BOROPHOSPHOSILICATE GLASS ETCHING IN A FLUORINATED PLASMA: EFFECTS OF BORON AND PHOSPHORUS.


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ABSTRACT

Dry etching of BPSG formed by PACVD was studied using fluorinated plasmas. Constant concentrations of boron and phosphorus were maintained in some films during etching over a wide range of plasma parameters, while for other films the concentrations were varied for selected constant plasma conditions.

1 INTRODUCTION

Several authors (1) have discussed the advantages and utility of BPSG films in MOS device manufacturing. Additional improvements in film properties were also reported using BPSG layers formed by PACVD (2). Considering the future requirements of the VLSI technology, the advantages associated with this film may be enjoyed only if delineation of BPSG is compatible with the rapidly advancing dry etch techniques (3). The films studied in this investigation were deposited by PACVD using a new gas mixture as reported below. Applying much of the knowledge accumulated during a previous study of the etching characteristics of PSG films formed by PACVD (4), the primary focus of this work was the dry etch mechanism.

2 EXPERIMENTAL

All of the films were formed on 100 mm diameter, (100) oriented silicon, using a commercially available Semy Eng. reactor, operating at 410 kHz. The deposition was performed using 100 % SiH4, 3 % PH3 Diluted in Ar, 0.5 % B2H6 diluted in N2, and NO. The concentration in the films was determined by Chemical Analysis (ICP). Dry etching of these films was then performed in different fluorinated plasmas, CHF3 + O2, CF4 + O2, and SF6 + O2, using a commercially available Hexode-style, RIE system from Applied Materials Inc. that operated at 13.56 MHz. The film thickness was always measured just before and after each process. To assure unambiguous data, previous thermal treatments were not
performed on these films. The standard film was doped with 2% P and 1.3% B, with a refractive index of 1.487.

3 RESULTS

Some of the previous experiments on PSG films were performed using constant power conditions and measuring the resulting D.C. bias associated with the plasma. To provide comparable data, the same absolute values for total gas flow were used. Figure 1 shows the etch rate of the standard film as a function of the R.F. power delivered by the automatic matching network. A linear correlation with power was found for all plasmas, indicating that a rate-limited mechanism exists for the generation of active species. In addition, the D.C. bias developed for each power condition was measured and compared with the trend in etch rate. Realizing that the etch rate may be a strong function of the free flourine available in the discharge, it was necessary to consider the following bonds that are involved for each gas mixture:

<table>
<thead>
<tr>
<th>CHF₃</th>
<th>CF₃ + H</th>
<th>104 kCal/m</th>
<th>98 kCal/m</th>
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</thead>
<tbody>
<tr>
<td>CHF²</td>
<td>CHF₂ + F</td>
<td>113 kCal/m</td>
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</tr>
<tr>
<td>CF₄</td>
<td>CF₃ + F</td>
<td>129 kCal/m</td>
<td>116 kCal/m</td>
</tr>
<tr>
<td>CF₃</td>
<td>CF₂ + F</td>
<td>88 kCal/m</td>
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</tr>
<tr>
<td>SF₆</td>
<td>SF₅ + F</td>
<td>68 kCal/m</td>
<td></td>
</tr>
<tr>
<td>SF₅</td>
<td>SF₄ + F</td>
<td></td>
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</table>

From energy consideration (5), the breaking of S-F bonds is more favorable than for C-F bonds. Experimentally, the observed etch value differences shown in Fig. 1 refutes this hypothesis. A comparison of the absolute values measured for both etch rate and D.C. bias voltage indicated a close relationship. Considering that in a RIE configuration the effect of ion bombardment is more significant towards etching than the chemical effect, the experimental observations seem to support the superimposition viewpoint suggested elsewhere (6). The different D.C. bias generated for constant power and flow conditions is directly related to the different electrical behavior of the plasma, i.e. impedance.

