Characterization and Control of Native Oxide on Silicon

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Characterization and control methods of native oxide growth on silicon (Si) surfaces at room temperature and during the temperature ramp-up are described. The native oxide growth on HF-cleaned Si surfaces can be controlled by lowering oxygen or water concentration in process ambience at room temperature and by passivation of Si surface for semiconductor processes at temperatures higher than 300 °C. In situ control methods of native oxide growth for semiconductor processes are developed based on analyses of factors dominating the native oxide growth.

1. INTRODUCTION

The characterization and control of native oxide growth on Si surfaces is essential in the fabrication of ultra large-scale integrated devices. The presence of native oxide on Si surfaces degrades low-resistance contact formation, low-temperature growth of high-quality epitaxial Si films, and high-quality gate oxide formation. Native oxide is unintentionally grown on Si surfaces under conditions before each process. The native oxides can be classified by growth condition parameters such as temperature and ambience as summarized in Table 1. Here, the uncontrolled oxide grown at elevated temperatures is defined as a type of native oxide.

In this paper, we discuss the factors controlling the native oxide growth in air and in ultrapure water at room temperature$^{1-5}$ and during the wafer temperature ramp-up in each process system,$^{9}$ and present in situ control methods of native oxide growth in W/n-Si(100) contact formation,$^{10}$ low-temperature Si epitaxy,$^{10}$ and very thin gate oxide formation$^{7,8}$ processes.

Table 1. Various native oxides.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Ambience</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room temperature</td>
<td>Air</td>
</tr>
<tr>
<td>Room temperature—95°C</td>
<td>Ultrapure water</td>
</tr>
<tr>
<td>Room temperature—95°C</td>
<td>Chemicals</td>
</tr>
<tr>
<td>Elevated temperatures</td>
<td>Process gas, Vacuum</td>
</tr>
</tbody>
</table>

2. NATIVE OXIDE GROWTH AT ROOM TEMPERATURE

The native oxide can be quantitatively analyzed by x-ray photoelectron spectroscopy (XPS).$^{3}$ Figure 1 shows Si_{2p} XPS spectra measured for native oxides on HF-cleaned n–Si(100) surfaces exposed to air at room temperature for various lengths of time, where the take-off angle of photoelectrons is 35°. The oxidation–induced chemically-shifted peak is easily observed after exposure to air for 1440 min (1 day), indicating that the native oxide grows for the initial exposure time. The peak from native oxide for 2880 min (2 days) overlaps with that for 1440 min (1 day). The native oxide growth for the additional exposure time of 1440 min (1 day) is minimal. The peak intensity increases during the period from 2880 min (2 days) to
21600 min (15 days). The peak does not change during the additional exposure of 21600 min (15 days). Therefore, XPS measurements clearly exhibit the step-wise increase in the native oxide thickness.

The amount of native oxide can be expressed as the film thickness by the calibration of the intensity ratio of SiO2 XPS signals from oxide to that from the Si substrate with thermal oxide film thickness measured by ellipsometry. The native oxide grown in air indicates a successive step-functionlike increase in native oxide. This is also observed in the measurement of physical thickness with atomic force microscope (AFM) calibrated by ellipsometry. These results suggest that layer-by-layer oxide growth occurred on HF-cleaned Si surfaces at room temperature. The native oxide hardly grows at all in air when the H2O concentration is suppressed bellow 0.1ppm. This shows that the native oxide growth on the HF-cleaned Si surface at room temperature requires the coexistence of oxygen and moisture.

The oxide thicknesses on n-Si wafers in ultrapure water at room temperature increase with increasing immersion time and dissolved oxygen concentration. This result suggests that the native oxide growth is suppressed in ultrapure water by decreasing the dissolved oxygen concentration. The initial growth rate of native oxide on n'-Si is very high. The oxide thickness on n'-Si also reduces as the dissolved oxygen concentration decreases.

3. OXIDATION AFTER HYDROGEN THERMAL DESORPTION

The thermal desorption spectra of hydrogen, oxygen and water from the HF-cleaned Si surface indicate that hydrogen is desorbed at about 300°C and has peaks at 400°C and 520°C, and intensities for both oxygen and water decrease at approximately 500°C and 800°C. The thermal desorption characteristics of hydrogen from the HF-cleaned Si surface in one atmospheric pressure Ar gas is reported to be similar to that in vacuum. The increase of oxygen concentration on the Si surface at about 500°C, as measured by XPS, coincides with the first consumption of oxygen and water. These results indicate that the desorption of hydrogen from the HF-cleaned Si surface occurs from about 300°C, and that the Si surface reacts with oxygen and water at temperatures higher than 500°C.

4. NATIVE OXIDE CONTROL IN SEMICONDUCTOR PROCESSES

Figure 2 shows contact resistances of W/n'-Si(100) contact areas. In a nitrogen gas sealed process, the Si wafer is chemically etched with diluted HF acid, rinsed in water with low dissolved oxygen concentration (20 ppb), and dried by N2 gas blowing in N2 sealed wet cleaning equipment, and then transported by N2 wafer carrier to the chemical vapor deposition (CVD) system, in order to suppress native oxide growth in ultrapure water and in gas ambient. In a conventional process, HF dipping, ultrapure water rinsing, N2 gas blowing and wafer transportation are carried out in clean room air. The resistance of the contact formed by the nitrogen gas sealed process is smaller than is seen in the conventional process, as reported for Al/n'-Si(100).

Figures 3 (a) and (b) show reflection electron
5. CONCLUSION

In situ control methods for the native oxide growth on Si surfaces are developed based on its ability for the enhancement of process performances. In situ control methods require no additional process step. Consequently, these methods promote high performance processing and investment savings.

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