Infrared laser-based monitoring of the silane dissociation during deposition of silicon thin films

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The silane dissociation efficiency, or depletion fraction, is an important plasma parameter by means of which the film growth rate and the amorphous-to-microcrystalline silicon transition regime can be monitored *in situ*. In this letter we implement a homebuilt quantum cascade laser-based absorption spectrometer to measure the silane dissociation efficiency in an industrial plasma-enhanced chemical vapor deposition system. This infrared laser-based diagnostic technique is compact, sensitive, and nonintrusive. Its resolution is good enough to resolve Doppler-broadened rotovibrational absorption lines of silane. The latter feature various absorption strengths, thereby enabling depletion measurements over a wide range of process conditions. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3141520]

One of the current major challenges of the thin-film silicon photovoltaic industry is the deposition of hydrogenated microcrystalline silicon (μc-Si:H) in large-area industrial plasma-enhanced chemical vapor deposition (PECVD) systems. A crucial parameter for high-rate deposition of device-grade μc-Si:H is the silane depletion fraction. In a recent study,[1] it has been shown that the growth of μc-Si:H occurs at low silane concentrations in the plasma, i.e., when the input SiH_4 flow is sufficiently diluted in H_2 or when the silane is sufficiently depleted within the plasma. In the latter case, device-grade μc-Si:H can even be grown from a pure SiH_4 flow.[2] In addition to investigations of the phase transition from amorphous silicon to microcrystalline silicon, silane depletion measurements enable—in the absence of polysilane dust particles—the monitoring of the film growth rate, as shown below. Another method to determine *in situ* the amorphous-to-microcrystalline transition is to monitor the SiH_4 density during a short postdeposition H_2 plasma etch.[3]

Prior attempts to directly measure the depletion fraction of silane were based upon mass spectrometers,[4–6] and a Fourier transform infrared spectrometer (FTIR) featuring a typical resolution of 0.5 cm^{-1}.[1,7] While the former are bulky and intrusive, the latter lacks of sensitivity.[8] Recently, optical emission spectroscopy has proven to be a compact and inexpensive technique to measure the depletion fraction in hydrogen-diluted plasmas,[8] but such measurements require the assumption of a plasma model in which the electronic temperature must remain constant. This is typically not fulfilled in dusty plasmas or plasmas with very high silane concentrations.[8] In this letter, we propose to measure the silane depletion fraction under any plasma condition using a tunable IR laser spectrometer.

Silane molecules feature intense rotovibrational absorption lines between 4.35 and 4.76 μm.[9,10] Unfortunately, this is also a mid-IR range that is not easily accessible with current laser sources. Noncryogenic-cooled tunable mid-IR laser sources in this wavelength range were basically limited to complex systems such as optical parametric oscillators and difference frequency generation sources.[11] Nowadays, with the advent of the room-temperature continuous-wave quantum cascade laser (QCL),[12] numerous opportunities are arising in the field of gas analysis.[13–15] In this letter, we operate a Peltier-cooled continuous-wave distributed-feedback QCL (Alpes Lasers SA, Switzerland).[16] Its single-mode emission is tunable between 2241 and 2245 cm^{-1}. This wavenumber range is particularly well suited for silane depletion measurements, as it is free from any known interferences with other absorbing species in the atmosphere. The QCL is mounted in a compact housing of the size of a cigar box. By varying the current supplied to the QCL, the wavenumber is tuned with a slope of −21 cm^{-1}/A. The highly divergent QCL beam is collimated by a telescope consisting of a custom-made Ge aspheric lens and a CaF_2 planoconvex lens. The mid-IR beam is modulated with a mechanical chopper at a frequency of 1 kHz. Before mounting the spectrometer on the PECVD chamber, the beam quality and collimation were controlled using a Hg–Cd–Te camera. Two Ag mirrors guide the mid-IR beam through a 3.7 m long evacuation line. The windows of the evacuation line are wedged to avoid the effect of overlapping multiple reflections. The mid-IR beam exiting the evacuation line is focused on a thermoelectric-cooled Hg–Cd–Te photovoltaic detector. The preamplified detector signal is read by a computer-controlled lock-in amplifier, the reference signal of which is provided by the chopper controller. The whole optical setup is pictured in Fig. 1.

