Real-time process sensing and metrology in amorphous and selective area silicon plasma enhanced chemical vapor deposition using *in situ* mass spectrometry

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(Received 11 July 1996; accepted 1 November 1996)

We have used mass spectroscopy to observe and analyze, in real-time, gas phase reactants and product species in plasma enhanced chemical vapor deposition (PECVD) of silicon. We describe a doubly differentially pumped mass spectrometry system to sample the exhaust stream of a large area plasma CVD reactor operating at 0.4–1.5 Torr. We show real-time quantitative analysis of silane consumption and hydrogen production for deposition of hydrogenated amorphous silicon and for pulsed-gas selective area silicon deposition. The ability of mass spectrometry to observe process faults in real time is also demonstrated. Mass spectroscopy is a useful nonintrusive process-state sensor for real-time metrology of plasma deposition, for example, to quantify gas phase species, and to characterize reactions occurring on the substrate surface. Based on our results, we discuss potential advanced manufacturing applications of real-time mass spectrometry in amorphous silicon and selective area silicon plasma deposition, including indirect wafer-state sensing, fault analysis and classification, and run-to-run and real-time process control. © *1997 American Vacuum Society.* [S0734-211X(97)01701-0]

I. INTRODUCTION

Increasing demands for improved product yields, throughput, and reproducibility in semiconductor manufacturing will require real-time process sensors for reaction monitoring, equipment analysis, and control.[1] Plasma enhanced chemical vapor deposition (PECVD) and etching processes used in semiconductor device manufacturing involve complex gas and surface reactions that are difficult to analyze, quantify and predict. Plasma deposition of hydrogenated amorphous silicon (*a*-Si:H) is widely used in active-matrix liquid crystal displays,[2] and the ability to sense the chemical process in real time could significantly impact the manufacturing of these devices. Also, low temperature plasma enhanced selective area silicon deposition offers advantages in thin film transistor fabrication and performance,[3,4] but is not currently used in manufacturing, in part because of perceived process complexity, and sensitivity to process fluctuations and chamber conditions. Monitoring of this process in real-time could lead to process improvements, and enable the transition of this process into a manufacturing environment.

Sensors that detect gas phase reactant and product species are ''process-state'' sensors, whereas, techniques that directly observe the deposited or etched surface are ''wafer-state'' sensors. Process-state sensors can be used to improve process reliability, for example, by quantifying run-to-run repeatability, detecting and characterizing process faults and perturbations, and by qualifying reactor preparation during conditioning or plasma cleaning steps.

Various techniques have been used as process-state sensors during thin film deposition and etching, including plasma optical emission interferometry[5] and quadrupole mass spectrometry.[2,6–9] Quadrupole mass spectrometry has been used as a real-time sensor in rapid thermal CVD of silicon,[6] epitaxial silicon CVD,[7] electron cyclotron resonance CVD of SiO_2,[8] and silicon nitride PECVD.[9] Mass spectrometry is attractive for gas phase process analysis and characterization because it is a relatively simple and robust technique for sensing neutral and ion species, and its application to residual gas analysis is well known. Mass spectroscopy also meets many of the criteria of an ideal *in situ* process sensor: it is relatively inexpensive, it can be used without disturbing the process itself, it requires only minor modifications of existing equipment, and it can be sensitive to equipment and process variations over a broad range of process conditions.

New approaches for real-time process sensors that are simple to implement and give direct information regarding the plasma process chemistry need to be developed for run-to-run and real-time process control. Run-to-run process control involves post-process comparison of equipment and process data to a simulation or reference data set. Information is then fed back, and set point deviations are adjusted for the next run. In real-time process control, the sensor and simulated data sets are compared and analyzed as the data is collected, and corrections are fed back as the process proceeds.

