Measurement of rotational temperature using $SiH(A^2\Delta\text{-}X^2\Pi)$ emission spectrum in SiH_4-H_2 plasmas

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(Received 27 May 2010; accepted 14 July 2010; published online 11 August 2010)

Based on the synthetic spectrum method of comparing with the experimental $SiH(A^2\Delta\text{-}X^2\Pi)$ diatomic molecular emission spectrum, the rotational temperatures of SiH_4-H_2 plasmas were investigated for various operating conditions. The plasma was generated between parallel plate electrodes biased at 40.68 MHz for thin film silicon deposition. Operating conditions of the gas pressure and the input power were varied from 2 to 8 Torr and from 200 to 600 W, respectively. Also, the total gas flow rate and H_2/SiH_4 gas flow ratio were changed. By increasing the input power, the rotational temperature was increased up to 865 K by more energetic electrons collisions. The magnitude of rotational temperature was reduced by 200 K due to particle cooling effects, with increasing the total flow rates and gas pressure. The experimental results were discussed further using Si/SiH emission intensity ratio to show the characteristics of electron temperature. © *2010 American Institute of Physics*. [doi:10.1063/1.3475438]

I. INTRODUCTION

In recent years, thin film silicon solar cells have been intensively studied as one of the possible solutions to worldwide energy problems due to its low cost and mass-productive characteristics. Hydrogenated amorphous silicon (a-Si:H) and hydrogenated microcrystalline silicon (μc-Si:H) are representative intrinsic materials making thin film solar cell devices.[1] However, each material reveals different material characteristics such as wavelength spectral sensitivity, stability against the light induced degradation, concentration of dangling bond, crystallinity, etc. Based on balancing of the aforementioned material characteristics, the stacked cells consisting of a-Si:H top cells and μc-Si:H bottom cells have been suggested for higher conversion efficiency, and they showed higher stable efficiencies than the single or a-Si:H/a-Si:H stacked solar cells.[2,3] However, since the μc-Si:H shows rather low absorption coefficient for wavelength larger than 800 nm, the μc-Si:H layer thickness of over 1 μm, which limits the prospective throughput by long deposition time, is required for enough light absorption.[4,5] In order to acquire a high growth rate and a high quality material, different silicon deposition techniques such as reactive sputtering, photochemical vapor deposition, hot-wire chemical vapor deposition, and plasma enhanced chemical vapor deposition (PECVD) have been applied.[1,4–6] Among them, the PECVD method is widely used because of its potential for uniform and high quality film fabrication on large area substrate over 1 m^2.[1,2,5–7] Since most parts of the solar cell layers are deposited by PECVD processes, the control and diagnostics of plasma properties are essential. For example, since SiH_3 radicals are known as key-playing precursors for high quality and high growth rate film deposition in solar cells, the generation of silane plasmas having a low electron temperature is crucial to increase the production rate of SiH_3 in the plasma.[8] However, it is not trivial to characterize the silane plasmas by conventional diagnostics such as electrostatic Langmuir probes because of its depositing gas property and high pressure operation regime over a few Torr. Therefore, optical emission spectroscopic (OES) methods using plasma emission spectra are frequently favored due to their nonintrusiveness and applications for wide operation ranges. The plasma emission spectrum provides important information about the plasma, such as identification of existing species (atoms, molecules, and radicals) as well as their temperatures and densities.[9] Especially, the optical emission intensity ratios of Si (281 nm) to SiH (414.2 nm band-head) and H_α (656.3 nm) to Si have been chosen to investigate the electron temperature tendency and the deposited film crystallinity in silane plasmas, respectively.[10–12] However, these line-ratio methods can give us only the atomic properties of the plasma and the relative trends about the plasma temperature. On the other hand, since the SiH emission spectrum is a convolution of rotational and vibrational energy bands of the diatomic molecule which is very important in chemical reaction in PECVD process, the information on the energy transfer between electrons and molecules and the collision characteristics among molecules can be obtained by measuring the molecular vibrational temperature (T_{vib}) and the rotational temperature (T_{rot}), respectively.[13–16]

Therefore, in this work, a $SiH(A^2\Delta\text{-}X^2\Pi)$ synthetic spectrum method was developed to measure the rotational temperature of SiH_4-H_2 plasma using a spectrometer of a modest resolution, and the effects of the operational conditions such as gas pressure, input power, total gas flow rates, etc., were discussed.