Depletion measurements were taken in the evacuation line of an industrial KAI-M PlasmaBox™ reactor,[17] the total inner surface of which was about 0.616 m^2. The interelectrode gap was 13 mm. Hydrogen and silane were introduced in the reactor through a uniform showerhead built in the
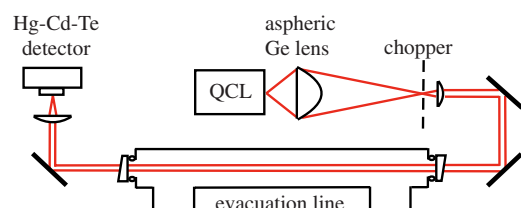

FIG. 1. (Color online) Optical setup of the QCL-based IR spectrometer.
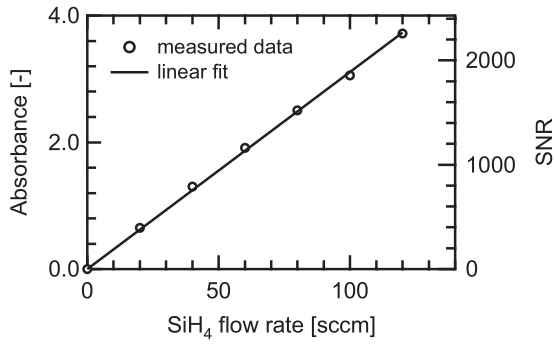
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FIG. 2. Silane absorbance and SNR at 2243.83 cm^{-1} vs the input SiH$_4$ flow rate before igniting the plasma. The input H$_2$ flow rate and the total pressure in the PECVD reactor were maintained at 700 SCCM and 4.5 mbars, respectively.

electrode. Exhaust gases were pumped from one side. A butterfly valve regulated the pressure inside the reactor. Thin Si films were deposited at a constant substrate temperature of 453 K and at a very high excitation frequency (VHF) of 40.68 MHz.

The input SiH$_4$ in a PECVD reactor can either contribute to the film growth, can polymerize to form powderlike particles,[18] or may not react at all and be pumped out of the reactor. Before ignition of the hydrogen-diluted plasma, the input SiH$_4$ mass flow rate $\dot{m}_{SiH_4}$ is completely pumped through the evacuation line. If $\dot{m}_{SiH_4}^{off}$ is the SiH$_4$ mass flow rate in the evacuation line before ignition of the plasma, we can write $\dot{m}_{SiH_4}^{off} = \dot{m}_{SiH_4}$. After ignition of the plasma, the SiH$_4$ mass flow rate in the evacuation line $\dot{m}_{SiH_4}^{on}$ can be expressed as

$$\dot{m}_{SiH_4}^{on} = (1 - D)\dot{m}_{SiH_4}^{off}, \qquad (1)$$

where D is the silane dissociation efficiency. If a beam of light and a constant flow of absorbing species are passed through a vacuum line, the mass flow rate $\dot{m}$ is given by

$$\dot{m} = \rho \cdot S \cdot v = \frac{M}{N_A} \cdot n \cdot S \cdot v = \frac{M}{N_A} \cdot \frac{A}{\sigma L} \cdot S \cdot v, \qquad (2)$$

where ρ is the mass density, S is the section of the line, v is the velocity, M is the molar mass, N_A is the Avogadro number, n is the number density, A is the absorbance defined in terms of the natural logarithm in the Beer–Lambert law, σ is the absorption cross section, and L is the absorption path length. In general, absorption cross sections depend on the wavelength, the total pressure, and the temperature. For small pressures below 10 mbars, as found in PECVD, the rotovibrational absorption lines of SiH$_4$ are Doppler-broadened. Their shape can be described by a Gaussian function that does not depend on the total pressure anymore. Preignition measurements, pictured in Fig. 2, together with Eq. (2), show that the SiH$_4$ number density in our evacuation line is proportional to the input SiH$_4$ mass flow rate. Therefore, with Eqs. (1) and (2), the dissociation efficiency can be expressed as

