AMINO VINYLISILANE PRECURSORS FOR STRESSED SIN FILMS

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Related U.S. Application Data

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Abstract

The present invention is a method to increase the intrinsic compressive stress in plasma enhanced chemical vapor deposition (PECVD) silicon nitride (SiN) and silicon carbonitride (SiCN) thin films, comprising depositing the film from an amino vinylsilane-based precursor. More specifically, the present invention uses the amino vinylsilane-based precursor selected from the formula: \([RR'N]_xSiR_y(R^3)_z\), where \(x+y+z=4\), \(x=1-3\), \(y=0-2\), and \(z=1-3\); each \(R\), \(R^1\), and \(R^3\) can be hydrogen, \(\text{C}_1\) to \(\text{C}_{10}\) alkane, alkene, or \(\text{C}_4\) to \(\text{C}_{12}\) aromatic; each \(R^2\) is a vinyl, allyl or vinyl-containing functional group.
FIG. 3

Absorbance (a.u.)

Wavenumber (cm⁻¹)

Film C

Film E

Si-N

N-H

Si-H
FIG. 4
AMINO VINYL SILANE PRECURSORS FOR STRESSED SIN FILMS

BACKGROUND OF THE INVENTION

The Present Invention is in the field of integrated circuit fabrication and particularly materials of construction in the films that are adjacent to or are a part of electronic devices in the integrated circuit, such as transistors, capacitors, vias, electrically conductive lines and bus bars. As the dimensions of such electronic devices continue to shrink and the density of such devices in a given area increases, the films adjacent to or a part of such electronic devices must exhibit higher electrical properties. Designing stress into such films can alter their electrical properties. Stress engineering of PECVD silicon nitride films is currently being used to enhance the performance of cutting edge metal oxide semiconductor field effect transistor (MOSFET) technology. Device speed has been significantly increased through the application of highly stressed SiN films deposited on top of MOSFET gate structures. Compressive stress enhances “P” type field effect transistors (pFET) devices through increases of hole mobility, while tensile stress is beneficial for “N” type field effect transistors (nFET) devices through enhancing electron mobility. Stress is generated from differences in the thermal expansion between two materials in contact. Plasma enhanced chemical vapor deposition (PECVD) silicon nitride films generally generate compressive stress.

Presently, compressively stressed films are deposited using silane and ammonia with reported compressive stresses up to ~3.5 gigapascals (GPa). Increasing compressive stress further is becoming particularly challenging. The industry is currently aiming for compressively stressed films of ~4 GPa or higher.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

FIGS. 1A and B are depictions of structural formulae of species of chemical precursors for the present invention.

FIG. 2 is a graph of stress values for films formed by PECVD depositions of BIPAVMS and ammonia under various process conditions.

FIG. 3 is a FTIR spectra of silicon nitride films deposited with PECVD using BIPAMS and ammonia.

FIG. 4 is a graph plotting the ratio of nitrogen bonded hydrogen (NHx) to silicon bonded hydrogen (SiH) content versus film stress.

FIG. 5 is a graph plotting NHx and SiH content versus film stress.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides amino vinylsilane-based precursors as a way to increase the intrinsic compressive stress in plasma enhanced chemical vapor deposition (PECVD) silicon nitride (SiN) and silicon carbonitride (SiCN) thin films. The main feature of these amino vinylsilane precursors is one or two vinyl functional groups bonded to the central silicon atom. The precursors have the general formula:

$$[RR'N],SiR_3^2(R^2)$$

where x+y+z=3, x=1-3, y=0-2, and z=1-3. R, R' can be hydrogen, C to C alkane, alkene, or C to C aromatic; each R' is a vinyl, allyl or vinyl-containing functional group.

Specifically the present invention uses the amino vinylsilane-based precursor selected from the formula:

$$[RR'N],SiR_3^2(R^2)$$

where x+y+z=3, x=1-3, y=0-2, and z=1-3. R, R' and R can be hydrogen, C to C alkane, alkene, or C to C aromatic; each R' is a vinyl, allyl or vinyl-containing functional group.
The particular precursor used in tests is Bis(iso-propylamino)vinylmethylsilane (BIPAVMS). Another similar precursor is Bis(iso-propylamino)divinylsilane (BIPADVS).

