MASS SPECTROMETRY AND POWER MEASUREMENTS FOR KINETICS AND MECHANISM INVESTIGATION OF SILANE GLOW DISCHARGES

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Measurements of silane consumption and hydrogen and disilane generation in an rf silane glow discharge, used for the deposition of a-Si:H, are presented as a function of the actual power dissipated in the discharge as measured by Fourier analysis. The influence of power at constant pressure and the pressure at constant power are discussed in relation to electron impact, surface and gas phase mechanisms.

Introduction

The properties of amorphous hydrogenated silicon films produced by rf silane glow discharges present large differences, beyond the characterization procedure experimental error, even when they are produced under the same conditions. This is partially due to the lack of controllability of the process, besides the large differences between the deposition systems. The only macroscopic parameters that are usually controlled accurately are the total pressure and the flow rate. This inefficiency, coupled with the limited plasma diagnostic techniques, is one of the major problems still encountered in order to understand and control the process. For the case of power, the values usually measured by conventional SWR bridges are not only far from the real values but also there is no constant or linear relation of the real power to that measured [1]. Recent efforts have succeeded in new relatively simple methods for the measurement of the discharge impedance and the accurate calculation of the power actually consumed by the discharge. This has permitted the design of series of new experiments using classic plasma diagnostic techniques, as mass spectrometry, emission and/or laser spectroscopy, or film characterization techniques, at constant power or as a function of power.

In this work, we present our first results using simultaneous measurements of the power consumption, using Fourier analysis of the voltage and current waveforms, and mass spectrometric determination of silane consumption together with the partial pressures of the main neutral gas products. These measurements are performed as a function of power, and as a function of pressure at constant power.

EXPERIMENTAL

The experimental arrangement used in our present work is schematically described in Fig. 1. The glow discharge chamber has been used in the past for depositing device quality a-Si:H films. The details of the chamber design are given in Ref [2]. Briefly the cell is a 160 mm wide, parallel-plate discharge chamber with 55 mm diameter electrodes. The electrodes are cylindrically symmetric having a 25 mm distance. One of the two electrodes is powered by a 13.56 MHZ rf generator isolated with an L-type matching network. Voltage and current signals are measured on the powered electrode lead using a high impedance 1:100 voltage probe and a 0.1 Ω transfer impedance rf current probe. The probe signals are digitized by a Lecroy 9400 oscilloscope and then transferred to the pc for Fourier analysis. The Fourier transform gives the amplitude and phase of the fundamental (13.56 MHZ) and the second through fifth harmonic components, which arise because of the non-linear impedance of the plasma. Voltage and current phases are corrected to account for propagation delays in the cables connecting the probes to the oscilloscope [3]. In addition, the cascade matrix of network of parasitics between the measurement point and the surface of the powered electrode is determined, in order to convert the measured waveforms to those at the powered electrode. A shunt circuit consisting of a coil and a variable capacitor is used for eliminating large displacement currents. Resistive losses on the shunt circuit and the cell's elements are also taken into account [1]. In all our measurements we have excluded the case of powder formation in the gas phase. For this purpose a laser light scattering technique has been applied. More specifically, the beam of a HeNe-laser is shaped into a light sheet and directed

