Investigation of optical and chemical bond properties of hydrogenated amorphous silicon nitride for optoelectronics applications

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Abstract

The aim of this work is to determine optimal deposition parameters of silicon nitride for optical applications. The authors present the investigation of hydrogenated amorphous silicon nitride SiNₓ:H deposited by the low temperature PECVD method in high frequency reactors. The study of hydrogen bonds in the SiNₓ:H thin films were detailed. The impact of NH₃, SiH₄ and N₂ flow ratio and radio frequency power on optical coefficients in relation to chemical composition and roughness of the film is studied. The correlation between chemical bonds (N–H, Si–H) and refractive index and extinction coefficients is systematically verified. The experimental results show that the films with high refractive indexes superior to 2.05 and low roughness of about 0.35 nm can be achieved for optoelectronics applications by tuning the flow ratio or decreasing the RF power. A variety of processes have been suggested as compatible with low thermal budget (under 350 °C) in order to integrate optical waveguides with lower loss. In particular, the incorporation of N₂ as dilution gas is suited to the fabrication of SiNₓ:H films optical waveguide requiring low N–H bonds, low concentration of hydrogen [H] and high refractive index.

1. Introduction

Thin silicon nitride films with a high refractive index are widely used in optoelectronics and optics applications. For example, silicon nitride is a good material for potential applications in photovoltaic and other thin film devices such as waveguides for visible-light. Silicon nitride fabricated at high temperatures (700–900 °C) by low-pressure chemical vapor deposition (LPCVD) presents excellent properties [1], and is a good candidate for optics applications. However, some technologies require fabrication processes at lower temperatures, usually from 200 °C to 400 °C. Hence, hydrogenated silicon nitride films SiNₓ:H prepared by Plasma Enhanced Chemical Vapor Deposition (PECVD) at low temperatures (typically 200–350 °C) have found a large number of applications in the semiconductor industry. However, due to the low temperatures and various chemical reactions, undesirable N–H and Si–H bonds are formed in the silicon nitride films called hydrogenated amorphous silicon nitride SiNₓ:H [2]. In fact, the amorphous hydrogenated silicon nitride films are strongly dependent on the deposition parameters which can prove to be quite critical in some application fields. The silicon nitride with a high refractive index is a potential candidate as an optical waveguide material [3]. However, SiNₓ:H films grown using PECVD contain significant amounts of hydrogen. Thus, due to the high concentration of hydrogen [H] arising from N–H bonds and Si–H bonds, optical waveguides using SiNₓ:H suffer from high propagation losses. Indeed, it is well known that the N–H bonds (stretching vibration) act as absorption centers and their low energy tails lead to undesirable absorption losses at a wavelength of 1.55 μm [4,5]. For passivation applications, PECVD films with much lower hydrogen contents are needed. In photovoltaic applications [6], SiNₓ:H is used for fabricating solar cells, which require anti-reflection coatings having high refractive indexes and low absorption coefficients [7]. For the thin films transistors (TFTs) using SiNₓ:H gate dielectric films are mainly governed by their chemical composition and surface roughness, which are strongly dependent on the deposition conditions [8,9]. Therefore, the surface roughness and chemical compositions of SiNₓ:H films must be considered simultaneously. Thus, in this paper, we study the effect of NH₃, SiH₄ and N₂ flow ratio and radio frequency power on the films' quality and on the stoichiometry. This study has been done to provide a simple method to determine growth conditions of the films. These investigations encompass characterizations in terms of roughness, refractive index, extinction coefficient and chemical composition in order to establish practical adjustment guidance to lessen optical loss properties in silicon nitride films.