In this article, we show that mass spectroscopy can be a valuable real-time process-state sensor for plasma deposition. We describe a two stage differentially pumped quadrupole mass spectrometric sensing tool that we have constructed that shows sensitivity to both equipment and process

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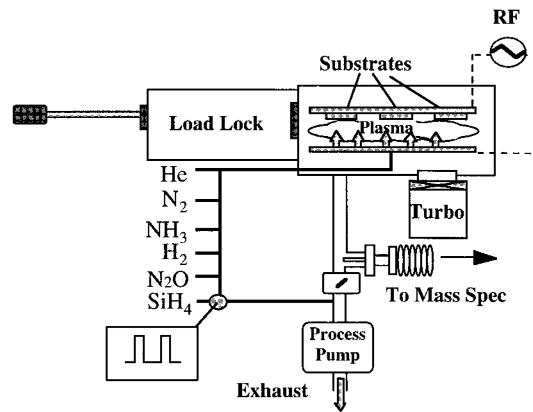

FIG. 1. Plasma CVD reactor used for thin film deposition. The deposition area is approximately 33×35 cm^2, and the mass spectrometer senses the exhaust stream as shown.

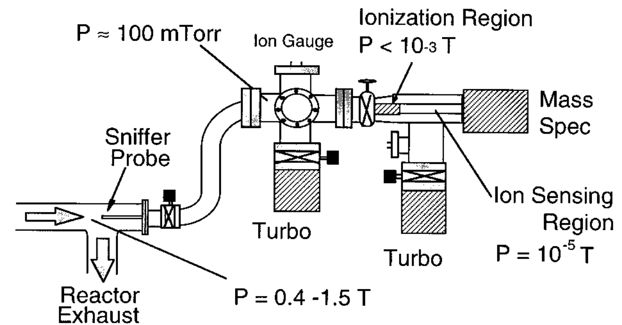

FIG. 2. Schematic of the double differentially pumped mass spectrometer sensing apparatus. The sniffer in the reactor exhaust is connected to the first pressure reduction stage through a flexible hose. Typical pressures in the exhaust, pressure reduction stage, ionization region, and ion sensing region during operation are indicated.

perturbations. We show process-state data obtained in real-time for plasma CVD, and use the data for ''process metrology'' to quantify and interpret the reactions occurring in the system. Specifically, for amorphous silicon deposition, we observe the extent of reaction in real time, and characterize the effect of process conditions on reaction stoichiometry. In pulsed-gas selective deposition, we observe silane depletion during deposition, and silane production (etching) during hydrogen plasma exposure. In addition, we show an example of real-time fault detection, and discuss other applications of real-time mass spectroscopic analysis in plasma deposition.

II. EXPERIMENTAL SYSTEM AND PROCEDURE

A. Silicon deposition processes

Film deposition studies were performed on a large area PECVD reactor shown in Fig. 1. Substrates are transferred through a load lock, and the reactor base pressure is 1×10^{-8} Torr. The plasma is powered at 13.56 MHz and the deposition pressure is between 0.4–2.0 Torr. Substrates are loaded face down on the grounded electrode which has an area of 40.5 cm×42 cm. Gas is delivered through a showerhead array of holes in the powered electrode which has an area of 33 cm×35.5 cm. The inter electrode spacing is 3 cm. Silicon deposition was performed using silane gas of 99.999% purity from Voltaix Inc. Amorphous silicon films were deposited using 50 standard cubic centimeters per minute (sccm) of SiH_4 at 0.4 Torr, substrate temperature of 250 °C, with rf power held constant between 10 and 50 W. Typical deposition time was 10 min, resulting in *a*-Si:H films with thickness between 500 and 2500 Å. In this reactor, we have also analyzed a pulsed-gas flow process for selective area silicon PECVD, where SiH_4 flow is modulated into a H_2 plasma.

For selective deposition, we used silane and hydrogen with flow rates of 10 and 1500 sccm, respectively. Typical process conditions are 1.5 Torr pressure, 70 W rf power, and a substrate temperature of 250 °C. Hydrogen gas flows continuously, while the silane flow is periodically pulsed into the reactor, or into the exhaust well downstream from the mass spectrometer sniffing point. The gas pulse cycle times are typically 20 s for deposition (silane flows into the system), followed by 50 s for hydrogen exposure (silane bypasses the system into the exhaust). Under these conditions, repeating the gas modulation for 100 cycles results in approximately 700 Å of silicon selectively deposited on silicon, with no deposition on glass or silicon dioxide surfaces.