Stress engineering of PECVD silicon nitride films is currently being used to enhance the performance of cutting edge MOSFET technology. Device speed has been significantly increased through the application of highly stressed SiN films deposited on top of MOSFET gate structures. Compressive stress enhances pFET devices through increases of hole mobility, while tensile stress is beneficial for nFET devices through enhancing electron mobility. Stress is generated from differences in the thermal expansion between the two materials in contact. PECVD silicon nitride films generally generate compressive stress. Presently, compressively stressed films are deposited using silane and ammonia with reported compressive stresses up to ~3.5 GPa. Increasing compressive stress further is becoming particularly challenging. The industry is currently aiming for compressively stressed films of ~4 GPa or higher.

The goal of ~4 GPa compressively stressed films may be realized through the use of the above described amino vinylsilane precursors. In the present invention, compressive stress of ~0.7 to ~4.5 GPa (~700 to ~4500 MPa) can be obtained. Up to now, most of the increases in stress generation have been through processing techniques, such as plasma surface treatment, multilayer deposition, dual frequency plasma and other similar methods. This invention is the first to specifically use a unique type of silicon-containing precursor to increase film stress.

Standard deposition methods have a limit to the amount of stress they can generate. Current targets for stress are 1.5 GPa for tensile stress and ~4 GPa for compressive stress.

It has been observed that higher hydrogen incorporation into SiN films leads to higher compressive stress. We propose that PECVD SiN films deposited using amino vinylsilanes such as BIPADVS and BIPAVMS can generate highly compressive stress due to overall hydrogen incorporation and, moreover, through the type of hydrogen incorporation, i.e. nitrogen bonded hydrogen vs silicon bonded hydrogen. We have shown for both bis(tertiary-butylamino)silane (BTBAS) and BIPAVMS a strong correlation between N—H to Si—H ratio and compressive stress, with high N—H to Si—H ratio leading to higher compressive stress. Films deposited using a mixture of an aminosilane and ammonia naturally lead to films containing high N—H to Si—H content through transamination reactions.

Furthermore, aminosilanes containing vinyl functional groups, such as BIPADVS and BIPAVMS, have been found to increase compressive stress further. Vinyl groups play important roles in creating film stress. Under plasma conditions, carbon-carbon double bonds may form cross-linking points, which increase the density of film by holding atoms closer. Si—H bonds of the precursor react with carbon-carbon double bonds with hydroxilation reaction, forming ethylene bridges between silicon atoms. Ethylene bridges hold the silicon atoms close, and are consequently replaced by ammonia, and that process helps the formation of Si—N— Si structure.

The present invention is directed to overcome limits of intrinsic stress generation through the use of this special class of aminosilane precursors, namely amino vinylsilanes, to deposit highly stressed silicon nitride (SiN) films or silicon carbonitride (SiCN) films using PECVD. The addition of a vinyl group to the aminosilane is found to increase the intrinsic compressive stress of SiN and SiCN films deposited using these precursors.

To deposit compressively stressed silicon nitride or silicon carbonitride films, the amino vinylsilane is reacted with a nitrogen-containing gas in a PECVD chamber at wafer temperatures of 500°C or less. The nitrogen containing gas can be ammonia, nitrogen, or a combination thereof. Additionally, a diluent gas such as, but not limited to, He, Ar, Ne, Xe, or hydrogen can be introduced to modify the film properties. For example, Bis(iso-propylamino)vinylmethysilane (BIPAVMS) (FIG. 1 A) or Bis(iso-propylamino)divinylsilane (BIPADVS) (FIG. 1 B) and ammonia are introduced into a PECVD chamber and allowed to react, resulting in the deposition of a compressively stressed SiN thin film. A suitable BIPAVMS flow rate may range from 50 to about 1000 mg/min. A suitable ammonia and/or nitrogen flow rate may range from 500 to 10,000 sccm, and the diluent gases can range from 50 to 50,000 sccm.

