Deposition of silicon nitride film at room temperature using a SiH₄–NH₃–N₂ plasma

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Silicon nitride films were deposited in SiH₄–NH₃–N₂ plasma at room temperature by using a plasma-enhanced chemical vapor deposition system. SiN film characteristics examined as a function of radio frequency bias power include a deposition rate, a refractive index, and a surface roughness. Ion energy diagnostics was also conducted to analyze in detail the bias power effect. An increase in ion energy and a decrease in ion energy flux were observed with increasing the bias power. Several relationships between ion energy variables and film properties were identified. For all the variations in the bias power, the deposition rate, the refractive index, and the surface roughness varied in the range of 185–532 Å/min, 1.89–2.48, and 0.24–0.96 nm, respectively. Very high refractive index could be achieved by controlling the bias power.

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Key-words : PECVD, Silicon nitride films, Room temperature, Ion energy diagnostics, Deposition rate, Refractive index, Surface roughness

1. Introduction

In fabricating Si-based solar cells, silicon nitride (SiN) films are used as anti-reflective or passivation layer. Attractive features of SiN films include a good thermal stability, a good chemical inertness, and a high electrical resistivity. SiN deposition has been conducted mostly by using a plasma-enhanced chemical vapor deposition at elevated temperatures. To exploit potential properties at low temperatures, SiN films were deposited at the temperatures less than 300°C. ¹⁻⁷ Promising features were reported for the SiN films deposited at room temperature by using a plasma-enhanced chemical vapor deposition (PECVD) system. Less than 3% of hydrogen content was reported. ¹³ This was also observed as SiN film was deposited by the electron cyclotron resonance (ECR) plasma ⁹⁻¹⁰ or ECR-enhanced magnetron sputtering. ⁷ Recently, the deposition of SiN films at room temperature was studied as a function of process parameters. A decrease in the radio frequency (rf) source power resulted in an increase in the deposition rate and a decrease in the surface roughness at SiH₄–NH₃ gas mixture. ⁸ This was similarly observed at SiH₄–N₂ gas mixture as the same rf source power was varied. ⁹⁻¹⁰ A decrease in the rf bias power at SiH₄–NH₃ gas mixture led to a decrease in the deposition rate, but an increase in the refractive index. ¹⁰⁻¹¹ However, to fully exploit the advantages of room-temperature deposition of SiN films, more studies on the SiN film properties at other gas mixtures or plasma conditions are still demanded.

In this study, SiN films were deposited in a SiH₄–N₂–NH₃ plasma at room temperature by using a PECVD system (PLASMART²⁸). Various impact of rf bias power on SiN film properties are studied. The film properties of concern include a deposition rate, a refractive index, and a surface roughness. A non-invasive ion analysis system (IEAS) (PLASMART²⁹) was used for ion energy diagnostics. Relationships between ion energy variables and film properties are examined.

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2. Experimental details

SiN films were deposited on p-type, single side polished Si wafers of (100) orientation. The thickness and resistivity of wafers were about 525 ± 25 µm and 1–30 Ω·cm, respectively. Using a PECVD system, SiN films were deposited in a SiH₄–NH₃–N₂ gas mixture. The equipment was detailed in the work.³⁻⁵ The deposition was conducted as a function of bias power. The flow rates of SiH₄, N₂, and NH₃ flow rates were set to 8, 22, and 10 sccm, respectively. The pressure was varied from 166 to 179 mTorr as bias power was varied. The deposition time was 5 min. The diagnostic parameters obtained from IEAS include a high ion energy (E₀), a low ion energy (E₁), a high ion energy flux (N₀), and a low ion energy flux (N₁). Both E₀ and E₁ represent the height of high and low energy peaks, respectively. The N₀ and N₁ correspond to the height of high and low energy peaks, respectively. From the main diagnostic parameters, a ratio of N₀/N₁ was also defined. The deposition rate and refractive index were measured by an ellipsometry. An atomic force microscopy was used to measure mean surface roughness.

3. Results

3.1 Ion energy diagnostics

Figure 1 shows E₀ and E₁ as a function of bias power. As shown in Fig. 1, increasing the bias power increases the E₀. The resulting enhanced ion bombardment is well expected because of a wider plasma sheath. The E₁ variation with the bias power is consistent with that for the E₀. One difference is that the magnitude of E₁ is much smaller than that of the E₀. This indicates that the E₀ is a more strong function of the bias power. Figure 2 shows N₀ and N₁ as a function of bias power. As shown in Fig. 2, the N₀ decreases with increasing the bias power. This contrasts with the variation in the E₀ and E₁. Compared to the N₀ variation, that of the N₁ is very similar. Figure 3 shows a N₀/N₁ as a function of bias power. The N₀/N₁ seems to gradually decrease with increasing the bias power.

