studies have been carried out in the wave number range of 400–4000 cm⁻¹ in attenuated total reflection (ATR) mode in order to identify various chemical bonding occurring between nitrogen, silicon, and hydrogen. Raman spectral measurements are carried out at room temperature using micro-Raman Spectrometer (inVia, Renishaw) with Ar⁺ laser excitation frequency of 514.5 nm, 1800 gr/mm grating, and thermoelectric cooled CCD detector in the backscattering configuration. Optical absorption spectra are recorded using UV-VIS spectrophotometer (Perkin Elmer Lambda 35) in the wavelength range of 200–800 nm. Swanepoel's method has been used in calculating the thickness and refractive index (η) values of the deposited films.

3. Results and Discussions

3.1. Fourier Transform Infrared Spectroscopy (FTIR) Analysis. FTIR analysis is a nondestructive versatile tool in identification of various vibrational modes that occur in the materials and in determining the nature of chemical bonds present in the material. Figure 1 shows the FTIR analysis of various a-SiN_x films deposited using PECVD at different N₂ concentrations. Generally, in silicon nitride films, three groups of bonds can be observed like Si-N, N-H, and Si-H. In the range from 2000 to 2200 cm⁻¹ various vibrational modes like H-Si-Si₃, H-Si-HSi₂, H-Si-NSi₂, H-Si-SiN₂, H-Si-H, and H-Si-N₃ will exist in a-SiN_x films [12]. Si-N vibrational mode is observed around 780–800 cm⁻¹ whereas around 1130–1160 cm⁻¹ N-H wagging mode is observed [12]. All the possible modes of vibrations present in the a-SiN_x films are tabulated in Table 2.

3.2. Raman Spectroscopy Analysis. Raman spectroscopy is a powerful analytical technique used for the analysis of inelastic scattering of light interacting with the material under test. The convoluted Raman spectra of SiN A and SiN D samples are shown in Figures 2(a) and 2(b). The broad peak maxima observed at 482 cm⁻¹ in SiN A and 485 cm⁻¹ in SiN D is due to the scattering of Si-Si bonds corresponding to the density of states of local TC like phonon modes in amorphous silicon peak [13]. Another peak observed at 400 cm⁻¹ in SiN A and 405 cm⁻¹ in SiN D corresponding to the scattering on the asymmetric Si-N bond stretching mode in which one of the neighboring Si atoms is removed and one of the central Si atoms is replaced with a nitrogen atom [13].

3.3. Optical Properties. Optical transmission spectra of a-SiN_x:H films have been recorded in the wavelength range of 300–900 nm. The transmission spectra of SiN A, SiN C, and SiN E are as shown in Figure 3. The refractive index (η) of the deposited films were calculated using Swanepoel's method [14], which is based on the parabolic fitting procedure of adjacent maximum T_M and minimum T_m of the transmission spectra. The refractive index (η) and the absorption coefficient of the film depend on the wavelength, λ .

The refractive index (η) of the film has been calculated as a function of wavelength using expression given below which is deduced from the maximum (T_M) and minimum (T_m) values

FIGURE 2: (a) Convolved Raman spectra of SiN A. (b) Convolved Raman spectra of SiN D.

of transmission spectra:

$$n = \left[N + (N^2 - s^2)^{1/2} \right]^{1/2}, \quad (1)$$

where

$$N = 2s \times \frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2}, \quad (2)$$

where “ s ” is the refractive index of the glass substrate, $S = 1.500$.

The refractive index values are calculated for SiN A, SiN C, and SiN E using above-mentioned Swanepoel’s method at $\lambda = 700$ nm, and the values are 2.68, 2.78 and 3.01,

FIGURE 3: Transmission spectra of a-SiN_x films.

respectively. These values lie between that of hydrogenated amorphous silicon ($\eta = 3.75$) and stoichiometric Si₃N₄ ($\eta = 2.0$). Efforts are being made to achieve the value of refractive index close to stoichiometric silicon nitride.

4. Conclusion

Hydrogenated amorphous silicon nitride thin films have been deposited by PECVD technique using SiH₄ and N₂ (instead of NH₃) as source gases. FTIR analysis has been carried out to identify various vibrational modes present in the deposited films. Raman spectroscopy analysis has been carried out, and peaks around 480 cm⁻¹ and 400 cm⁻¹ are observed, which are mainly due to the Si-Si and Si-N bonds, respectively. Optical transmission spectra are recorded in order to calculate the refractive index of the deposited films. Refractive index values are calculated using Swanepoel’s method and are found to be in between amorphous silicon and stoichiometric silicon nitride.

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