RELATION BETWEEN FLOW, POWER AND PRESENCE OF CARRIER GAS
DURING PLASMA DEPOSITION OF THIN FILMS

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ABSTRACT

Plasma deposition processes have become an integral part of the manufacturing of microelectronic devices. Control of proper deposition parameters, understanding their relation to the composition of the plasma, and therefore to the film properties, is essential for depositing films in a repeatable and a predictable way.

Using mass spectrometry, we have studied the influence of input RF power, reactant gas flow, and the presence and concentration of carrier gas on the decomposition of a wide range of starting materials used during plasma deposition. It is shown that all three parameters influence the decomposition of the starting material and therefore the composition and properties of the deposit. It is also shown that different degrees of decomposition for different materials cannot always be predicted from the bonding energy between species being dissociated by a plasma.

Using silicon nitride as an example it is shown that the composition of films deposited with various conditions corresponds to the composition of the plasma as measured by mass spectrometry.

INTRODUCTION

Plasma deposition and plasma enhanced chemical vapor deposition of thin films of silicon nitride, oxide and oxynitrides are established as important processes in manufacturing microelectronic devices. The main uses of films made in such a way are as passivation and diffusion barrier layers.(1-3) More recently attempts were made to use silicon nitride as gate insulators in thin film transistors.(4-5) Plasma deposition of such films has been studied in great detail and there is a huge body of literature describing both the deposition conditions and properties of the materials. The main concern of the literature is the properties of deposited materials as they relate to the application in the semiconductor industry. The deposition parameters are studied only as they relate to the final properties and less emphasis is placed on the technological aspects and chemistry involved.

The purpose of this paper is to study, using mass spectrometry, the influences of the deposition power, reactant gas flow, and presence and flow of inert carrier gas on the decomposition of NH\textsubscript{3}, N\textsubscript{2}O, SiH\textsubscript{4} and other starting materials used in plasma deposition. Particular attention will be paid to the relation between the plasma composition and the composition of the deposit.
EXPERIMENTAL

The mass spectrometer measurements and film depositions described in this study were made in the vacuum system shown schematically in Fig. 1. This system is a plasma discharge reactor utilizing a continuous flow of the reactant gases and parallel plate electrodes. The size of the bell jar is 46 x 76 cm. The electrodes are capacitively coupled and are supported by a magnetron structure to confine the primary glow to a "racetrack" on the electrode surface. The electrodes are shown schematically in Fig. 2. The gases were introduced into the bell jar directly into the glow area and if more than one gas was employed they were premixed before introduction into the bell jar. The pressure in the system was measured using an MKS Baratron capacitance probe and was maintained constant during each experiment by controlling the pumping rate.

A 13.56 MHz power supply with a power density in the racetrack region of 0.1 - 5.0 w/cm$^2$ was used. During the depositions, substrates to be coated were placed on a grounded plate located in the center between the electrodes. To obtain uniform deposition, the substrates were rotated perpendicularly to the racetrack. The distance between the electrodes was 5 cm. All the depositions were made with substrates at room temperature and without dilution of the reacting gases.

In order to monitor the gas phase a MA-1 Bendix time-of-flight mass spectrometer was attached to the system. The sampling point at the mass spectrometer (MS) inlet was placed at the location of interest in the given experiment. Since the distance between the sampling point and MS chamber was about 50 cm only relatively stable species could be measured.

Film composition was evaluated using Rutherford back-scattering.

The thickness and index of refraction (n) of the films were determined by ellipsometry. A commercial ellipsometer (O.E. Rudolph and Sons, Inc.) and a computer program developed by McCrackin(6) for calculating the thickness and index of refraction of the films were used.

Fig. 1
Schematic of the plasma deposition system

Fig. 2
Magnet arrangement in the electrode
RESULTS AND DISCUSSION

In an earlier work (7-8) we have shown that SiH₄, N₂O, and NH₃ decompose to a different degree for a given power density. This resulted in different quantities of reactant being available for coating forming reaction. Thus coatings of different composition result from the same starting materials at different power densities.

![Graph showing % decomposition vs. power] Fig. 3
Degree of decomposition as a function of power applied to the electrodes for different starting materials

We have investigated several other commonly used starting materials and the degree to which they decompose as a function of power. The results are shown in Fig. 3. It can be seen from Fig. 3 that there are substantial differences when different starting materials decompose in plasmas of the same power density. This should be expected since different materials have different bonding strengths and different levels of energy are needed for activation and decomposition. However, when the degree of decomposition for different materials at constant power is compared with the bonding energy (9) (Table I), it becomes obvious that there are factors other than bond strength that influence the degree of decomposition of various starting materials and in the composition and properties of the coatings.

**TABLE I**

<table>
<thead>
<tr>
<th>Material</th>
<th>% of decomposition at 100 w</th>
<th>Bond strength (K cal/mol)</th>
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</thead>
<tbody>
<tr>
<td>SiH₄</td>
<td>86</td>
<td>71.4</td>
</tr>
<tr>
<td>N₂O</td>
<td>80</td>
<td>40</td>
</tr>
<tr>
<td>NH₃</td>
<td>72</td>
<td>103</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>47</td>
<td>112.3</td>
</tr>
<tr>
<td>CF₄</td>
<td>47</td>
<td>128</td>
</tr>
<tr>
<td>C₆H₆</td>
<td>9</td>
<td>105</td>
</tr>
</tbody>
</table>

One factor influencing the compositions may be the different recombination rates of materials already decomposed. Others may include relative pumping rates of the starting material or their by-products. In
this paper we will limit ourselves to examining the influence of changing flows and pumping rates on the degree of decomposition and film properties.

