

In-Situ ATR-FTIR of Hafnium (IV) Tert-Butoxide Adsorption and Decomposition on Ge

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INTRODUCTION

Attenuated Total Reflectance (ATR) FTIR is widely used by researchers to examine a variety of sample types including solids, powders, pastes and liquids for food analysis, biomedical applications, polymers, and thin films. In addition to the identification of functional groups during more routine analysis, ATR-FTIR spectroscopy is useful for mechanistic studies of vapor-solid inter-actions during chemical vapor deposition or heterogeneous catalysis by *in situ* real time monitoring of surface species¹. These experiments typically require the IR beam to exit the spectrometer, pass through a vacuum system or pressure reactor containing the ATR crystal and gas phase molecules of interest via IR transparent windows, and finally to return to the spectrometer for detection.

In this note, a [Horizon™](#) accessory in conjunction with a heated trough-plate design with VCO vacuum fittings was used to introduce gaseous reactants to the vicinity of a heated ATR crystal element under low pressure in order to observe absorption and decomposition of Hf (IV) t-butoxide (HTB) on Ge. HTB is a widely used organometallic precursor for HfO₂, and a leading candidate to replace SiO₂ gates in metal oxide semiconductor field effect transistors (MOSFETs).^{2,3} With this method, adsorption of hafnium tert-butoxide (HTB), was observed.

EXPERIMENTAL

The Horizon™ accessory (Figure 1) with a Ge crystal element was placed in the sample compartment of an

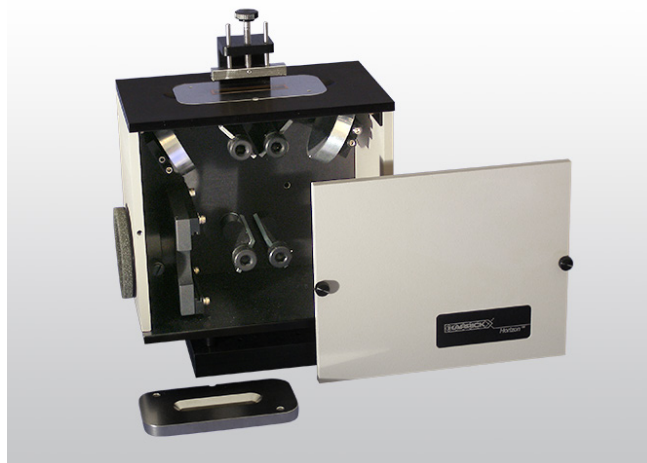


Figure 1. The Horizon™, shown here with its solid sampling plate.

FTIR spectrometer. The inlet of the flow-through cell was connected via VCO fittings with Kalrez gaskets to a heated gas line (50-55°C) for delivery of the HTB through a gas-liquid bubbler at a temperature of 52°C. HTB is a clear liquid at room temperature with a vapor pressure of 1 torr at 65°C.³ The outlet of the flow through cell was connected to a 2.3 ft³min⁻¹ rotary vane pump resulting in a pressure of 1 torr in high throughput mode measured by a convection pressure gauge on the outlet side and with a flow rate of 5 sccm of N₂ carrier gas plus 0.67 sccm of HTB when vapor-liquid equilibrium is assumed. Before the experiment the Ge ATR crystal was cleaned with trichloroethylene and dipped in a buffered 1:500 hydrofluoric acid solution to remove the native oxide and to obtain an H-terminated surface.⁴ A back-

