

REAL-TIME CHEMICAL SENSING IN THIN FILM MULTICOMPONENT CVD

Theodosia Gougousi, Department of Materials and Nuclear Engineering and Institute for Systems Research, University of Maryland, College Park, MD 20742-3285

Yiheng Xu, Department of Materials and Nuclear Engineering and Institute for Systems Research, University of Maryland, College Park, MD 20742-3285

Laurent Henn-Lecordier, Department of Materials and Nuclear Engineering and Institute for Systems Research, University of Maryland, College Park, MD 20742-3285

John Kidder Jr., Department of Materials and Nuclear Engineering and Institute for Systems Research, University of Maryland, College Park, MD 20742-3285

Gary W. Rubloff, Department of Materials and Nuclear Engineering and Institute for Systems Research, University of Maryland, College Park, MD 20742-3285

Charles R. Tilford, National Institute of Standards and Technology, Process Measurement Division, Gaithersburg, MD 20899

ABSTRACT

A quadrupole mass spectrometer (QMS) and an acoustic sensor have been used for real-time process monitoring and thickness metrology in W-CVD ($3\text{ H}_2 + \text{WF}_6 \rightarrow \text{W} + 6\text{ HF}$) using an Ulvac cluster tool. The QMS recorded the time evolution of the partial pressures for the reactants (H_2/WF_6) and the HF product, while the acoustic sensor monitored variations in the average molecular weight of the gas mixture in the reactor through the process cycle. Integrated signals from both sensors gave *in-situ* thickness estimates accurate to within ~7% cf. actual post-process thickness measurements, despite the poor reactant conversion rate (just a few percent) in the tool. For mainstream processes involving blanket CVD, where much higher conversion rates (~50%) are typical, we expect thickness metrology capability in the range of 1-2%, making these techniques attractive for thickness metrology and associated process control, in addition to fault detection and process chemistry determination.

INTRODUCTION

In this paper we present the use of two commercially available compact sensors, an RGA (Residual Gas Analyzer) and an acoustic sensor, for real-time process-status monitoring and thickness metrology in a W CVD process. In addition, we have used the RGA-based metrology for run-to-run process control and for fault detection. Due to space limitations, we will not be able to provide details on the metrology establishment and present examples on all these applications. However, the interested reader may find more details in upcoming publications (1),(2).

EXPERIMENT

An RGA is a compact Quadrupole Mass Spectrometer (QMS) that is widely used for vacuum failure/contamination detection. The instrument used for this work is a Leybold-Inficon 300 CIS Transpector 2. The Leybold-Inficon Composer measures the resonance frequency of an acoustic cavity, a parameter that depends on the average molecular weight of the gas filling the cavity. Although such a sensor can not identify the individual components of a multicomponent gas mixture, it is very sensitive on even small variations in the composition of the gas mixture due to process, equipment or vacuum failures. Both sensors have specific pressure operation requirements ($P < 10^{-5}$ torr in the quadrupole region for the RGA, and $P > 50$ torr in the cavity for the Composer) and are attached to the reactor via suitable sampling systems.

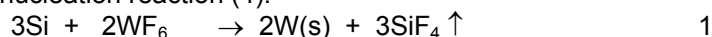
The experiments are carried out with an ULVAC ERA-100 cluster tool that is equipped with two cold wall CVD reactors, a load lock, and a buffer chamber. Heating lamps positioned outside and above the reactor provide heating to the wafer. The gas supply system is designed so that H_2 is delivered through a quartz

showerhead on the top of the reactor, and the WF₆ through a slit inlet at the wafer lever. The tool operation is limited to pressures below 1 torr, which is significantly lower than the 40 torr industrial standard for the same process. As a result the reagent conversion is very poor, limited to only a few percent. A more detailed description of the tool can be found in an upcoming publication (3).

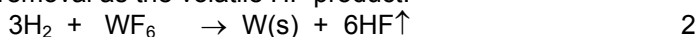
All the RGA experiments presented in this article are performed at 0.5 torr, temperature around 350-400° C, with flow rates of 40 sccm for H₂ and 10 sccm for WF₆. The composer experiments are performed under similar conditions except for WF₆ flow rates that is 5 sccm.

The films are deposited on 4" (10 mm) Si wafers that undergo HF cleaning (10% HF in H₂O), de-ionized (DI) water rinsing and N₂ drying.

When H₂ and WF₆ molecules collide with a heated Si surface initially a seed W layer covers the surface via the fairly rapid self-limiting nucleation reaction (4):



Once W covers the entire available Si surface, it provides the active sites for the H₂ reduction of WF₆ through adsorption and F atom removal as the volatile HF product.



For each W atom deposited on the wafer, one molecule of WF₆ and 3 molecules of H₂ are consumed and 6 molecules of HF are produced. Both the SiF₄ and the HF gas phase products have been identified by the RGA.