Fig. 4 shows the degree of decomposition as a function of flow of \( \text{NH}_3 \) and \( \text{N}_2\text{O} \) into the system at constant pressure of 45u and 400W power applied to the electrode. The degree of decomposition for both gasses decrease as their flow into the system increases. The drop is substantial - a ten fold increase in flow has the same result as the change in power from 600W to 50W. This is caused by a decrease in residence time of the species in the glow and a diminished probability of their decomposition. The degree of decomposition drops much faster with flow for \( \text{NH}_3 \) than for \( \text{N}_2\text{O} \). This is consistent with the higher degree of decomposition for \( \text{N}_2\text{O} \) than for \( \text{NH}_3 \) for a given power (Fig. 3). The circled points and crosses on Fig. 4 represent the degree of decomposition for \( \text{NH}_3 \) and \( \text{N}_2\text{O} \) when the increase in flow was obtained by addition of argon rather than the active gas itself. When the increase in flow is obtained by argon addition, we also observe a drop in the degree of decomposition with increased flow. However, it is somewhat smaller than when argon is absent. We believe the small difference in the degree of decomposition when argon is added to the flow is caused by relatively heavy argon ions present in the argon plasma. These ions can by themselves cause additional decomposition of reacting gas.

When a mixture of two gasses is used during the decomposition, an additional factor influences the decomposition of the stining materials and hence the composition of the coating i.e., the pumping rate. Gasses with different densities will be pumped at a different rate by the same pumps and the products of their decomposition will be pumped at still different rates. Therefore any change in the pumping speed during the deposition process (e.g. change in the main valve opening) may cause changes in film composition.
The effect of the influence of pumping rate on the film properties is demonstrated in Fig. 5. Fig. 5 shows the variation of the index of refraction of a silicon nitride coating as a function of argon flow introduced into the system. The introduction of argon causes a change in the index of refraction of the coating from 1.87 to 2.00. Such a change in index corresponds to a change in the N/Si ratio in these films from 1.3 to 0.8. The effect shown in Fig. 5 is a combination of N\textsubscript{2} being pumped faster than SiH\textsubscript{4}, a decreased NH\textsubscript{3}/SiH\textsubscript{4} ratio and, as discussed earlier, the influence of increased total flow resulting in shorter residence times in the glow region for both NH\textsubscript{3} and SiH\textsubscript{4}. Based on the dependence of the index of refraction of such coatings on total flow of reactants (10-11), it is estimated that about one third of the change in Fig. 5 can be attributed to the differences in pumping rate and the rest to the shorter residence caused by the increased flow. To show further that the composition of the coating depends not only on the concentration of starting materials but also on their degree of decomposition in the plasma, we have compared the N/Si ratio in the deposited film as measured by RBS with the calculated ratio of ammonia to silane decomposed and available for reaction at different powers and at constant flow ratio and pressure. The calculations were based on the relative decomposition of ammonia and silane as a function of power and flow.

Results are shown in Table II. The data in Table II are for a SiH\textsubscript{4} flow of 30 sccm, a NH\textsubscript{3} flow of 45 sccm and a pressure of 45u. The ratio for stoichiometric Si\textsubscript{3}N\textsubscript{4} is 1.33.

<table>
<thead>
<tr>
<th>Power Applied to Electrodes (W)</th>
<th>NH\textsubscript{3}/SiH\textsubscript{4} Flow Ratio</th>
<th>Calculated NH\textsubscript{3}/SiH\textsubscript{4} Ratio Available for Reaction</th>
<th>N/Si in the Deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.5</td>
<td>.3</td>
<td>.8</td>
</tr>
<tr>
<td>150</td>
<td>1.5</td>
<td>.55</td>
<td>.91</td>
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<td>200</td>
<td>1.5</td>
<td>.79</td>
<td>1.1</td>
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<tr>
<td>300</td>
<td>1.5</td>
<td>1.02</td>
<td>1.40</td>
</tr>
<tr>
<td>400</td>
<td>1.5</td>
<td>1.17</td>
<td>1.45</td>
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</table>
The data in Table II shows an agreement between the ratio of constituents available for reaction, ammonia and silane, and the composition of the deposit. The discrepancy is probably due to differences in the pumping rate between NH$_3$, SiH$_4$ and their decomposition products.

CONCLUSIONS

The properties of plasma deposited films depend not only on the nature and quantity of starting materials being introduced into a deposition chamber but also on that portion of those materials that are decomposed or activated by the glow. The extent of decomposition and activation is affected by the power density in the substrate vicinity, the gas flow in the system, flows and nature of additional gas flows into the system (both inert and reactive) and the pumping rate of the system.

ACKNOWLEDGMENTS

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REFERENCES


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