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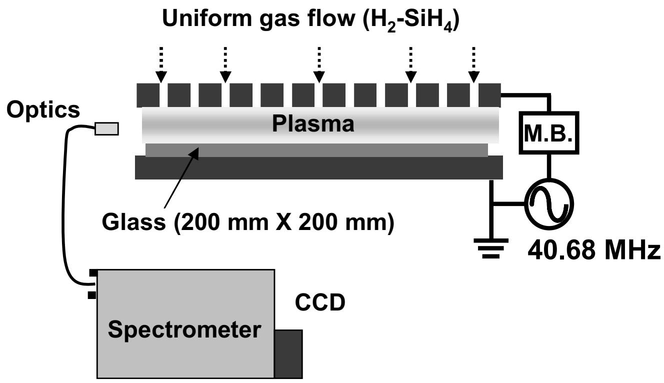

FIG. 1. Schematic illustration of the PECVD setup and optical instruments for plasma analysis.

II. EXPERIMENTAL SETUP

As illustrated in Fig. 1, the silane plasma, produced in a capacitivley coupled PECVD reactor, was studied by OES using an optical fiber and a spectrometer (Dongwoo Optron, MonoRa500i, 1200 grooves/mm, 600 grooves/mm) with a charge coupled device (Andor DV401A). The PECVD reactor has the same size (240×240 mm^2) parallel-plate electrodes for minimizing the self-bias effect. The top electrode with a shower-head configuration for the uniform gas distribution was powered by a very high frequency (VHF) 40.68 MHz power supply (NRF, NR1N40M) via matching circuit. The silicon thin film was deposited on the glass substrate (200×200 mm^2) by controlling pure SiH_4 and H_2 gas flow rates and their gas flow rate ratio R ($=H_2/SiH_4$) through mass flow controllers (Lintec). In this work, the susceptor temperature and the discharge gap were fixed in the ranges of 160–200 °C and 10–20 mm, respectively.

III. RESULTS AND DISCUSSIONS

In order to measure the rotational temperature of the plasma, experimentally obtained SiH spectra were compared with SiH synthetic spectra described elsewhere in detail.[13–18] Theoretically, the rotational emission intensity of the SiH band, $I_{v'v''}$, as a function of both T_{rot} and T_{vib} is given by[14–19]

$$I_{v'v''} \propto q_{v'v''} S_{J'J''} (\nu_{J'J''})^4 \exp\left(-\frac{F_{J'}hc}{kT_{rot}}\right) \exp\left(-\frac{G_{v'}hc}{kT_{vib}}\right), \quad (1)$$

where $q_{v'v''}$ is the Frank–Condon factor, $S_{J'J''}$ denotes the rotational band strengths, $\nu_{J'J''}$ is the emission light frequency, h is the Planck constant, c is the speed of light, and k is the Boltzmann constant. Subscripts J', J'' and v', v'' are the upper and the lower states of rotational and vibrational transitions, respectively, and $F_{J'}$ and $G_{v'}$ are the rotational and the vibrational terms of the excited states in cm^{-1}, respectively.[18,19] In this work, T_{rot} is obtained based solely on the SiH band $(v', v'' = 0, 0)$ in the 408–415 nm range since it is pretty much isolated from other transition bands. Since the wavelength region has the same vibrational state (0,0), the only rotational term in Eq. (1) is considered during the temperature measurement. Besides, the dependency of each