Example

Depositions conditions for Runs A-F and the corresponding film stress obtained in Table 1, below, are as follows. Deposition temperature was 400°C. In these examples, properties were obtained from sample films that were deposited onto medium resistivity (8-12 Ωcm) single crystal silicon wafer substrates. All depositions were performed on an Applied Materials Precision 5000 system in a 200 mm DXZ chamber fitted with an Advanced Energy 2000 RF generator. The plasma is single frequency of 13.56 MHz.

In the Table 1 examples, thickness and optical properties, such as refractive index of the dielectric films, were measured on an SCI Filmtek Reflectometer. The refractive index is measured using 632 nm wavelength light. Fourier Infrared Spectroscopy (FTIR) data was collected on the wafers using a Thermo Nicolet 750 system in a nitrogen purged cell. Background spectra were collected on similar medium resistivity wafers to eliminate CO₂ and water from the spectra. Data was obtained in the range of from 4000 to 400 cm⁻¹ by collecting 32 scans with a resolution of 4 cm⁻¹. The OMNIC software package was used to process the data. Film stress measurements were made using a laser beam scattering tool (Toho Technology Corp., Model: FLX2320S).
TABLE 1

<table>
<thead>
<tr>
<th>Film</th>
<th>BIPAVMS flow</th>
<th>NH3</th>
<th>P</th>
<th>Power</th>
<th>Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>250</td>
<td>2500</td>
<td>2.5</td>
<td>400</td>
<td>-1849</td>
</tr>
<tr>
<td>B</td>
<td>250</td>
<td>2500</td>
<td>2.5</td>
<td>400</td>
<td>-934</td>
</tr>
<tr>
<td>C</td>
<td>250</td>
<td>2500</td>
<td>2.5</td>
<td>600</td>
<td>-757</td>
</tr>
<tr>
<td>D</td>
<td>125</td>
<td>2500</td>
<td>2.5</td>
<td>400</td>
<td>-2249</td>
</tr>
<tr>
<td>E</td>
<td>125</td>
<td>2500</td>
<td>2.5</td>
<td>600</td>
<td>-2357</td>
</tr>
<tr>
<td>F</td>
<td>125</td>
<td>2500</td>
<td>2.5</td>
<td>600</td>
<td>-2260</td>
</tr>
</tbody>
</table>

Example 2

Under process condition A listed in Table 1, the stress of films using non-vinyl precursor (such as BTBAS) is lower than that for (BIPAVMS)

TABLE 2

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Thickness (nm)</th>
<th>Dep. Rate (nm/min)</th>
<th>RI</th>
<th>Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIPAVMS</td>
<td>208</td>
<td>13.9</td>
<td>1.97</td>
<td>-1849</td>
</tr>
<tr>
<td>BTBAS</td>
<td>136</td>
<td>13.6</td>
<td>1.97</td>
<td>-1034</td>
</tr>
</tbody>
</table>

Example 3

Under process condition A listed in Table 1, but an alternative tool and showerhead configuration, the stress of films deposited increases as the number of vinyl groups increases in precursor.

TABLE 3

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Vinyl groups</th>
<th>Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIPAVMS</td>
<td>1</td>
<td>-1200</td>
</tr>
<tr>
<td>BIPADVS</td>
<td>2</td>
<td>-1705</td>
</tr>
</tbody>
</table>

1. A method to increase the intrinsic compressive stress in plasma enhanced chemical vapor deposition (PECVD) of silicon nitride (SiN) and silicon carbonitride (SiCN) thin films, comprising depositing the film from an amino vinylsilane-based precursor.

2. The method of claim 1 wherein the amino vinylsilane-based precursor is selected from the formula: [RR"N]SiR^3, (R^3).

where x+y+z=4, x=1-3, y=0-2, and z=1-3; R, R^4 and R^2 can be hydrogen, C_1 to C_10, alkane, alkenes, or C_4 to C_12 aromatic; each R^2 is a vinyl, allyl or vinyl-containing functional group.

3. The method of claim 2 wherein the amino vinylsilane-based precursor is selected from the group consisting of Bis(iso-propylamino)vinylmethyilsilane (BIPAVMS), Bis(iso-propylamino)divinylsilane (BIPADVS) and mixtures thereof.