The RGA monitors in real-time the partial pressures of both reagents and the HF product while the composer records the influence of the changes in the gas-mixture average molecular weight on the acoustic cavity resonance frequency. We will demonstrate that the HF and H₂ RGA signal as well as the composer signal is correlated with the thickness of the produced W film. The film thickness is calculated from the wafer area, the known W density and the measured film weight (by weighing the wafer before and after the deposition with a microbalance).

The process cycle is fairly complicated including purging steps in the beginning and the end of the cycle, a background, a wafer heating and a signal recording step. The background step was introduced so as to provide a baseline for both the RGA (H₂ and HF) and the composer signals. The background and the deposition signal recording steps are of equal duration to facilitate integrated signal comparison.

RESULTS

For the establishment of the RGA-based metrology both the HF (see Fig. 1a) and H₂ signals undergo significant mathematical manipulation: initially both the background and the deposition signals are integrated for a time period equal to the deposition time. Subsequently the background signal is subtracted from the deposition signal to determine the net reaction HF production (the opposite for H₂ so as to determine the reagent depletion), and the result is normalized to the background signal. Finally, the normalized signal is multiplied by the deposition time to derive a signal (S_{HF} and S_{H₂} for the HF and H₂ data respectively) proportional to the extent of the reaction. This somewhat lengthy analysis of the data is necessary so as to correct for errors resulting from sensor/process drifts. The relationship between the W film thickness and the HF and H₂ normalized mass spectrometer signals is given on Fig. 2a and 2b. In both cases the data exhibit good linearity with the HF data providing a more accurate metrology due to the larger signal to background ratio.

For the HF product the regression analysis generates the expression:

$$\text{Film thickness (nm)} = 30.99 (\pm 3.94) + 53.00 (\pm 1.74) * S_{\text{HF}}$$

For the H₂ data the regression line is given by the expression:

$$\text{Film thickness (nm)} = 41.56 (\pm 7.98) + 586.19 (\pm 43.14) * S_{\text{H}_2}$$

The positive y-intercept in both metrology graphs is attributed to the nucleation reaction 1. The existence of this step is confirmed by the observation of SiF_3^+ (major product of the SiF_4 fragmentation) in the mass spectrum, and the thickness indicated by the regression analysis is in very good agreement with nucleation experiments we performed and with other measurements in the literature (5),(6).

Deposition of W on the heated wafer leads to depletion of the reagents H_2 and WF_6 and generation of the gaseous HF product resulting in a change in the average molecular weight of the gas filling the acoustic cavity. This is accompanied by a very distinguishable change in the cavity resonance frequency between the background and the deposition steps (see Fig. 1b). For metrology purposes the average film thickness is plotted as a function of this frequency difference (Δf). The relationship is fairly linear (Fig. 2c) and described by the expression.

$$\text{Film thickness (nm)} = 4.76 (\pm 5.90) + 4.44 (\pm 0.26) * \Delta f$$

Both the RGA HF-based metrology and the composer-based metrology have an accuracy of about 7% as determined by statistical analysis of the data. For the H_2 -based metrology the accuracy is somewhat worse, about 15%.

CONCLUSIONS

In this paper we present the application of two commercially available, compact sensors, a CIS-RGA and the Composer acoustic sensor for real time chemical sensing and thin film thickness metrology in a W-CVD process. Both sensors estimate the average film thickness within ~7% of the post process measurement. In many ways, this application is a worst case test for both techniques due to the very poor reagent utilization (process operated at 0.5 torr compared with 40 torr industrial standard), extraneous sources of signal and the high reactivity of reagents and products (for more details see (1)). For processes with reasonable reagent conversion (around 50%), H_2 is expected to provide the best RGA-metrology signal, free of many of the complications associated with the HF monitoring. For such processes, the metrology for both sensors is expected to improve significantly in accuracy (1-2%), making both techniques attractive for run-to-run or real-time process control applications.

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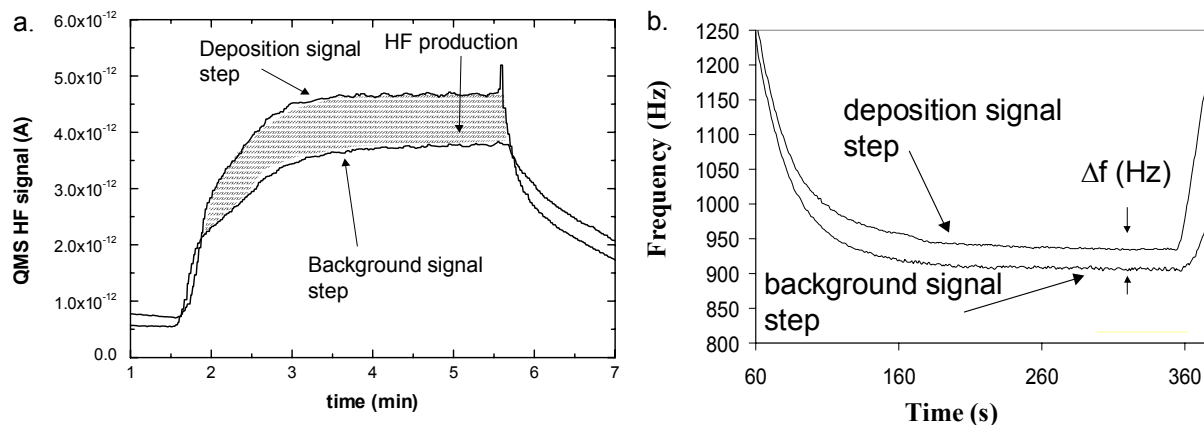