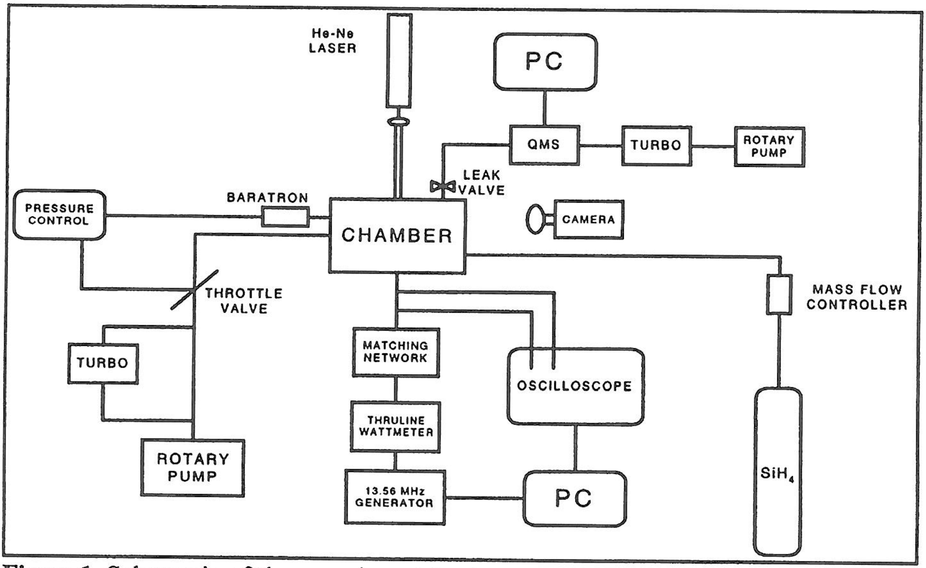

Figure 1. Schematic of the experimental setup.

into the inter-electrode region of the reactor. The scattered light from the particles is observed at right angles to the propagating beam through a monochromator set at the specific wavelength of the laser beam and a photomultiplier. A video camera is alternatively used for observation of the red stray light from particles in the discharge. The gas from the plasma chamber is sampled through a variable leak valve and is analysed by a Quadrupole Mass Spectrometer (QMS) after 70 eV electron impact ionization. The partial pressures of H_2, SiH_4, Si_2H_6, in the reaction chamber are determined by measuring ion currents at values of m/e=2,32, and 62 respectively. In this way, the fragmentation pattern of higher homologues has a minimal contribution to the peaks measured. The partial pressure of a species x is proportional to the respective ion current with the proportionality constant K_x being a function of the leak valve aperture diameter, the mass spectrometer chamber pumping speed for species x and the relative abundance of the ions having the specific m/e value for the parent compound x [4]. These sensitivity constants were directly determined for pure H_2, SiH_4, and Si_2H_6 at exactly the same conditions, by measuring the output current at the above m/e values for various pressures of H_2, SiH_4 and Si_2H_6 in the plasma chamber with no discharge. The slope of each of the obtained least square fittings is used to convert ion currents to partial pressures. The measurements reported here, were performed for certain fixed chamber pressure, flow rate and leak valve aperture. The chamber pressure was kept constant by a downstream throttle valve controller using an MKS 227A Baratron, while the flow rate was independently adjusted to 22 sccm using mass flow controllers. Ultra high purity gases were used at all cases.

RESULTS AND DISCUSSION.

Simultaneous mass spectrometric and power consumption measurements were performed in order to reveal the influence of power and pressure to the consumption of silane and the respective production of hydrogen and disilane. The measurements were performed under mild discharge, low deposition rate conditions that usually lead to low defect density a-Si:H films. The flow, pressure and power conditions used are not favourable to the formation of dust particles in the gas- phase, which is an essential condition in order to have meaningful power consumption and partial pressure results. This condition is continuously controlled by the intensity of laser scattering. This limits the discharge conditions region to be examined from 80 to 200 V for the peak to peak voltage (V_{pp}) and around 100 mTorr for the total pressure. It must be kept in mind that these limits depend on the deposition chamber characteristics (mainly the size of the chamber and the electrodes). In Fig. 2 we have plotted the variation of silane consumption as a function of the discharge power consumption, for a 50 mTorr glow discharge. V_{pp} was varied in the range 100-200 V. Error bars have been calculated by the standard deviation of several measurements at identical conditions. What is obvious from this figure is that there is no simple linear type dependence. In fact the dependence of silane consumption upon dissipated power is of a sigmoidal type with tendency of saturation at low and high power levels respectively. The contribution of the additional silane produced by secondary gas phase reactions, mainly through the reactions of radicals with atomic hydrogen, or from the decomposition of higher silanes, is considered to be negligible.