B. Mass spectrometric process sensing system

A two stage differentially pumped mass spectrometric process sensing system has been developed for real-time sensing of the plasma process, and a schematic is shown in Fig. 2. The system is arranged to sample the exhaust port, but the system design will allow us to use the same mass spectrometer to sense the plasma directly. In its present configuration, the sensing system consists of a changeable sniffing aperture (1.5 mm) attached to a 6 in. long 1/4 in. SS tube connected through a T connector to the exhaust of the PECVD tool. The butterfly valve for reactor pressure control is downstream from the sniffer port, so that the pressure in sampling area is the same as in the deposition zone. The first pumping stage consists of the sniffer tube, connected with a flexible tube to a chamber, with a 50 ℓ/s turbomolecular pump to reduce the pressure to near 10^{-3} Torr. For the apertures used, and a reactor pressure of 1.5 Torr, the flow in the thin sniffer tube is in the transition zone between molecular and viscous flow regimes, and the flow is molecular in the larger flexible tube and the chamber. At a process pressure of 0.4 Torr, the flow is close to molecular in the sniffer tube and molecular in the first stage. Under these flow conditions, the absolute measured concentrations are expected to be affected by differences in diffusivity and pumping rate, whereas the relative values will not be significantly affected. Therefore, the gas composition at the aperture leading into the mass spectrometer can be related to the composition of the gas at the sniffer aperture in the reactor exhaust. From the first stage, gas flows through an aperture into the ionization region of the quadrupole mass spectrometer. We have used an MKS PPT430 quadrupole mass spectrometer with a 0–300 amu range. This unit is configured with a partial enclosure

around the ionization region, allowing the ionizer to be maintained at a higher pressure (10^{-4}–10^{-3} Torr) than at the filament in the housing manifold (10^{-7}–10^{-5} Torr). The signal is collected in the Faraday cup. The pressure in the manifold is maintained with a 50 ℓ/s (N_2) turbomolecular pump.

The mass spectrometric sensor system was designed using a fluid-mechanical gas flow model to determine the aperture sizes for optimum pressures in each zone of the sensor system. The model was constructed as a dynamic simulator including a throughput balance and standard conductance expressions.[10] In the simulation, using the desired reactor pressure, known volumes of each pumping zone, and the given pumping speeds, we adjust the aperture sizes and estimate pressure in the first pumping stage and in the ionization and ion sensing regions of the mass spectrometer. We then choose the aperture sizes to optimize the signal intensity in the mass spectrometer for the particular process being analyzed. For the amorphous silicon deposition experiments at 0.4 Torr, the sniffer aperture was 1.5 mm, and the mass spectrometer input aperture was 0.23 mm. For the selective silicon deposition at 1.5 Torr, the same apertures were used, with a larger pump on the mass spectrometer manifold. These apertures were not precisely optimum, but gave good signal-to-noise performance, and were sufficient for the initial experiments reported here.

Spectral data for both amorphous silicon and selective silicon deposition was collected at 2, 30, and 31 amu, corresponding to H_2^+, SiH_2^+, and SiH_3^+ fragments of SiH_4, respectively. The data was collected using a dwell setting of 8 for each mass point monitored, corresponding to approximately a 1 s collection time for a data set containing three mass points.

III. RESULTS

A. Hydrogenated amorphous silicon deposition

The overall reaction for silicon deposition from SiH_4 can be written as

$$SiH_{4(g)} \leftrightarrow Si_{(s)} + 2H_{2(g)}. \quad (1)$$

In plasma processes, in addition to deposition, silicon is often consumed in undesired homogeneous reactions that form higher silanes. With these reactions, the silicon mass balance is given by

$$Si_{Input} = Si_{Output} + Si_{Deposited} + Si_{Homogeneous}, \quad (2)$$

where Si_{Input} represents the total amount of silicon flowing into the reactor (as silane) over a given time, $Si_{Deposited}$ is the amount of silicon deposited on the substrate and on the chamber walls, $Si_{Homogeneous}$ is the amount of silicon consumed in gas phase reactions, and Si_{Output} represents the silicon not consumed in the reaction and output through the exhaust. The value for Si_{Input} is directly proportional to the silane partial pressure measured by the mass spectrometer system, prior to initiating the plasma. The value for Si_{Output} is measured while the plasma is on, and generally depends on process conditions. Real-time signals obtained at 30 and 2 amu corresponding to the SiH_2^+ silane fragment and H_2^+ respectively, are plotted as a function of time in Figs. 3 and 4. In Fig. 3 the rf power was 40 W, and 20 W was used for the data in Fig. 4. These experiments were conducted at 0.4 Torr, 250 °C with 50 sccm SiH_4. Each plot shows the signal baseline (plasma off, before and after the run) and the signal when the plasma is running. The baseline signal at 2 amu corresponds to hydrogen produced during the cracking of SiH_4 in the ionizer. The change in the baseline signal before the plasma is initiated is observed because an insufficient filament warm-up time was used in these early runs. When the plasma is initiated, we observe a distinct decrease in the silane related signal, and a sharp increase in the hydrogen related signal, indicating real-time sensitivity to silane con-

