Silicon nitride deposited by ECR–CVD at room temperature for LOCOS isolation technology

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Abstract

For LOCOS application, silicon nitride (SiNₓ) insulators have been deposited by ECR–CVD at room temperature and with N₂ flows of 2.5, 5, 10 and 20 sccm on pad-SiO₂/Si or on Si substrates. The obtained SiNₓ/Si structures were used to analyze the SiNₓ characteristics. FTIR analyses reveal the presence of Si–N and N–H bonds. The refractive indexes between 1.88 and 2.48 and the thickness between 120 and 139 nm were determined by ellipsometry. With these thickness values, the deposition rates of 9.6–10.1 nm/min and the BHF etch rates of 2–86 nm/min were determined. On the SiNₓ/pad-SiO₂/Si structures, the LOCOS process was performed. Optical and SEM microscopy analyses were used to investigate the SiNₓ resistance to thermal oxidation, made at 1000°C, and the bird’s beak in the obtained LOCOS structures, respectively. These analyses reveal that SiNₓ insulator performed with N₂ flows higher than 2.5 sccm presented high quality to LOCOS isolation technology.

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1. Introduction

Electron cyclotron resonance (ECR) plasma has been widely utilized for low temperature, low pressure and low damage chemical vapor deposition (CVD). High degree of dissociation of SiH₄ gas molecules under high discharge power conditions can be obtained by ECR plasmas, and the maximum rate of deposition can be expected for radicals with intermediate hydrogen content (like SiH₂). Therefore, in terms of deposition rate, for the process optimization a certain (intermediate rather than the highest) degree of silane dissociation should be achieved. On the other, in order to optimize the composition and microstructure of the film deposited, the H incorporation should be controlled at a low level. SiH₂ diluted in 98% of Ar permits low silane concentration in the ECR plasma that, with high degree of dissociation, can reduce the Si–H bond incorporation in the films deposited. Insulators deposited by ECR–CVD at low temperatures (<200°C) have presented high quality, with low H incorporation levels, and good uniformity [1]. Silicon nitride (SiNₓ) films have received considerable attention due to their electrical and physical properties [1].

Usually, the silicon nitrides are deposited by conventional low-pressure chemical vapor deposition (LPCVD) at temperatures higher than 600°C for LOCOS (LOCal Oxidation of Silicon) isolation tech-
nology used to CMOS device fabrication [2–6]. As recent alternative, silicon nitrides have been deposited by plasma enhanced chemical vapor deposition (PECVD) for LOCOS isolation without field implant of CMOS integrated circuits [3,6].

In this work, for LOCOS application, silicon nitride (SiNₓ) insulators have been deposited by electron cyclotron resonance—plasma enhanced chemical vapor deposition at room temperature (20 °C), at low pressure (5 mTorr), with N₂ flows of 2.5, 5, 10 and 20 sccm, with fixed SiH₄/Ar flows of 200/20 sccm, and at microwave power of 1000 W on SiO₂/Si or on Si substrates. The obtained SiNₓ/Si structures were used to analyze the silicon nitride physical characteristics. Chemical bonding characteristics of the SiNₓ films were determined using Fourier transform infrared (FTIR) spectrometry analyses. The refractive indexes and the thickness of SiNₓ films were determined by ellipsometry. With these thickness values and with deposition and buffered HF etching times, the deposition rates and the etch rates were determined, respectively. On the SiNₓ/SiO₂/Si structures, the LOCOS process, with sequential photolithography, silicon nitride and pad oxide BHF wet etching and thermal oxidation steps, was performed. The SiNₓ/pad-SiO₂ thickness ratio of about 3:1 to minimize the stress effect in the structure was employed [4].

The AZ1350J resist and AZ312MIF developer in photolithography step were used. The conventional thermal wet oxidation at 1000 °C, for 180 min and in O₂/H₂O ambient was performed. Optical and scanning electron microscopy analyses were used to investigate the silicon nitride resistance to thermal oxidation, made at high temperature (1000 °C), and the bird’s beak in the obtained LOCOS structures, respectively.

2. Experimental

The silicon nitride layers were formed on p-type Si(1 0 0) or on pad silicon oxide (50 nm)/p-type Si(1 0 0) wafers. The substrates were cleaned by RCA method. Based on the better condition established by [1], the silicon nitride ECR depositions were carried out at different N₂ flows of 2.5, 5, 10 and 20 sccm and with the samples with these nitrides were named as N2.5, N5, N10 and N20, respectively. The substrate temperature, process pressure, SiH₄ and Ar flows, microwave (frequency = 2.45 GHz) and rf (frequency = 13.56 MHz) powers were fixed at 20 °C, 5 mTorr, 200 sccm (diluted in 98% of Ar) and 20 sccm, 1000 and 1 W, respectively.