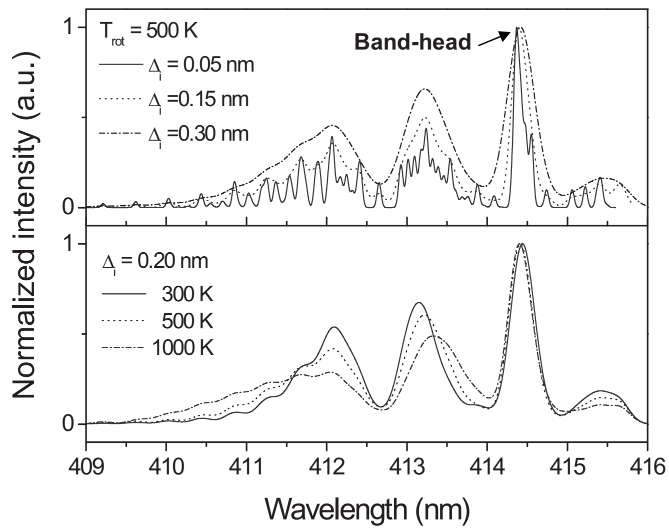

FIG. 2. The synthetic SiH($A^2\Delta$-$X^2\Pi$) spectrum for various Δ_i at T_{rot}=500 K (top) and various T_{rot} at Δ_i=0.20 nm (bottom).

temperature and line broadening effect on the spectrum shape were considered first. Since the instrumental broadening in our experimental setup and condition was dominant compared to others such as Doppler and Stark broadening, etc., and was found to have a Gaussian shape, the intensity profile becomes the convolution of Eq. (1) and a Gaussian function with a full width at half maximum, Δ_i.[17,18]

A typical SiH synthetic spectrum using Eq. (1) at T_{rot}=500 K, with various spectral resolution Δ_i =0.05–0.30 nm with appropriate constants by Herzberg[19] is presented in Fig. 2(a). Since the most prominent band is around 414 nm denoted as band-head in the figure, the SiH emission spectrum was normalized by the intensity of the band-head for convenience. As seen in Fig. 2(b), describing the T_{rot} effects on the SiH spectral features, the SiH spectrum is shown as a good thermometer for the rotational tempera-

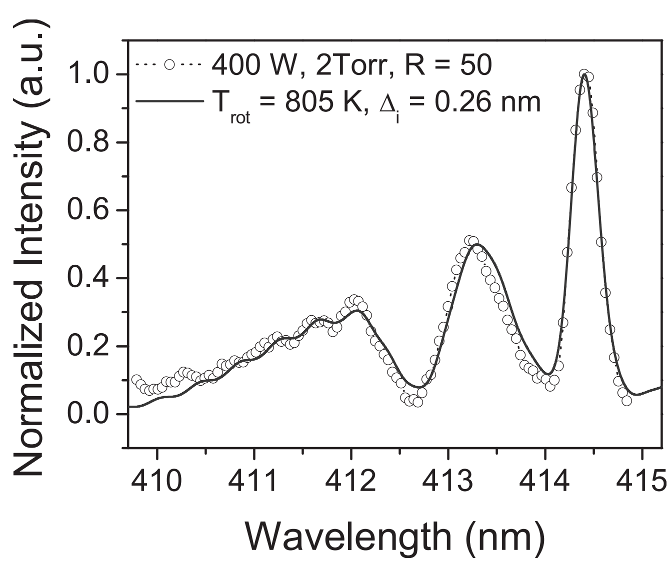

FIG. 3. T_{rot} obtained by the comparison between the experimental result (-○-) and the synthetic spectrum (−) of SiH (0,0) band is 805 K.