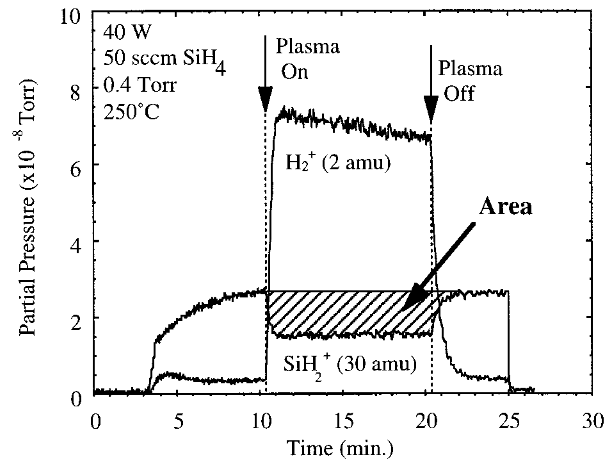

FIG. 3. Real-time hydrogen (2 amu) and silane (30 amu) signals vs time during amorphous silicon deposition at 40 W of rf power. The SiH_2^+ signal is proportional to the silane partial pressure in the reactor. The total deposition time was 10 min and the times at which the plasma was turned on and off are indicated. The integrated area corresponds to the silane consumed during the deposition.

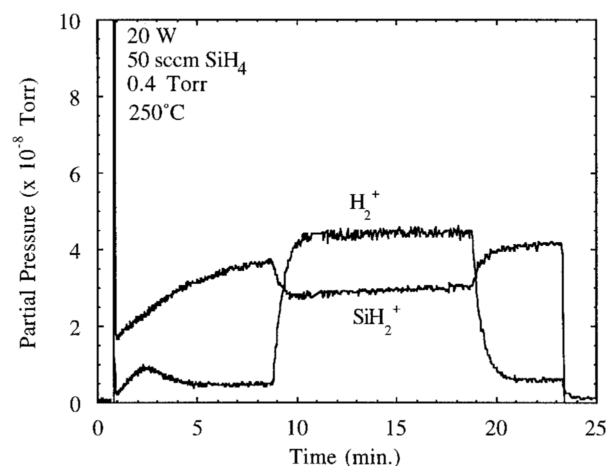

FIG. 4. Real-time mass spectrometer signal for amorphous silicon deposition at 20 W shown on the same scale as in Fig. 3. All other conditions are the same as those used in Fig. 3. The large signal at 1 min resulted from the initial flow of gas into the sensor.

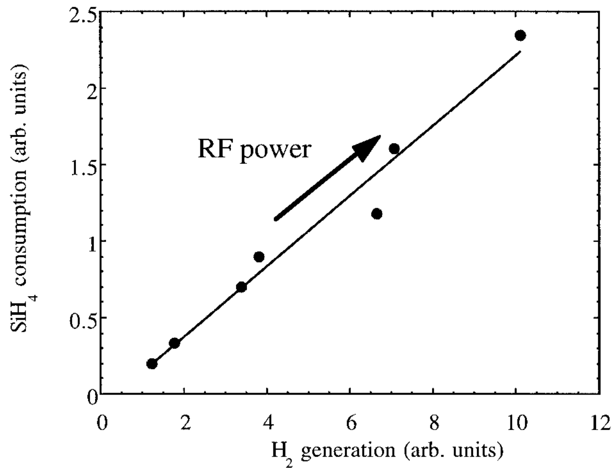

FIG. 5. Correlation between SiH_4 consumption and H_2 generation calculated from time integrated differential area under the SiH_2^+ and H_2^+ signals as shown in Fig. 3. The linear trend observed indicates stability in overall reaction stoichiometry with changing rf power.