The second series of experiments were designed to demonstrate the effects of pressure on the same plasmas, as shown in Fig. 2. For these experiments, it was observed that the D.C. bias was inversely related to the pressure. It should also be noted that the residence time increased from approximately 4 seconds to approximately 20 seconds. As a result, for CF₄ and CHF₃, a sharp increase in the etch rate was found in increasing the pressure from
20 mT to 40 mT. Continuing to increase the pressure finally shows a decrease in the etch rate as a result of the decrease in the D.C. bias. For the SF6 plasma, the slope of the etch rate curve follows the slope of the D.C. bias. Recalling from (7), that Vdc = 2Vpp and Vpp/P is a function of active species rate generation, the reduced etch rate at higher pressures is understandable. For this case, it was also observed that the D.C. bias was essentially constant at a value of about 10 volts over a relatively wide pressure range. In the low pressure regime, i.e. (20-50 mT), it was found that a change in Vpp/P is dominant with respect to a pressure change, i.e. the flourine available, coupled with the high D.C.bias voltage is sufficient to assist in providing a high etch rate, even with a low residence time. It was previously pointed out (8), that by adding O2 to the flourine-based plasma, it is possible to sustain the etching rate. In these experiments, the six different O2 flows reported in sccm in Fig. 3 were used for each plasma. For these flows, the maximum difference in residence time was approximately 4 seconds. It is clear that for both CF4 and CHF3, the increase in etch rate resulting from the addition of a small amount of O2 is large. This is suggested to be due to the mechanism proposed by several authors (9). It is further suggested that the presence of greater than 10% O2 in the discharge may result in a competition between F and O in a CF4 plasma that is sufficient to suppress the chemical etch component, leaving only the sputtering component to provide the etch yield. For CHF3, this phenomenon is not so evident as the recombination process associated with the presence of the H does not affect the etching.

In the SF6 plasma, for this range of O2, stable behaviour accompanied with stable values of D.C. bias was observed. The final experiment using the standard film was performed as a function of the total flow of etchant gas, as shown in Fig. 4. In the CHF3 plasma, deposition of a thin, teflon-like polymer film on the BPSG surface was found at high flow rates, as is already well-known to be typical for this chemistry (10). The shape of the curve for the CF4 etch rate suggests that increasing the flow results in a power-limited situation, i.e. the efficiency of the discharge is not optimized. For SF6, the shape of the curve may be divided in two sections: the lower one for working in the low flow rate regime, i.e. less than 40 sccm, and an upper section for flow rates above 40 sccm. In the upper section, a significant decrease in etch rate was observed due to a reduction in residence time. This phenomena was not observed for either CF4 or CHF3 plasmas. It is proposed that the reason for this are respectively as follows:

a) the concentration of active species is so high that the decrease in residence time is completely masked, and

b) the role of polymer formation obscures other effects.

The second family of experiments concerns the role of dopant inside the film. All the films were etched using constant plasma parameters.

Table 1 summarizes the physical properties of these films. As clearly shown in Fig. 5, a markedly different behaviour was found for boron and phosphorus. It was possible to produce a boron variation over only a narrow
range. For this range, a purely physical etch was observed. In contrast, a chemical etch of phosphorus-doped films was seen, as previously reported for PSG (4). In Fig. 5, the curves marked as '1' refer to the etch rate versus boron concentration, and the curves marked '2' refer to etch rate versus phosphorus concentration.

4 CONCLUSION

BPSG film deposited by PACVD was studied in flourine plasma chemistries over a wide range. It was observed that the yield was related more to high D.C. bias voltages than high flourine concentration. In addition, neither contamination nor residues of any kind were found using SF₆ and CF₄ plasmas, whereas for CHF₃ polymer formation occurs at high flow rates. The presence of phosphorus dopant inside the film alters the etch rate with a spread in values. Over the experimental range studied here, it may be concluded that the presence of boron does not affect the etch behavior of BPSG.

5 REFERENCES

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Fig. 2

Table 1

<table>
<thead>
<tr>
<th>film type</th>
<th>n</th>
<th>P wt/o</th>
<th>B wt/o</th>
</tr>
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<tbody>
<tr>
<td>low B</td>
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<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>medium B</td>
<td>1.487</td>
<td>2</td>
<td>1.3</td>
</tr>
<tr>
<td>high B</td>
<td>1.478</td>
<td>1.5</td>
<td>1.2</td>
</tr>
<tr>
<td>low P</td>
<td>1.468</td>
<td>0.6</td>
<td>1.3</td>
</tr>
<tr>
<td>medium P</td>
<td>1.487</td>
<td>2</td>
<td>1.3</td>
</tr>
<tr>
<td>high P</td>
<td>1.490</td>
<td>5</td>
<td>0.7</td>
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