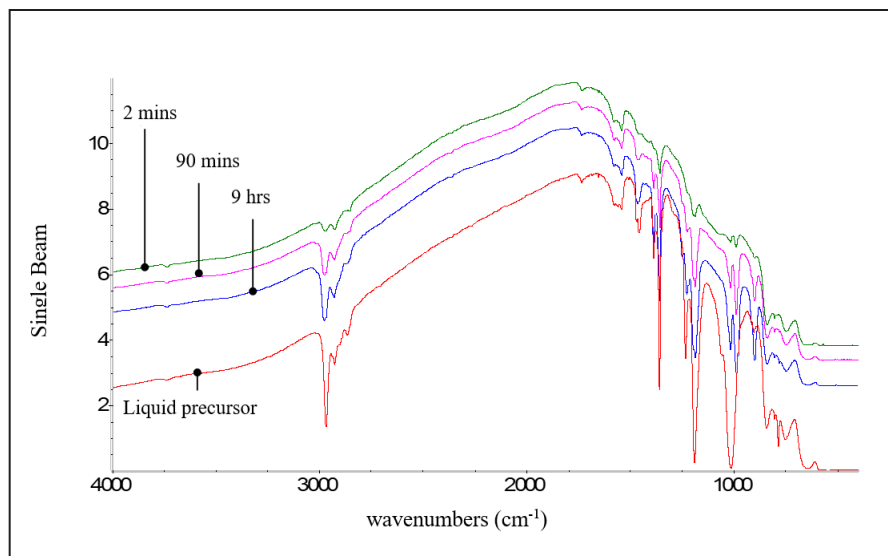


Figure 2. Single beam spectra of adsorbed HTB on Ge at 100°C and 1 torr and applied liquid precursor at atmospheric pressure and room temperature

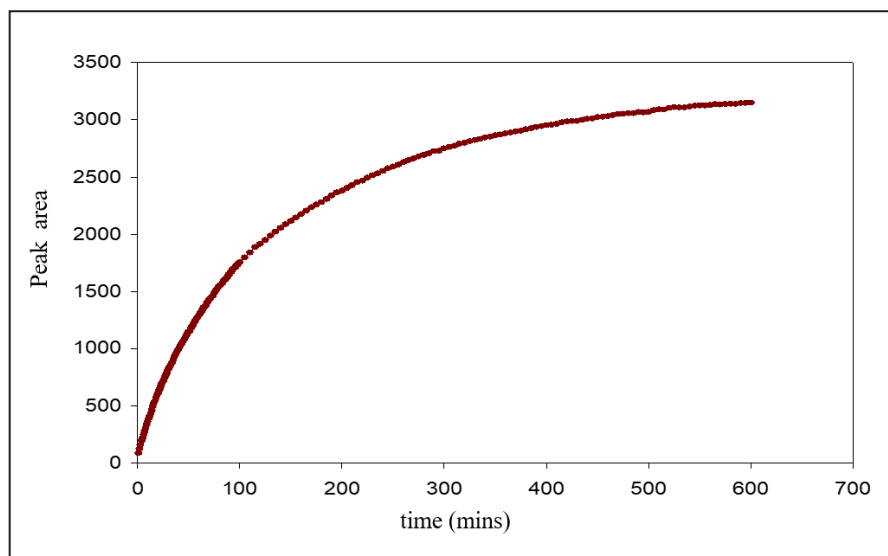


Figure 3. C-H stretch peak area vs. time for HTB absorption on Ge crystal at 100°C and 1 torr.

ground spectrum was recorded for an ATR crystal temperature of 100°C under 0.01 torr pressure without N₂ or HTB flow. Using N₂ as the carrier gas, HTB vapor was delivered to the ATR cell where the crystal was maintained at 100°C, with a total pressure of 1 torr. During the exposure of precursor on the crystal surface, IR spectra were collected at 5 min intervals. For comparison, liquid HTB was directly applied to the crystal under an inert atmosphere and an IR spectrum was collected at room temperature and atmospheric pressure.

RESULTS AND DISCUSSION

A Ge crystal was chosen instead of the more application relevant Si (100) surface as Ge has a wider range of IR transparency. Figure 2 shows the single beam spectra obtained after 2 min, 9 min, and 9 hrs as well as the applied liquid HTB for comparison. Absorbance peaks between 3000-2800 cm⁻¹ are due to *asym* and *sym* C-H stretches of the tert-butyl groups, and are a useful feature for monitoring surface coverage of the precursor.⁵

Figure 3 shows the time dependence of the C-H stretching mode peak area as it increases and then saturates. The saturated absorbance is 5% lower than the applied liquid value indicating that the thickness of a physisorbed layer may have exceeded the depth of penetration of the evanescent wave.