The nitride formation at the SiNₓ/Si structures were investigated by FTIR and ellipsometry. With the thickness values obtained by ellipsometry and with deposition and buffered HF (BHF) etching times, the deposition rates and the etch rates were determined, respectively. The BHF etching step was performed to verify the silicon nitride porosity, which is related to the hydrogen concentration into the films.

On the SiNₓ (150 nm)/pad-SiO₂ (50 nm)/Si structures, the LOCOS process, with sequential photolithography, silicon nitride and pad oxide BHF wet etching and thermal wet oxidation steps, was performed. The SiNₓ/pad-SiO₂ thickness ratio of about 3:1 to minimize the stress effect in the structure was employed [4]. The AZ1350J resist and AZ312MIF developer in photolithography step were used. The conventional thermal wet oxidation at 1000 °C, for 180 min and in O₂/H₂O ambient was performed. Optical and scanning electron microscopy analyses were used to investigate the silicon nitride resistance to thermal oxidation, made at high temperature (1000 °C), and the bird’s beak in the obtained LOCOS structures, respectively.

3. Results

Thickness and refractive index (n_N) of the silicon nitride deposited on Si wafers were measured by ellipsometry. A fixed wavelength of 632.8 nm and an incidence angle of 70° were used. A complex refractive index nₛ of 3.858-i.0.018 was used for the substrate. The deposition and BHF etch rates were calculated from the nitride thickness values and the deposition and etching times, respectively. Table 1 shows the thickness, refractive index (n_N), deposition and BHF etch rates for each nitride. For the stoichiometric nitride, the refractive index is 2.0. For n_N lower

<table>
<thead>
<tr>
<th>Samples</th>
<th>DR (nm/min)</th>
<th>BHF-ER (nm/min)</th>
<th>T_N (nm)</th>
<th>n_N</th>
<th>Si–N bond peak position (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2.5</td>
<td>9.6</td>
<td>&lt;2</td>
<td>120</td>
<td>2.48</td>
<td>833</td>
</tr>
<tr>
<td>N5</td>
<td>10.5</td>
<td>29.2</td>
<td>132</td>
<td>1.94</td>
<td>852</td>
</tr>
<tr>
<td>N10</td>
<td>11.1</td>
<td>69.4</td>
<td>139</td>
<td>1.90</td>
<td>860</td>
</tr>
<tr>
<td>N20</td>
<td>10.3</td>
<td>86.2</td>
<td>130</td>
<td>1.88</td>
<td>864</td>
</tr>
</tbody>
</table>

DR, BHF-ER, T_N and n_N are defined as deposition rates, etch rates in BHF, thickness and refractive index of silicon nitrides, respectively.
than 2.0, the films are nitrogen rich. For \( n_N \) higher than 2.0, the films are silicon rich [1]. The refractive indexes of 1.88, 1.90, 1.94 and 2.48 for N20, N10, N5 and N2.5 samples, respectively, indicate the formation of nitrogen rich films, except to N2.5 samples, which were formed with low N2 flow of 2.5 sccm. Table 1 and Fig. 1 present the deposition rates between 9.6 and 10.1 nm/min and the BHF etch rates between 2 and 86 nm/min. From Fig. 1, it was observed that the deposition rate increased with N2 flow up to 10 sccm and decreased for 20 sccm, indicating that the deposition process saturation occurred, and the BHF etch rate is increased with N2 flow. High BHF etch rate values indicate the nitride formation with high porosity, which can be due to high hydrogen concentration into the films. Therefore, the BHF etch rate results (Table 1 and Fig. 1) indicate a higher porosity for N5, N10 and N20 nitrides, which are nitrogen-rich films.

