In situ ATR-FTIR analysis of TDMAH adsorption on silicon(111) and metallic thin films

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Introduction

- Hard disk storage is by far the most important member of the storage hierarchy in modern computers, as evidenced by the fraction of system cost devoted to that function.
- Heads and media used in extremely high recording density hard-disk drives are protected against corrosion and wear by an overcoat.
- Hafnium dioxide can be a good candidate for this overcoat application due to its mechanical characteristics and thermal and chemical stability.

In situ analysis of ALD process by ATR-FTIR

- Atomic layer deposition (ALD) is a promising way to make thin HfO2 films on silicon wafer or other substrates. However some concerns still exist in HfO2 ALD studies, such as interfacial layer formation and presence of foreign atoms, which will affect the electrical properties of the films.
- The beginning of the ALD reaction between the precursor and substrate surface is quite important for us to understand the whole process.
- As a nondestructive and highly sensitive surface analysis method, ATR-FTIR (Attenuated total reflection- Fourier transform infrared spectroscopy) can be used to do an in situ analysis of the chemical reactions during deposition and process evaluation.
- Schematic of ATR configuration

Experimental setup

- Schematic diagram of ATR-FTIR system
- Tetrakis dimethylamido hafnium (TDMAH) was used as hafnium precursor in this research. The adsorption behavior of TDMAH molecules on H-terminated silicon crystal (111), platinum thin film coated silicon crystal, germanium crystal and zinc selenide crystal (ZnSe) was analyzed by in situ ATR-FTIR

Results

- Peak Assignment

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>3100</td>
<td>3.0</td>
</tr>
<tr>
<td>2800</td>
<td>2.5</td>
</tr>
<tr>
<td>1600</td>
<td>0.5</td>
</tr>
<tr>
<td>1100</td>
<td>0.2</td>
</tr>
<tr>
<td>800</td>
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</table>

Comparison of DFT generated vibrational spectrum to TDMAH liquid drop measurement

IR spectra under different crystal T were compared. The emergence of peak Hf-OH indicated the beginning of the decomposition of TDMAH.

Oxidation of TDMAH on ZnSe crystal

Under room temperature, TDMAH molecules were adsorbed on the ZnSe crystal in our vacuum ATR system. Oxidation happened when the crystal was exposed to the air.

Peak assignment of air oxidized TDMAH

This spectrum was taken after a long time crystal exposure to the air. The apparent peak happened around 1580cm⁻¹ was assigned to Hf-OH stretching mode.

Conclusion

- Density Functional Theory was used to modeling the TDMAH adsorption on Si crystal, which matched well with the liquid drop experiment.
- At 160°C the TDMAH molecule begins to thermally decompose, which is indicated by the emergence of Hf-OH vibration peak in the IR spectra.
- The adsorption of TDMAH on Si(111) and Pt coated Si under 160°C doesn’t saturate but proceeds multilayer adsorption complicating ALD process design.
- The adsorption on platinum thin films gets enhanced IR absorption due to the surface roughness or surface-plasmon effect.