2. Experimental

In this study, the PECVD reactor (Oxford Plasma 80 plus) with a plasma frequency of 13.56 MHz is used for the SiNₓ:H
film deposition. Before being introduced in the PECVD reactor, the silicon substrate (3 ̊, (1 0 0) crystallographic orientation, p-type, 25.5–425.5 Ω cm −1) is cleaned by the RCA method [10] to remove the contaminants on the substrate (the substrate was etched in HF:H2O in the ratio 1:10 for 20 s). We used NH3 and 5% SiH4 diluted in N2 as a precursor and N2 as a diluent. The thickness, the refractive index and the extinction coefficient were measured by Spectroscopic Ellipsometry, for different NH3/SiH4 flow ratios and N2 dilution conditions. The thickness of the film was around 200 nm. The chemical bonds were determined by Fourier Transformed InfraRed (FTIR) spectroscopic measurements (Perkin–Elmer 1710 FTIR). FTIR measurements are realized in the 400–4000 cm −1 range. A base Line correction was performed. Peaks corresponding to Si–H and N–H bonds were identified from the absorption spectra. The roughness was characterized by the Atomic Force Microscope (AFM). Table 1 presents the process parameters employed to study the dielectric at different adjusted parameters. Two kinds of SiN x–H films deposited by PECVD at 1 torr pressure, at a low temperature (200 °C) are characterized. One utilizes flow ratio with typical precursors SiH4 5% diluted in N2 (360 sccm and 500 sccm), NH3 (20 sccm and 40 sccm) and N2 (240 sccm). For our comprehension, pure SiH4 (18 sccm and 25 sccm), corresponding to the SiH4 5% diluted in N2, was taken into account, in the flow ratio expression R = NH3/SiH4.

Among them, NH3 and SiH4 are used as reactants and N2 is employed to enhance the plasma. Another kind of film is based on the effect of RF power varied from 10 W to 100 W with reactants NH3/s SiH4 fixed at 360 sccm/20 sccm.

3. Results and discussion

3.1. The influence of gas flow ratio

The homogeneity, uniformity, conformality and adhesion of the films are strongly dependent on the deposition parameters which can prove to be quite critical in some application domains. The main parameter that controls uniformity and homogeneity in this investigation is the pressure. In our experiment, the pressure fixed at 1 torr enabled us to achieve good uniformity and homogeneity. In order to study the chemical bonds optical properties, deposition rate and roughness of the SiN x–H films deposited by PECVD, the gas mixtures flow ratio (R = NH3/SiH4) was varied and N2 used to enhance the plasma. Fig. 1 presents the FTIR absorbance spectra of the typical PECVD SiN x–H, whose process parameters were described in the previous section (Table 1). For hydrogenated amorphous silicon nitride films, it is well known that the main vibration mode in FTIR is around 850 cm −1 for Si–N in stretching mode; at 1150–1200 cm −1 in bending mode and 3360–3460 cm −1 in stretching mode for N–H bonds; and at 2000–2150 cm −1 in stretching mode for Si–H bonds [11].

As shown in Fig. 2, the plasma PECVD deposition conditions can develop different stoichiometry of SiN x–H (e.g. Si–H and N–H ratio can vary significantly). For the gas mixtures SiH4/NH3/N2, the main plasma generated reactions [2] are given by:

$$\begin{align*}
    N_2 + e^- & \rightarrow 2N + e^- \\
    SiH_4 + e^- & \rightarrow SiH_2 + H_2 + e^- \\
    NH_3 + e^- & \rightarrow NH_2 + H + e^- 
\end{align*}$$

For zero N2 dilution, when the flow ratio (R = NH3/SiH4) is increased (1.11–2.22), the N–H bonds proportion is higher as shown in Fig. 2a and c. However, as it is presented in Fig. 2b the concentration of [Si–H] is larger than that of nitrogen [N–H]. This can be explained by the fact that the energy of Si–H bonds is lower than the energy of N–H bonds, so NH3 is more difficult to dissociate than SiH4. Therefore, the films deposited under such conditions are expected to be silicon-rich SiN x–H ([Si] > [N]). The SiN x–H films deposited with higher NH3 flows also present higher hydrogen concentrations.