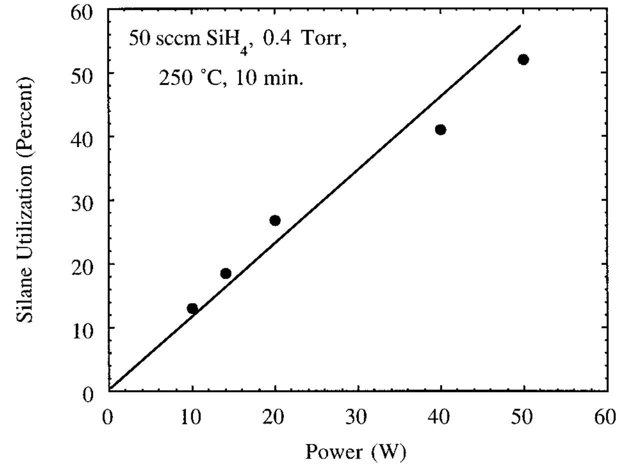

FIG. 6. Silane utilization plotted versus rf power, showing a linear increase in utilization with power.

sumption and hydrogen production during plasma deposition. The decrease in the silane signal from the baseline represents the difference $Si_{Input}-Si_{Output}$ so that the integrated signal over the run time corresponds to silicon lost to deposition and homogeneous reactions. Comparing Figs. 3 and 4, the integrated difference is clearly larger for the larger value of rf power, consistent with the observed higher deposition rate. The integrated decrease in the silane related signal at amu 30 is compared to the integrated increase in the hydrogen signal in Fig. 5. A linear trend is observed indicating that the stoichiometry of the overall reaction does not change appreciably with varying conditions.

The data in Figs. 3 and 4 can also be used in real-time to determine the extent of the silane consumption in reaction (1) and the silane utilization fraction. Silane utilization is defined as the ratio $(Si_{Input}-Si_{Output})/Si_{Input}$, where the input value is the baseline, and the output is the average value over the run period. Silane utilization is plotted versus rf power in Fig. 6. The data shows the relatively low silane utilization in this process, with a linear increase in silane consumption with increasing rf power.

Real-time process sensing can also be used for fault detection. An example fault during amorphous silicon deposition detected in real-time is shown in Fig. 7. After 2 to 3 min into this run, we noted that the silane (amu 30) and hydrogen (amu 2) signals showed an erratic behavior, which led us to inspect the reactor. The plasma was fluctuating and the automatic matching network was not correctly tuned. By manually adjusting the matching network for 1–2 min, the plasma was stabilized, and the run proceeded. The data in Fig. 7 clearly shows the effect of plasma instability and network tuning on the gas phase reactant and products in real time.

B. Plasma enhanced selective area silicon deposition

Substrate selective silicon deposition can be achieved at low temperature by plasma enhanced processes using time modulated flow of silane into a hydrogen plasma. Selective deposition allows silicon to be deposited only on receptive areas of a patterned substrate, and be eliminated from other areas. The mass spectrometry system has been used to analyze the silane and hydrogen gas output during plasma enhanced pulsed-gas selective area silicon deposition using the process conditions described above. Figure 8 shows the intensity of the amu 30 silane signal plotted versus time for both the plasma off and plasma on conditions. With the plasma off, the sensor clearly shows the time dependence of the SiH_2^+ signal corresponding to the partial pressure modulation. The asymmetric shape, with a gradual tail after silane flow is turned off, is due to the gas residence time in the chamber. From an exponential fit we estimate the residence time to be ~5 s, consistent with the known flow rate and pressure, and the estimated reactor volume. When the plasma is turned on, the silane signal in Fig. 8 shows a similar time