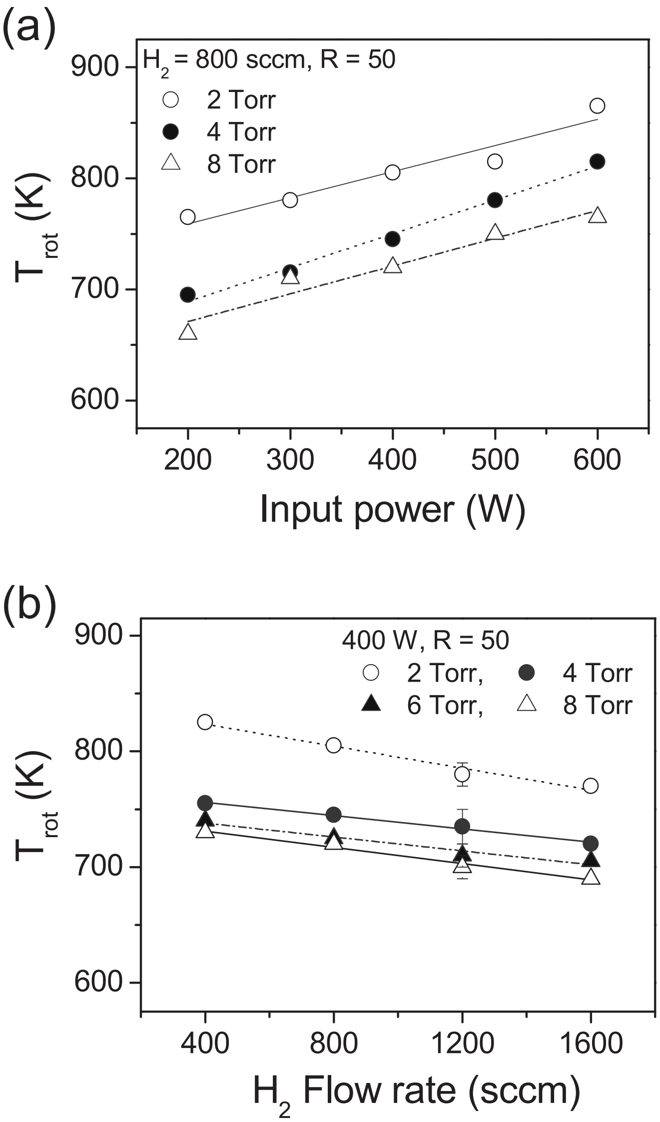

FIG. 4. (a) As the input power is increased, T_{rot} is also increased from 765 to 865 K at 2 Torr and 400 W, but (b) T_{rot} shows lower value at higher total gas flow rates because of gas cooling effects. In all cases of pressures, 2–8 Torr, the similar effects of input power and total gas flow rates are observed.

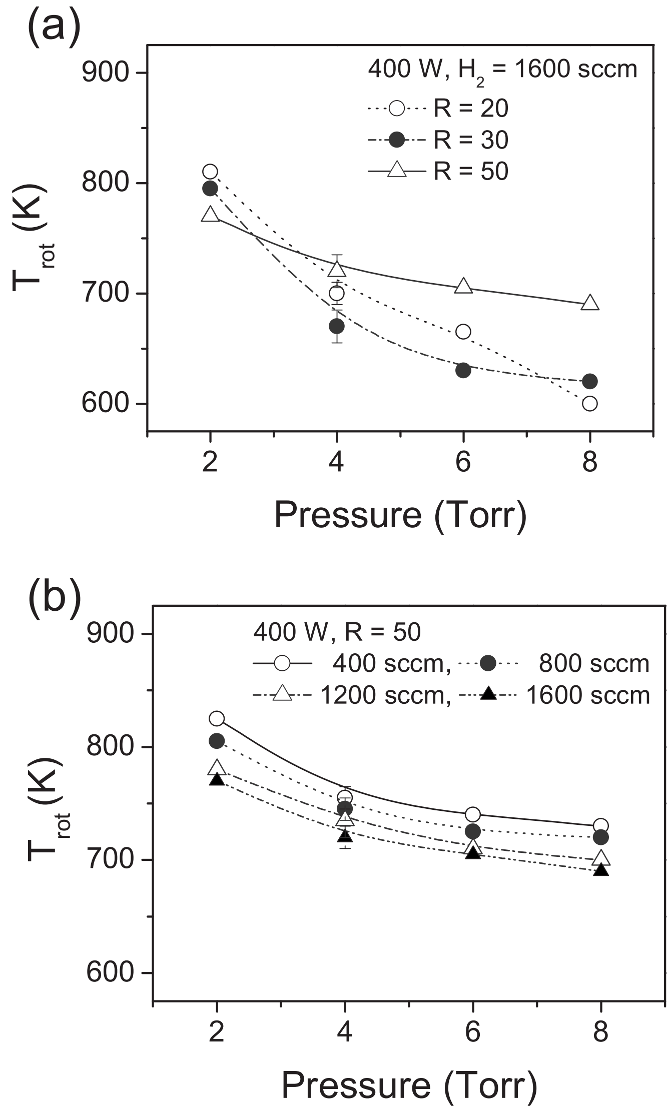

FIG. 5. (a) Gas pressure effects on T_{rot} for various H_2/SiH_4 gas ratios (denoted as R) and (b) for various total gas flow rate at 400 W. Increasing gas pressure, T_{rot} was decreased by frequent collisions between electron and neutrals.

ture measurements because of the different dependencies of the temperature in short and long wavelength regions with respect to around 412 nm.