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3.2 Film properties

Figure 4 shows a deposition rate as a function of the bias power. From the figure, it is found that deposition rate varies from 185 to 532 Å/min for all the variations in bias power, and has the maximum at 60 W of bias power. However, the deposition rate seems to have no correlation with the ion energy, ion energy flux, or $N_{h}/N_{l}$. Meanwhile, SiN films grow by the insertion of nitrogen into the Si–Si bonds. In Fig. 4, the deposition rate decreases significantly as the bias power increases from 60 to 80 W. This indicates a significantly reduced concentration of N-related species (such as $N_{2}^{*}$, $N_{2}^{+}$) at 80 W, responsible for nitridation of Si–Si. The expected higher Si/N ratio is clearly supported by the higher refractive index at 80 W in Fig. 5. The relationship between the Si/N and refractive index is detailed later. It has been reported experimentally$^{11}$ and from an empirical model$^{12}$ that plasma density is influenced by the bias power. The relative concentration of plasma species generated by the bias power depends on the dissociation energy. Actually, the dissociation energy of N–N is 945.33 kJ/mol,
which is much larger than those of Si–H and N–H, less than 299.2 and 339 kJ/mol, respectively.\textsuperscript{13} Once a bias power is given, the concentration of N-related species responsible for nitridation of Si–Si bonds is hence expected to be much lower than that of Si. Eventually this leads to a decrease in the deposition rate, which accounts for the decreased deposition rate at 80 W. It is expected that in our experiment the dissociation of N–N is little affected at lower bias power. In other words, the film growth depends nearly on the production of Si and N from the dissociation of Si–H and N–H bonds. From the smaller dissociation energy of Si–H than N–H, a larger amount of Si than N is expected. Therefore, the increased deposition rate at 60 W with respect to that at 40 W is attributed to the larger Si/N ratio.

Figure 5 shows a refractive index as a function of bias power. As shown in Fig. 5, increasing the bias power increases the refractive index. A similar variation was noted in SiH\textsubscript{4}–N\textsubscript{2}–Ar\textsuperscript{21} or SiH\textsubscript{4}–NH\textsubscript{3}–Ar plasma.\textsuperscript{22} It should be noted that the refractive index was closely related to the [Si–H]/[N–H].\textsuperscript{13} This is further supported by the strong relationship between the N/Si and [N–H]/[Si–H].\textsuperscript{14} From these facts, the increasing refractive index in Fig. 5 indicates the formation of Si-richer films. Compared to Fig. 1, the refractive index variation is strongly related to the \( E_{0} \) or \( E_{i} \) variation. This shows that ion bombardment plays a considerable role in determining the refractive index. The refractive index variation in Fig. 5 is unable to be explained by the typical bond breaking mechanism. This is because a higher breakage rate of [Si–H] than [N–H] at higher bias power leads to a larger [N–H] by bonding excess hydrogen to N. It should be noted that the [Si–H] is broken more easily than [N–H] due to less bonding energy. The refractive index is varied between 1.89 and 2.48 in Fig. 5. It is noticeable that the refractive index is large enough to be used as an anti-reflective layer of solar cells.

Figure 6 shows a surface roughness as a function of the bias power. As shown in Fig. 6, increasing the bias power increases the surface roughness. The bias power impact becomes drastic as it is increased from 80 to 100 W. This is closely related to the \( E_{0} \) and \( E_{i} \), indicating that enhanced ion bombardment creates a rougher surface. The surface roughness varied from 0.24 to 0.96 nm in Fig. 6. The corresponding AFM images are shown in Figs. 7(a)–(d). The AFM images show that the drastically increased surface roughness is due to the creation of many unbalanced columns. Meanwhile, as conducted earlier,\textsuperscript{9} the surface morphology was more detailed by calculating the range of pixel heights. The results are shown in Table 1. Here the occupancy is the ratio of the number of pixel heights included in a range to the total number. Table 1 shows that each surface is covered with columns, ranging between 1 and –1 nm. This is indicative of the formation of very dense and homogeneous surface. From all these observations, the bias power of 60 W is selected to be the best condition, at which high deposition rate, high refractive index, and smaller surface roughness are achieved.

<table>
<thead>
<tr>
<th>Bias power (W)</th>
<th>Total Range (nm)</th>
<th>Range (nm)</th>
<th>Occupancy (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>–1–3</td>
<td>–1–1</td>
<td>99.6</td>
</tr>
<tr>
<td>60</td>
<td>–2–3</td>
<td>–1–1</td>
<td>98.1</td>
</tr>
<tr>
<td>80</td>
<td>–2–5</td>
<td>–1–1</td>
<td>97.6</td>
</tr>
<tr>
<td>100</td>
<td>–2–14</td>
<td>–2–1</td>
<td>98.1</td>
</tr>
</tbody>
</table>

4. Conclusions

Using a plasma-enhanced chemical vapor deposition system, SiN films were deposited in SiH\textsubscript{4}–NH\textsubscript{3}–N\textsubscript{2} plasma. Compared to previous studies, the experiment conducted here is very helpful in that it provide useful data for SiN film characteristics conducted at room temperature. The ion energy diagnostic data also proved effective in analyzing ion bombardment impact on the film characteristics. A strong dependency of the refractive index or the surface roughness on the ion energy was identified. Denser surface morphology was achieved at lower bias power. Most of all, it is noteworthy that very high refractive index was achieved simply by controlling the bias power.

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References