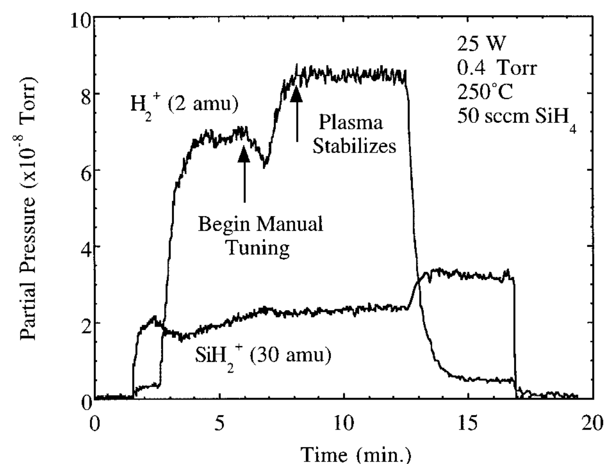

FIG. 7. Real-time SiH_2^+ and H_2^+ signals for an amorphous silicon deposition run where a process fault is observed. The plasma fluctuated for the first 3 min due to improper tuning of the plasma. The plasma was tuned manually for 1–2 min, then the process stabilized for the final 5 min.

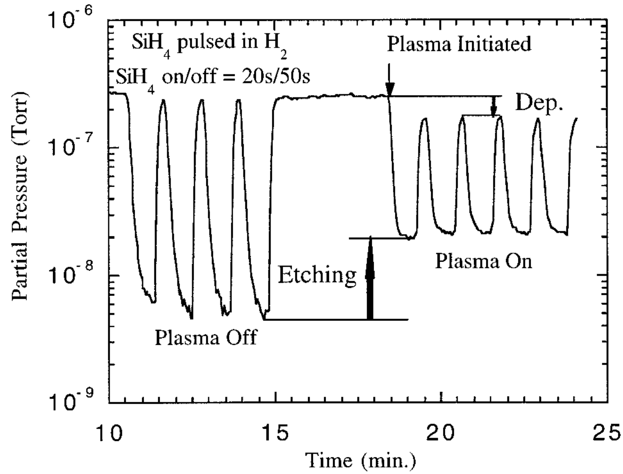

FIG. 8. SiH_2^+ signal vs time during selective area silicon deposition with modulated gas flow. The time dependence is consistent with the gas residence time in the chamber. Note that when the plasma is initiated, the maximum silane signal is reduced, corresponding to deposition, and the minimum silane signal is enhanced, corresponding to etching.

dependence as in the plasma off condition. However, when the plasma is turned on, the silane signal during the time that silane flows to the reactor is smaller than measured when the plasma is off. Also, during the time that silane bypasses the reactor, turning the plasma on results in larger signal than when no plasma was present. When silane flows to the reactor, the silane signal is expected to decrease due to deposition when the plasma is initiated, similar to data in Figs. 3 and 4. During the part of the cycle where silane bypasses the reactor, the larger silane signal when the plasma is on results from etching of silicon by atomic hydrogen in the plasma. This difference between the plasma on and plasma off states is more clearly shown in Fig. 9 where the signal intensities before and after plasma initiation are superimposed. Integrating the difference between the plasma on and plasma off

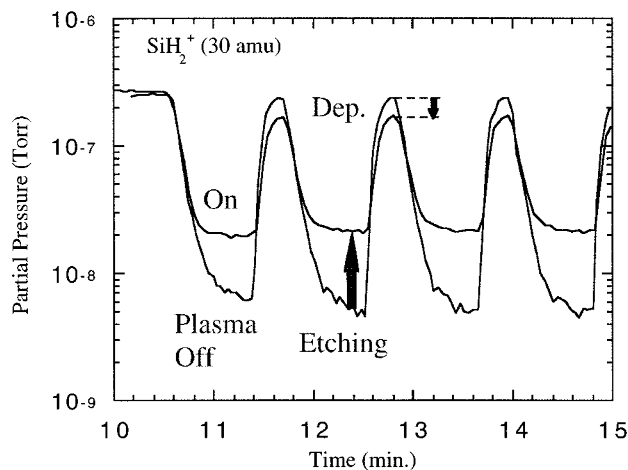

FIG. 9. SiH_2^+ signals with and without plasma from Fig. 8 superimposed on a logarithmic scale to show the difference due to deposition and etching. The integrated silane consumption per gas-pulsing cycle is a factor of 2–3 larger than the silane generated during the etching.

signals on the logarithmic scale indicates that the amount of silane lost to deposition is a factor of 2 to 3 larger than the amount of silane produced during the hydrogen exposure (etching) cycle.