Absorbance peaks in the lower wavenumber region, 1500 to 500 cm^{-1} , are attributed to C-O (1230cm^{-1}), Hf-O-Ge (1017cm^{-1}), Hf-O-C (985cm^{-1}) and Ge-O (900cm^{-1}) stretching and are shown in Figure 4 with the liquid applied HTB for comparison. Some major differences between the applied liquid and vapor adsorption experiments elucidate the chemical bonding of the precursor to Ge. Specifically, the observed Ge-O and Hf-O-Ge stretches, which are absent in the liquid HTB measurement, show the HTB molecule bonds to the surface through oxygen atoms.

CONCLUSION

The Horizon™ ATR accessory was used to observe the adsorption and decomposition of HTB vapor molecules on a heated Ge crystal and the spectra were compared to HTB applied as a liquid drop to the crystal element at room temperature. The spectra indicate attachment of the HTB groups through Hf-O-Ge bonds. The results show that ATR-FTIR is an extremely useful surface sensitive

technique to determine functional groups and bonds *in situ* during thin film deposition at moderately elevated temperatures and under vacuum.

ACKNOWLEDGEMENT

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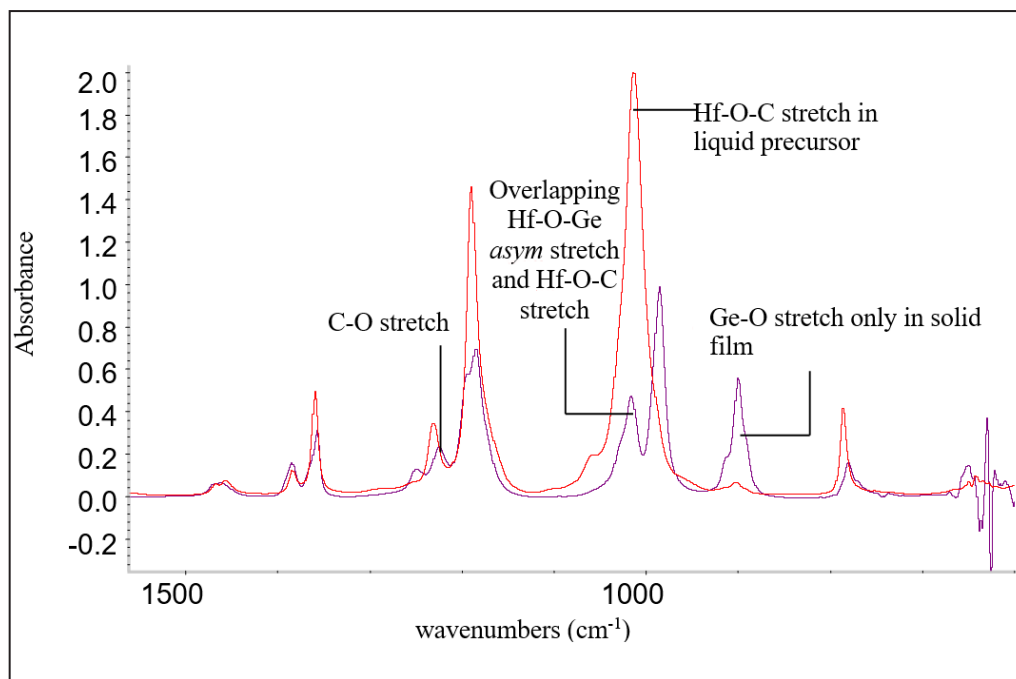


Figure 4 Absorbance spectrum of adsorbed HTB on Ge at 100°C and 1 torr (purple) and applied liquid precursor at 1 atm and 25°C (red).