$$D = 1 - \frac{\dot{m}_{SiH_4}^{on}}{\dot{m}_{SiH_4}^{off}} = 1 - \frac{A_{SiH_4}^{on}}{A_{SiH_4}^{off}}, \qquad (3)$$

where $A_{SiH_4}^{on}$ and $A_{SiH_4}^{off}$ are the absorbances in the evacuation line measured at a given wavenumber before and after ignition of the plasma, respectively. In literature,[1,7] the right hand side of Eq. (3) formally defines the depletion fraction, whereas the dissociation efficiency is defined by Eq. (1). In this letter, both expressions are found to be equivalent, in agreement with Ref. 5.

In the absence of polysilane particles, the silicon deposition rate $\dot{m}_{Si}^{dep}$ is given by

$$\dot{m}_{Si}^{dep} = D \cdot \dot{m}_{SiH_4} \cdot \frac{M_{Si}}{M_{SiH_4}}, \qquad (4)$$

where M_{SiH_4} and M_{Si} are the molar masses of silane and silicon, respectively. The silicon deposition rate $\dot{m}_{Si}^{dep}$, expressed in units of kg/s, is related to the film growth rate R_g,
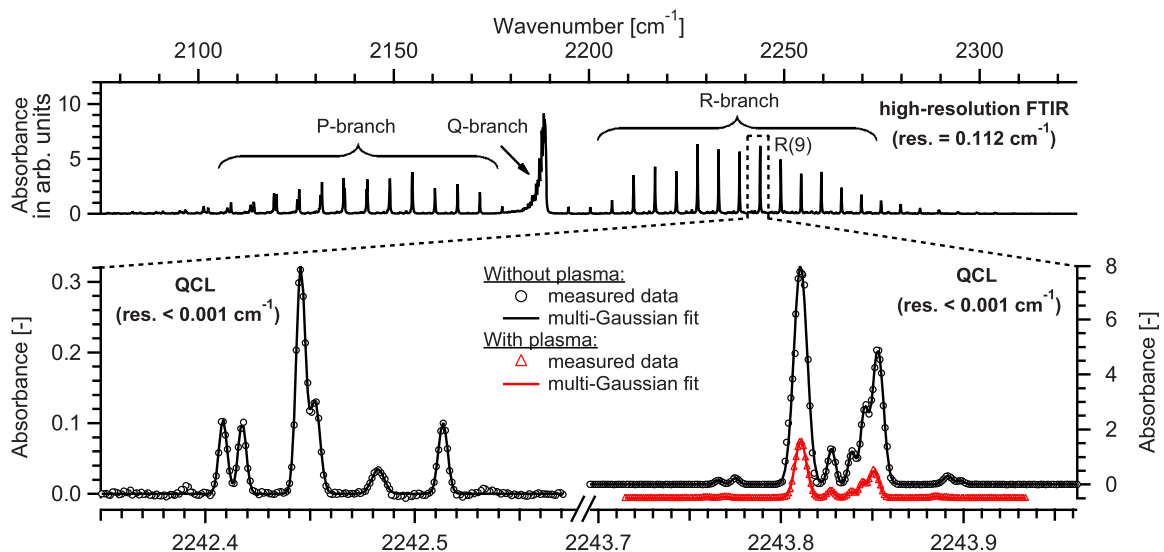

FIG. 3. (Color online) The ν_3 band of SiH$_4$ acquired by a high-resolution FTIR (upper part of the figure; see Ref. 10), the Doppler-resolved R(9) multiplet of SiH$_4$ acquired by the QCL before and after igniting the plasma in the high-deposition-rate regime (right hand side of the inset), and weak unassigned absorption lines of SiH$_4$ that only appear in the spectrum acquired by the QCL (left hand side of the inset). For illustrative purposes, the spectrum of SiH$_4$ acquired after igniting the plasma is slightly shifted in the vertical axis.