Using the ''pulsed gas'' process, selective deposition proceeds as follows: when the silane flows to the reactor, a thin layer of silicon (typically less than 50 Å) is deposited on all substrate surfaces. The structure and bonding in this thin nucleated layer is dependent on the structure of the substrate surface. When silane flow is diverted from the chamber, the thin silicon layer is exposed to atomic hydrogen generated in the plasma. Atomic hydrogen is sensitive to the structure of the deposited surface, and is likely to insert into more highly strained Si–Si bonds. The difference in nucleation of thin silicon layers on different substrates results in a higher preference for etching by atomic hydrogen. The ability to tune the deposition thickness and the hydrogen exposure time allows us to achieve selective area deposition on a variety of substrates. This picture of the selective deposition process has been developed through a series of experimental results.[3,11,12] However, the mass spectroscopic results presented here are the first direct demonstration that etching by atomic hydrogen is a critical process for achieving selective deposition.

IV. DISCUSSION AND CONCLUSIONS

The data presented above shows that quadrupole mass spectroscopy can be a valuable diagnostic tool during plasma deposition of silicon to obtain equipment, process, and chemical information in real-time. For amorphous silicon deposition processes, we have shown that reactant and product signals are clear and discernible, and that mass spectroscopy can give immediate information concerning the reactor state, including gas phase species and concentrations, before, during, and after deposition proceeds. For this analysis, we routinely use collection times near 1 s per mass set, which is sufficient resolution in reactor systems where the typical gas residence time is a few seconds or more. Similar to other studies of mass spectroscopy sensing of rapid thermal CVD processes,[6] we find that using mass spectrometry for real-time analysis of plasma deposition can give significant insight into the deposition reaction chemistry. Through measurements of silane utilization and analysis of reaction stoichiometry, for example, process mechanisms and performance can be easily analyzed. This could be used to improve process design and efficiency. Also, by developing a correlation between the silane utilization and the film thickness, mass spectrometry may be suitable as an indirect wafer-state sensor for on-line process metrology in manufacturing.

As shown in Fig. 8 above, the mass spectrometer is useful for real-time fault and fluctuation detection. In intelligent manufacturing systems, a real-time mass spectrometer sensor could be used for fault classification, where data is compared to a simulation output which includes categorized fault modes and potential corrections. Process control may also be important in silicon thin film manufacturing. Run-to-run or real-time control could include real-time mass spectroscopy

for direct and rapid monitoring of multiple gas phase species. Control is then achieved by comparing a reaction data set, including the mass spectrometer and other sensor outputs, with a simulated or previously measured ''optimum'' data set, and making corrections to minimize deviations in real-time, or before the next run.

Selective deposition enables some distinct improvements in thin film transistor device fabrication and performance. For example, self-aligned devices with significantly reduced gate/source overlap capacitance could be formed, which will help enable large resolution large area active matrix display systems. For the pulsed gas selective silicon deposition process, real-time mass spectroscopy can be used to characterize gas flow dynamics, quantify the rate of change of reactants and products in the reactor, and identify product species formed during the etching of silicon by plasma generated atomic hydrogen. Selective deposition techniques are not widely used in manufacturing, in part because of perceived process complexity, and sensitivity to process fluctuations and chamber conditions. Mass spectroscopy could be used to detect and analyze these problems in real-time. The ability to characterize deposition and etching, coupled with real-time fault and reactor analysis, could help enable the transfer and use of selective deposition in a manufacturing environment.

In this article, we have demonstrated that mass spectrometry can be a valuable *in situ* real-time equipment-state and process-state sensor for hydrogenated amorphous silicon and selective area silicon PECVD. The real-time partial pressure analysis allows us to identify and quantify gas phase reactants and product species, evaluate equipment performance, and to sense process faults and fluctuations, demonstrating the suitability of mass spectrometry as an on-line metrology tool. The ability to monitor the process ambient with easily available equipment and only slight reactor modification suggests that mass spectrometry could be a valuable sensor in PECVD thin film manufacturing applications. Coupling these sensors with process simulation capability can allow for fault classification and in-line process control.

ACKNOWLEDGMENTS

The authors acknowledge support from the NSF Engineering Research Center Program through the Center for Advanced Electronics Materials Processing (Grant No. CDR 8721505) and the DARPA High Definition Systems Program, Contract No. DABT 63-94-C-0004.

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