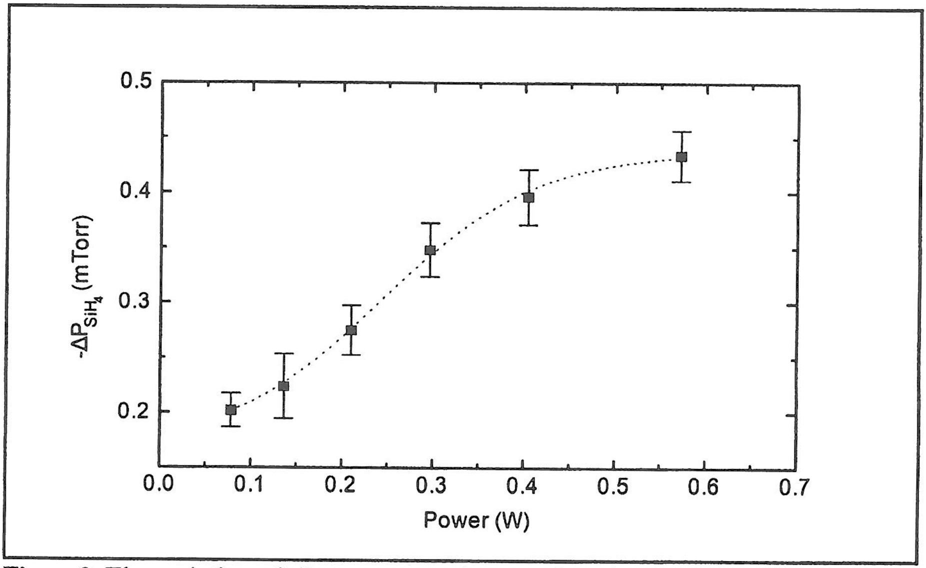

Figure 2. The variation of silane consumption as a function of the dissipated power.

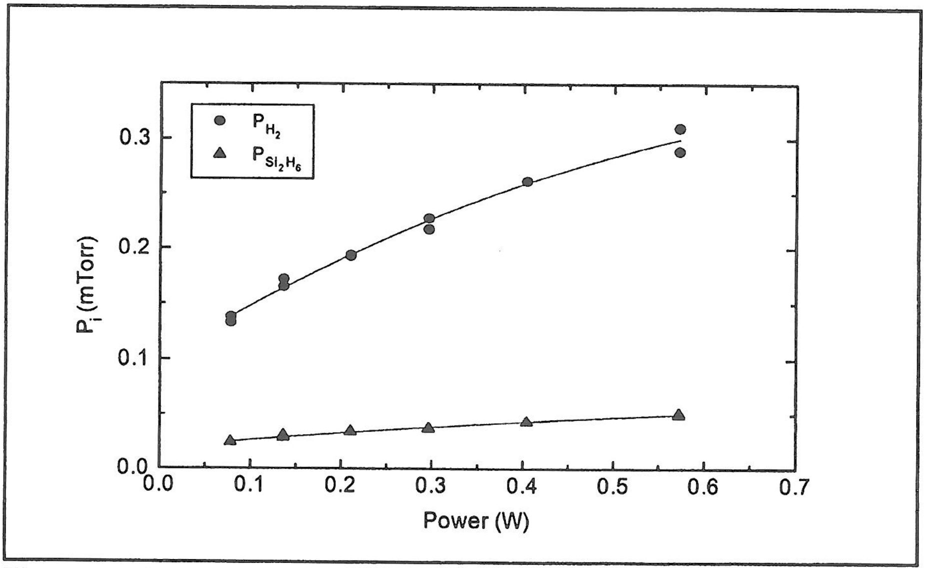

Figure 3 Hydrogen and disilane partial pressures as a function of power.

Therefore, this behaviour depicts the influence of the change in electron heating mechanisms which results in an increase of both electron temperature and electron density. Moreover, only a part of this power is consumed in electron impact dissociation of silane, the rest being spent for momentum transfer, dissociative excitation, ionization and even attachment collisions. As the electron temperature increases the elementary collision processes having higher energy requirements are favoured, thus taking a larger piece of power [5].

On the other hand the outcome of the total reaction scheme towards stable neutral products, is much more influenced by secondary reactions at the surfaces as well as in the gas phase. Therefore, the production of hydrogen and disilane is much more smoothly influenced by the variation of power. This can be seen in Fig. 3 which presents the variation of the partial pressure of these products as a function of power, under the same conditions.