expressed in units of m/s, through the following equation:

$$\dot{m}_{Si}^{dep} = R_g \cdot A_{react} \cdot \rho_{Si}, \tag{5}$$

where A_{react} is the inner surface of the reactor and ρ_{Si} is the silicon mass density of the film. Given the low atomic percentage of H_2 in such films, ρ_{Si} can be approximated by the mass density of the film itself $\rho_{Si:H}$, which is 2.2–2.3 g/cm³ for μc-Si:H thin films.[19,20] The growth rate R_g can be determined by comparing Eqs. (4) and (5),

$$R_g = \frac{D \cdot \dot{m}_{SiH_4} \cdot \dfrac{M_{Si}}{M_{SiH_4}}}{A_{react} \cdot \rho_{Si}}. \tag{6}$$

During preliminary measurements, the QCL was calibrated with an accuracy of 0.01 cm⁻¹ with the help of the well-documented N_2O ν_3-band rotational lines R(23), R(24), R(25), and R(26). As pictured in Fig. 3, silane spectra were then acquired by scanning the injection current of the QCL with steps of 50 μA at a rate of 1.7 s per step. Given the step width, the precision of the spectrometer is better than 0.001 cm⁻¹ (the linewidth of the laser emission itself is much lower). The QCL-based spectrum of SiH_4 features nine absorption lines that have been assigned to the R(9) multiplet of the ν_3 vibrational band.[21] These lines are centered at 2243.766, 2243.775, 2243.810, 2243.827, 2243.839, 2243.847, 2243.852, 2243.891, and 2243.898 cm⁻¹. Furthermore, six unassigned weak absorption lines of SiH_4 appear at 2242.408, 2242.418, 2242.445, 2242.453, 2242.483, and 2242.514 cm⁻¹. The peak centered at 2243.810 cm⁻¹ is saturated in Fig. 3 and not suited for quantitative measurements under our process conditions. By comparing the peak centered at 2243.827 cm⁻¹ under steady-state conditions before and after ignition of the plasma, depletion fractions of 22.4 ± 1.3% and 80.0 ± 1.3% were measured when μc-Si:H films were deposited at a low-deposition rate and at a high-deposition rate, respectively. In the low-deposition-rate regime, the total pressure in the reactor was maintained at 3.5 mbars, the upper electrode was powered at 0.05 W/cm², and the input SiH_4 and H_2 flow rates were 50 and 2000 SCCM (SCCM denotes cubic centimeter per minute at STP), respectively. In good agreement with an *ex situ* profilometric measurement on the film thickness that yielded a growth rate of 1.53 ± 0.03 Å/s, a growth rate of 1.7 ± 0.1 Å/s is derived from the depletion measurement and Eq. (6). In the high-deposition-rate regime, the total pressure in the reactor was maintained at 4.5 mbars, the VHF power was 0.12 W/cm², and the input SiH_4 and H_2 flow rates were 40 and 700 SCCM, respectively. In good agreement with an *ex situ* profilometric measurement on the film thickness that yielded a growth rate of 4.37 ± 0.17 Å/s, a growth rate of

4.8 ± 0.2 Å/s is derived from the depletion measurement and Eq. (6). Nonuniform deposition regimes would account for larger discrepancies between *in situ* and *ex situ* measurements.

In conclusion, the silane dissociation efficiency was measured in this letter with an unprecedented level of precision using an IR laser spectrometer. This diagnostic technique is compact, sensitive, and nonintrusive. It was mounted on an industrial PECVD system for *in situ* monitoring of the film growth rate. Doppler-resolved rotovibrational absorption lines of SiH_4 have been resolved. Given their various absorption strengths and the excellent signal-to-noise ratio (SNR) of the spectrometer, depletions measurements over a wide range of process conditions are feasible.

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