The influence of SiH4 flow rate is presented in Fig. 2. For this test, the SiH4 flow rate ranged from 18 to 25 sccm, while NH3 is kept constant at 20 sccm. In these conditions, when the SiH4 flow rate is too high, it is not easy to modify the stoichiometry of SiN x–H since there is not sufficient NH3 to consume the redundant SiH4 in the reactor PECVD. Thus, at the critical SiH4 flow rate R3 (SiH4: 25 sccm) no significant modification is obtained for the stoichiometries of SiN x–H whatever the rate of SiH4.

The influence of the N2 gas flow rate on the gas mixture NH3/SiH4 is illustrated in Fig. 2b. We can observe that the concentration of [Si–H] decreases considerably. This result is somewhat unexpected: like the SiH4/NH3 flow rate ratio with N2 dilution, the films present a high N content. Thus, the N2 gas flow contributes to the development of nitrogen rich SiN x–H films.

Table 2 summarizes the deposition rate and roughness of the SiN x–H films for different gas ratios. We show that the deposition rate varies from 160 to 120 Å/min and the root means square (RMS) surface roughness ranges from 0.35 nm to 1 nm.

It can be noticed that the increase of the NH3 flow rate (from R1 = 1.11 to R2 = 2.22) leads to a deposition rate decrease (from 160 Å/min to 120 Å/min) and the increase of the RMS surface roughness (from 0.46 nm to 1 nm) as shown in Fig. 3. This phenomenon is due to the variation of the chemical N–H and Si–H bond concentrations as shown in Fig. 2. Moreover the deposition rate decreases when the N–H bond concentrations increase which is correlated with higher NH3 flows. Indeed, N–H bonds are formed from NH3 dissociation which happens at higher energy than Si–H bonds formed from SiH4 dissociation. Considering that N2 also supplies the N atom for reaction, the presence of N2 leads to an N-rich

| Table 1 Process parameters of PECVD SiN x–H films. |
|-----------------|---|---|---|---|
| Flow ratio R = NH3/SiH4 | R1 | R2 | R3 | R1–N2 |
| NH3 (sccm) | 20 | 40 | 20 | 20 |
| SiH4 (sccm) | 18 | 18 | 25 | 18 |
| N2 (sccm) | 240 | 240 | 240 | 240 |
| R | 1.11 | 2.22 | 0.8 | – |

Fig. 1. FTIR spectra of the absorption bonds corresponding to Si–H and N–H bonds concentration with the gas flow ratios (R = NH3/SiH4 and R in presence of N2).

Fig. 2. The influence of the N2 gas flow rate on the gas mixture NH3/SiH4.
SiN\textsubscript{x}:H film that shows a lower deposition rate (135 Å/min) and a lower roughness (0.35 nm).

Table 2

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<tr>
<th>T = 200 °C, Pressure = 1 torr, P\textsubscript{RF} = 10 W</th>
<th>Flow ratio R = NH\textsubscript{3}/SiH\textsubscript{4}</th>
<th>R\textsubscript{1}</th>
<th>R\textsubscript{2}</th>
<th>R\textsubscript{3}</th>
<th>R\textsubscript{1}–N\textsubscript{2}</th>
</tr>
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<tbody>
<tr>
<td>RMS roughness (nm)</td>
<td>0.46</td>
<td>1</td>
<td>0.57</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>Deposition rate (Å/min)</td>
<td>160</td>
<td>120</td>
<td>160</td>
<td>135</td>
<td></td>
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Fig. 2. Zoom from Fig. 1 of the variation in the concentration bonds with the gases flow ratio (R = NH\textsubscript{3}/SiH\textsubscript{4}) (a) N–H stretching bonds (b) Si–H stretching and (c) N–H rocking bonds by FTIR.

Fig. 3. AFM pictures of surface of the SiN\textsubscript{x}:H films deposited by PECVD. (a) Flow ratio R\textsubscript{1} = NH\textsubscript{3}/SiH\textsubscript{4} = 1.11 and (b) flow ratio R\textsubscript{3} = NH\textsubscript{3}/SiH\textsubscript{4} = 0.8.