4. The method of claim 1 wherein the compressively stressed films have a compressive stress of -4 GPa or higher.

5. The method of claim 1 wherein a nitrogen containing reactant is reacted with the amino vinylsilane-based precursor.

6. The method of claim 5 wherein the nitrogen containing reactant is selected from the group consisting of ammonia, nitrogen and mixtures thereof.

7. The method of claim 1 wherein the deposition is conducted at an elevated temperature at or below 500°C.

8. The method of claim 1 wherein the deposition is conducted in the presence of a diluent gas selected from the group consisting of helium, argon, neon, xenon and mixtures thereof.

9. The method of claim 1 wherein the flow rate of the amino vinylsilane-based precursor is 50 to 1000 mg/min.

10. The method of claim 5 wherein the flow rate of the nitrogen containing reactant is 50 to 10,000 mg/min.

11. The method of claim 8 wherein the flow rate of the diluent gases is 50 to 50,000 mg/min.

12. The method of claim 1 wherein the deposited thin film has a compressive stress of -700 to -2400 MPa.

13. The method of claim 1 wherein the deposited thin film has a N—H to Si—H ratio of 25 to 85.

14. The method of claim 1 wherein the deposited thin film has a N—H derived H content cm^2×10^15 in the range of 3.3 to 3.6.

15. The method of claim 1 wherein the deposited thin film has a compressive stress of -700 to -4500 MPa.

16-18. (canceled)

19. A method for depositing a film selected from a silicon nitride film or a silicon carbonitride film comprising:

reacting a nitrogen-containing gas with a precursor having the general formula:

[R"N]SiR^3(R^2)}
where \( x+y+z = 4 \), \( x = 1-3 \), \( y = 0-2 \), and \( z = 1-3 \) and wherein \( R \), \( R' \) and \( R'' \) are individually selected from the group consisting of hydrogen, \( C_1 \) to \( C_{10} \) alkane, \( O_2 \) to \( C_{12} \) alkene, or \( C_4 \) to \( C_{12} \) aromatic; \( R' \) is selected from the group consisting of a vinyl, allyl or other vinyl-containing functional group and wherein when \( R' \) is vinyl, \( x = 2 \), \( y = 0 \), and \( z = 2 \); \( R \) and \( R' \) cannot both be methyl to provide the film.

20. The precursor of claim 19 selected from the group consisting of Bis(isopropylamino)divinylsilane (BIPADS), Bis(isopropylamino)diallylsilane, Bis(t-butyramino)divinylsilane, Bis(t-butyramino)diallylsilane, Bis(diethylamino)diallylsilane, Bis(methylthiylamino)diallylsilane, and Bis(methylthiylamino)divinylsilane.

21. A composition for depositing a film selected from a silicon nitride and a silicon carbonitride film comprising:

- an aminosilane precursor which is at least one selected from the group consisting of Bis(isopropylamino)divinylsilane (BIPADS), Bis(isopropylamino)vinylmethylsilane (BIPAVNS), Bis(isopropylamino)vinylsilane, Bis(isopropylamino)allylthiylsilane, Bis(isopropylamino)allylsilane, Bis(t-butyramino)vinylmethylsilane, Bis(t-butyramino)vinylsilane, Bis(t-butyramino)allylthiylsilane, Bis(t-butyramino)allylsilane, Bis(diethylthiylamino)vinylsilane, Bis(diethylthiylamino)allylsilane, Bis(diethylthiylamino)divinylsilane, Bis(diethylthiylamino)allylsilane, Bis(dimethylamino)vinylsilane, Bis(dimethylamino)allylsilane, Bis(dimethylamino)divinylsilane, Bis(dimethylamino)allylsilane, Bis(methylthiylamino)vinylmethylsilane, Bis(methylthiylamino)vinylsilane, Bis(methylthiylamino)vinyilsilane, Bis(methylthiylamino)allylsilane, Dipiperidinovinylmethylsilane, Dipiperidinoallylsilane, and Dipiperidinodiallylsilane.