Figure 1.a. Overlay of the background and the deposition step HF signals for a 4 min deposition process. The difference in the level is the HF product of the W deposition reaction. The large HF background signal is mainly due to Hf generating reactions in the RGA ion source **b.** Overlay of the cavity resonance frequency vs. time plots for the deposition and the background steps of a typical deposition process. The change in the resonance frequency is due to the reagent depletion and the HF formation during W deposition.

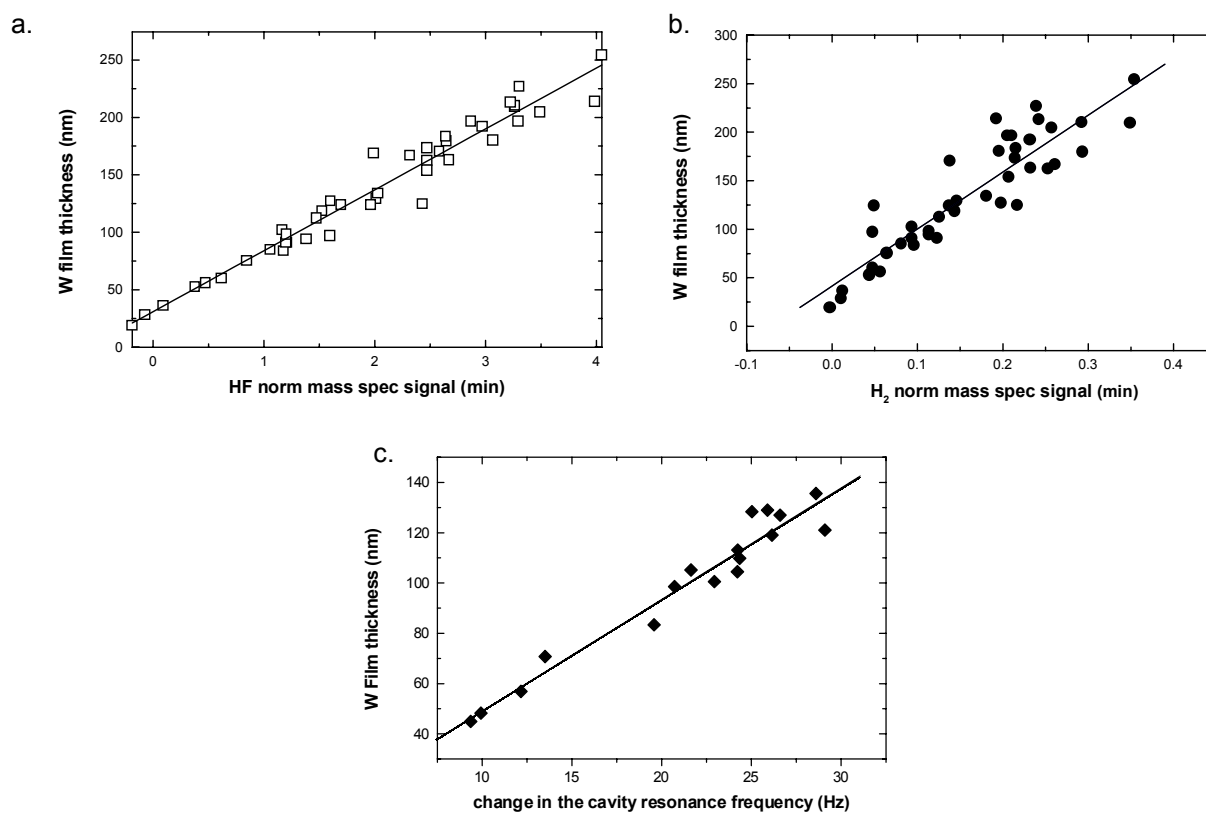


Figure 2. a. A plot of the average W film thickness vs. the HF mass spectrometer signal (normalized HF production above background times deposition time). **b.** A plot of the average W film thickness vs. the H_2 mass spectrometer signal (normalized H_2 depletion times deposition time). **c.** A plot of the average W film thickness vs change in the resonance frequency of the acoustic cavity. In all three plots, the solid line is a linear regression through all data points.