FTIR spectrometry was performed in order to evaluate chemical bonds and to investigate the H incorporation. Table 1 shows the absorption peak wavenumbers related to Si–N bonds (stretching mode) for each SiNx deposited on Si substrate. In Fig. 2, the infra-red spectrum of the SiNx films, which were deposited with N2 flows between 2.5 and 20 sccm, is presented. Absorption peaks occur at 833–864 cm\(^{-1}\) (stretching mode) and at 470 cm\(^{-1}\) (wagging mode) which are due to Si–N bonds [1]. The FTIR analyses revealed the presence of absorptions at 3340–3350 cm\(^{-1}\) which are related to the N–H stretching mode, and the absence of absorptions at 2000–2300 cm\(^{-1}\) related to Si–H bonds, except in the N2.5 samples, which were deposited with low nitrogen flow of 2.5 sccm. Fig. 3 presents the silicon nitride refractive index behavior in relation to the Si–N bond (stretching mode) peak position shifts, which were observed in Fig. 2. For Si–N peak position values higher than 847 cm\(^{-1}\), the films are nitrogen rich, such as N5, N10 and N20 nitrides. For Si–N peak position values lower than 847 cm\(^{-1}\), the films are silicon rich (N2.5 nitride). From Fig. 2, it was observed that the N–H bond peak intensities for N5, N10 and N20 nitrides are higher than Si–H bond peak intensity for N2.5 sample, therefore, the nitrogen-rich films present higher hydrogen concentration than the silicon rich nitrides. These considerations confirm the BHF etch rate results (for stoichiometric ECR silicon nitride, with refractive index of 2.0, the Si–N bond (stretching mode) peak position is of about 847 cm\(^{-1}\) (Table 1 and Fig. 1)), which indicate a higher porosity for N5, N10 and N20 nitrides. This can be explained by high degree
of dissociation of silane gas molecules under the high discharge power conditions in ECR plasmas rich in nitrogen, that permit high N–H and low Si–H bond incorporation in the deposited films [1]. The LOCOS process was performed on the SiNx (150 nm)/pad-SiO2 (50 nm)/Si structures, with SiNx/pad-SiO2 layer total thickness values of about 200 nm measured before thermal oxidation. Optical and scanning electron microscopy analyses were used to investigate the silicon nitride resistance to thermal oxidation, made at high temperature (1000 °C), and the bird’s beak in the obtained LOCOS structures, respectively. Fig. 4 shows top side optical microscopy pictures of patterns obtained on the SiNx (150 nm)/pad-SiO2 (50 nm)/Si structures, before and after of the thermal wet oxidation, for LOCOS process. This

![Fig. 4. Top side optical microscopy pictures of patterns obtained on the SiNx (150 nm)/pad-SiO2 (50 nm)/Si structures, before and after thermal wet oxidation, for LOCOS process.](image)

![Fig. 5. The post-oxidation pattern cross-section SEM micrographs of (a) N2.5, (b) N5 and (c) N20 nitrides for LOCOS structures.](image)
analysis reveals that rich nitrogen SiN$_x$ insulator formed with N$_2$ flows higher than 2.5 sccm are resistant to subsequent thermal oxidation, because the post-oxidation patterns were not modified. The N2.5 nitrides are not resistant to an additional thermal treatment at high temperatures. The post-oxidation pattern cross-section SEM micrographs of N2.5, N5 and N20 nitrides for LOCOS structures are presented in Fig. 5. For LOCOS structures formed by the N2.5 nitride (Fig. 5(a)), the SiN$_x$/pad-SiO$_2$ layer total thickness values were modified and increased from about 200 nm (as measured before thermal oxidation) to 400 nm, indicating that these N2.5 nitrides were oxidized and not effective mask against oxidation, as previously observed by the optical microscopy analyses. This nitride oxidation can be related to the high silicon concentration in silicon rich nitrides, which supply silicon to react with oxygen during the thermal oxidation [7]. For LOCOS structures formed by N5 and N20 nitrides (Fig. 5(b) and (c)), it was observed that the lengths of the bird’s beak are of about 1 mm and the SiN$_x$/pad-SiO$_2$ layer total thickness values of about 200 nm were kept. Similar results were obtained by N10 nitrides, confirming the optical microscopy analyses, which indicates that SiN$_x$ insulating films formed with N$_2$ flows higher than 2.5 sccm, present high quality for LOCOS isolation technology; similar to the PECVD nitrides used to CMOS device manufacturing [3,6].

4. Conclusions

For LOCOS application, silicon nitride (SiN$_x$) insulators have been deposited by electron cyclotron resonance—chemical vapor deposition at room temperature (20 °C), at low pressure (5 mTorr), with N$_2$ flows of 2.5, 5, 10 and 20 sccm, with fixed SiH$_4$/Ar flows of 200/20 sccm, and at microwave power of 1000 W on pad-SiO$_2$/Si or Si substrates. The obtained SiN$_x$/Si structures were used to analyze the silicon nitride physical characteristics. Fourier transform infrared spectrometry analyses reveal the presence of Si–N and N–H bonds and the shifts of main peak position Si–N bond (stretching vibration mode) in the silicon nitride films are related to N$_2$ flows in gas mixture. The refractive indexes, between 1.88 and 2.48, and the thickness, between 120 and 139 nm, were determined by ellipsometry. With these thickness values and with deposition and buffered HF etching times, the deposition rates of 9.6–10.1 nm/min and the etch rates of 2–86 nm/min were determined, respectively.

On the SiN$_x$/pad-SiO$_2$/Si structures, the LOCOS process, with sequential photolithography, silicon nitride and pad oxide BHF wet etching and thermal oxidation steps, was performed. Optical and scanning electron microscopy analyses were used to investigate the silicon nitride resistance to thermal oxidation, made at high temperature (1000 °C), and the bird’s beak in the obtained LOCOS structures, respectively. These analyses reveal that SiN$_x$ insulating films, performed with N$_2$ flows higher than 2.5 sccm, presented high quality for LOCOS isolation technology, indicating that these nitrides can be used to CMOS device manufacturing.

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References