SiN\textsubscript{x}:H film that shows a lower deposition rate (135 Å/min) and a lower roughness (0.35 nm).
ficient determined at a wavelength 350 nm varies from 0.03 to 0.016. The value of the coefficient absorption $k$ versus the wavelength increases when the concentration $[\text{Si–H}]/[\text{N–H}]$ ratio decreases.

In fact, SiN$_x$:H films deposited by PECVD without post-annealing have become attractive for instance, for the active devices that require a low thermal budget. However, due to the hydrogen bonds and especially $[\text{N–H}]$ bonds, the silicon nitride waveguide fabricated by PECVD suffers from high propagation loss compare to the low loss (<1 dB/cm) optical waveguides[1] with Si$_3$N$_4$ grown by LPCVD. In this work, an attempt is made to identify possible drawbacks of the different gases mixture.

In these experiments, the hydrogen absorption peaks of N–H bonds were measured by FTIR. The relative hydrogen concentrations $[\text{H}]$ have been estimated using the following relationship [13]:

$$[\text{H}] = \frac{[\text{Si–H}] + [\text{N–H}]}{[\text{Si–H}] + [\text{N–H}] + [\text{Si–N}]}$$

The results of physical characterization are summarized in Table 3. As shown in Fig. 2, the N$_2$ gas flow contributes to the development of nitrogen rich SiN$_x$:H films with lower concentration $[\text{H}]$ as proposed in Table 3. In the previous work [14], at 340 °C the use of N$_2$ decreases the Si–H bonds, the concentration $[\text{H}]$ (less than 12 at.%) and the N–H bonds. However, even if the concentration $[\text{H}]$ is higher for lower temperatures, the gas mixture NH$_3$/SiH$_4$/N$_2$ enables us to reduce this concentration. This flow mixture is then suited to the fabrication of SiN$_x$:H films optical waveguide used in the applications requiring low loss and high refractive indexes.

### 3.2. The influence of RF power

In order to investigate the influence of the RF power on the variation of roughness, the deposition rates, the chemical bonds and the optical properties of the SiN$_x$:H films deposited by PECVD, RF power ranging from 10 W to 100 W has been applied. In this section, special attention is given to analyze N–H bond stretching absorption at 3300–3400 cm$^{-1}$. During these experiments, the gas mixture ratios $R$ = NH$_3$/SiH$_4$ are kept constant ($R_1$ = 1.11) as well as the deposition condition pressure (1 torr) and the temperature (200 °C), as proposed in Table 1. The effects of RF power on roughness and deposition rates are presented in Fig. 5. One can note that the energy increase of the electrons contributes to the
dissociations of the gas mixture and, as a result, the deposition rate increases (from 160 Å/min to 480 Å/min). The higher RF power enhances the plasma in the reactor chamber, which subsequently yields higher energy electrons. As for the roughness measurements by AFM, they are strongly linked to the presence of the hydrogen concentration [H] due to the N–H and Si–H bonds concentration on SiN$_x$:H films. The roughness remains low at about 0.35–0.6 nm.

The effects of different RF powers on the FTIR absorption spectra of SiN$_x$:H films are presented in Fig. 6.

As shown in Fig. 7, the RF power conditions of plasma in the PECVD reactor can develop different SiN$_x$:H film properties. The results indicate that the concentration of the N–H bonds increases with RF power. One can note that we have no correlation between RF power conditions and the concentration of the Si–H bonds. However, the lowest Si–H bonds concentration and the lowest roughness are obtained at the RF power of 50 W.