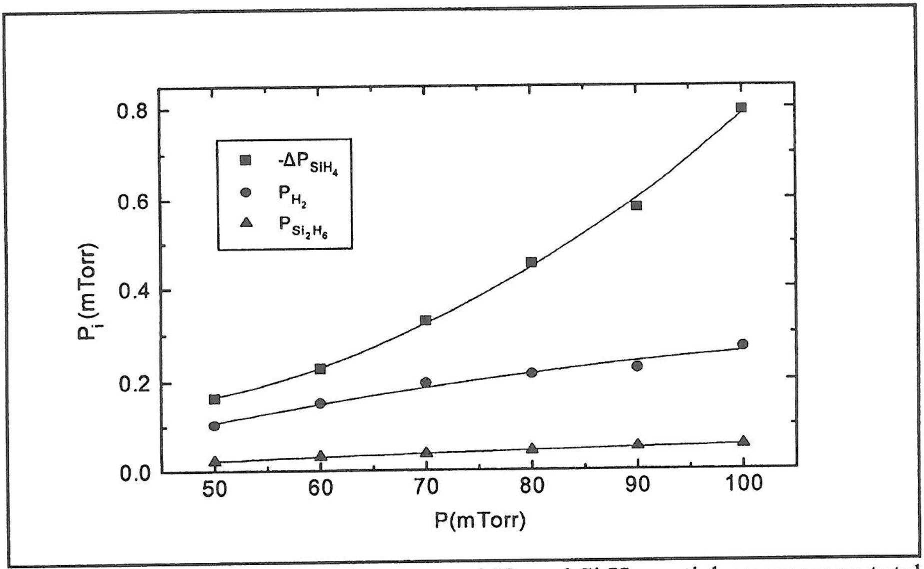

Figure 4. The silane pressure decrease and H_2 and Si_2H_6 partial pressures vs total chamber pressure. The discharge is maintained by an 80 V_{pp} rf driving voltage.

Fig. 4 shows the variation of pressure of H_2 and Si_2H_6 as well as the change in the silane pressure as a function of total chamber pressure, for a constant V_{pp} driving voltage of 80 V. In this case silane consumption has a parabolic dependence upon total pressure, which is generally expected by the increase of both silane and electron density, although one has to take also into account the variation of the electron energy distribution function with pressure, to extract the order of the silane dissociation. In addition, it is important to consider the small but significant change of the power with pressure at constant V_{pp}. Thus, in order to investigate further the influence of both the dissipated power and the process pressure, on the silane consumption we have replotted Fig. 4 with an additional axis for power.

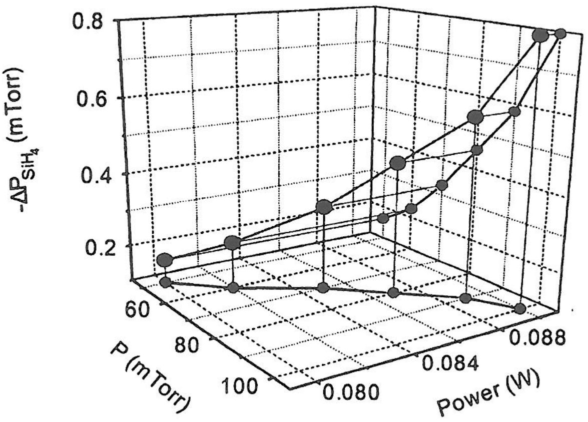

Figure 5. Silane consumption, $-\Delta P_{SiH4}$, as a function of total pressure and dissipated power. V_{pp} is kept constant at 80 Volts.

The results of this plot are represented in Fig. 5. It is observed that for a certain V_{pp} driving voltage, the dissipated power has a dependence upon the process pressure that is drawn on the power-pressure plane.

Conclusions

The variation of silane pressure and of the partial pressures of the main stable products of the electron impact dissociation reveals the complexity of the relation between macroscopic plasma parameters and the primary and secondary gas phase products. The dissimilar trends of silane consumption and product formation depict the differences between electron impact dissociation and secondary reactions chemistry. The first one indicates the importance of the electron heating mechanisms while the second depends on surface and gas phase chemistry.

References

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