An analysis by ellipsometry measurements, shown in Fig. 8, has provided additional observations concerning FTIR measurements. The relationship between the refractive indexes and RF power is experimentally demonstrated. Meanwhile, a similar phenomenon is observed at 400 nm wavelength for extinction coefficients. The refractive index determined by a single wavelength (630 nm) ellipsometry varies from 2.01 to 1.89 while the RF power is increased from 10 W to 100 W. The extinction coefficient determined at a wavelength of 350 nm varies from 0.086 to 0.025. These results show that the refractive indexes and the extinction coefficients of the SiN$_x$:H films increase continuously with a RF power decrease. This is explained by an enrichment of the Si–H bonds formation with lower RF power and an enrichment of the N–H bonds formation with higher RF power. The nitrogen-rich SiN$_x$:H has a lower refractive index due to increased N–H bond concentrations. The value of the extinction coefficient k versus the wavelength increases when the concentration [Si–H]/[N–H] ratio decreases. The silicon-rich SiN$_x$:H has a higher refractive index.

A strong correlation between optical properties, chemical bonds, deposition rate and roughness is demonstrated. An increase of RF power clearly reveals that the precursor gases with a higher dissociative energy results in an increase in the deposition rate and in a decrease of the refractive indexes and the extinction coefficient. The results show that with a lower RF power we obtain an enrichment of the Si–H bond formations and an enrichment of

Fig. 7. Zoom from Fig. 6 of the variation in the concentration bonds with the RF power (a) N–H stretching bonds (b) Si–H stretching and (c) N–H rocking bonds by FTIR.

Fig. 8. Effect of RF power on refractive index (a) and extinction coefficient (b) of the SiN$_x$:H films.
the N–H bond formations with higher RF power. The nitrogen-rich SiN$_x$:H has a lower refractive index due to increased N–H bond concentrations. The value of the extinction coefficient $\kappa$ versus the wavelength increases when the concentration [Si–H]/[N–H] ratio decreases. The silicon-rich SiN$_x$:H has higher refractive indexes exceeding 2.05 over a wavelength range of 300–800 nm due to increased Si–H bond concentrations.

Silicon waveguide suffers from the high propagation loss problem, due to hydrogen content. Indeed, H concentration in silicon nitride film is directly influenced by the optical properties of waveguide. As shown previously the amount of hydrogen depends on the method of deposition and precursor gases. From Table 4, we see that for both types of thin-films, there is a tendency towards an increased [H] concentration and especially the N–H bonds stretching as RF power is increased.

Similarly, the N–H concentration also increases with increasing RF power (350–500 W with a step of 50 W) in which the ratio of N$_2$/SiH$_4$ flow rates fixed at 4000 sccm/80 sccm [15] at 4.2 torr pressure, with refractive indexes’ variations from 1.89 to 2.32. The author explains that the lowest loss (2.1 ± 0.2 dB/cm @ 1.55 µm, with refractive indexes’ variations from 1.89 to 2.32. The nitrogen-rich SiN$_x$:H has a lower refractive index due to increased N–H bond concentrations.

Table 4

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<th>$P_{RF}$ (W)</th>
<th>[H] at %</th>
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<tr>
<td>10</td>
<td>28.75</td>
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<tr>
<td>25</td>
<td>28</td>
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<tr>
<td>50</td>
<td>33</td>
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<td>100</td>
<td>35</td>
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To conclude, optical properties of silicon nitride films due to surface roughness and low [H] concentration can be improved by reducing the RF power. In particular, refractive indexes superior to 2.05 over a wavelength range of 300–800 nm were obtained on films deposited with a 10 W RF power.

4. Conclusions

A comprehensive study of the hydrogenated silicon nitride films SiN$_x$:H deposition in PECVD reactor at low temperatures is reported in this paper. The uniformity and the homogeneity of the SiN$_x$:H layers in this investigation are mainly obtained at a pressure fixed at 1 torr. In these experiments, it is shown that both NH$_3$/SiH$_4$/N$_2$ flow ratio and RF power affect the density of the N–H bonds and Si–H bonds. We can conclude that for a specific application such as the optical waveguide, the SiN$_x$:H-PECVD films’ properties can be adjusted as a function of the process parameters. In particular, we have shown that high refractive indexes and low roughness can be reached by tuning flow ratios and RF power.

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References