Figure 3 depicts a comparison of the experimentally obtained SiH band (-○-) and the synthetic rotational spectrum (−), showing T_{rot} of 805 K which is in a good agreement with the experimental SiH spectrum. Based on the methods, we investigated the parametric effects of the plasma operation conditions on the T_{rot}.

As seen in Fig. 4(a), T_{rot} was increased by increasing the input power from 200 to 600 W because more energetic electrons heated the neutrals through the collisions. However, increasing H_2 gas flow from 400 to 1600 SCCM (SCCM denotes cubic centimeter per minute at STP), which means the increase of SiH_4 flow rate due to the fixed H_2/SiH_4 gas ratio (R=50), T_{rot} was slightly decreased by the gas cooling effect. In Fig. 4, the higher pressure showed lower T_{rot} values even though the tendency of the parametric effects is similar in all cases of the pressure. Since the pressure increase results in the frequent collisions between the electrons and the heavy particles, it is well known that rotational, vibrational, and electron temperature decreases toward the equilibrium state with the gas temperature although the electron temperature is still higher than the gas temperature.[16,20] The pressure effects were also investigated in various H_2/SiH_4 gas flow ratio R in Fig. 5(a) and total gas flow rates in Fig. 5(b). Increasing the gas ratio R, which means the decrease of SiH_4 flow rate, enhanced the gas pressure effect relatively due to the less loss channels of the electron energy via electron-neutral collision. In addition, the high gas flow rate results in the lower T_{rot} at the same gas pressure due to the gas cooling effect by more pumping as described in Fig. 5(b). The similar influences of the gas pressure and the gas flow rate were also observed for electron temperature, measured by emission intensity ratio Si/SiH.[10] The optical emission intensity

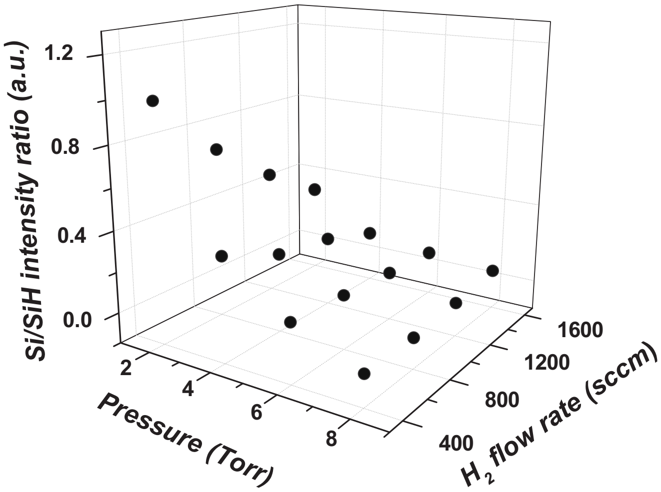

FIG. 6. Emission intensity ratio Si/SiH, which gives the information about electron temperature (Ref. 10), decreased as increasing gas pressure and total gas flow rate.

ratio of Si (281 nm) to SiH (414.2 nm band-head) gives information on the electron temperature because of the similar electron energy dependence on Si and SiH generation cross sections. Therefore, the low value of Si/SiH emission intensity ratio means the low electron temperature in plasmas.[10] As illustrated in Fig. 6, the emission intensity ratio of Si/SiH was also decreased by the increment of both gas pressure and total gas flow rate due to the energy losses by more collisions between particles, which results in the decrease of T_{rot} in plasmas.

IV. SUMMARY

Using the SiH molecular spectrum ($A^2\Delta$-$X^2\Pi$) emitted from H_2-SiH_4 plasmas for thin film silicon solar cells fabrication, the rotational temperatures were evaluated by the optical spectroscopic methods. In order to obtain the accurate measurement with a modest spectral resolution, the synthetic method considering both temperatures and the instrumental line broadening was developed. By increasing the VHF power from 200 to 600 W, the increase of about 15% in T_{rot} was observed due to more energetic electron collisions. On the other hand, the rotational temperatures reduced with higher gas pressure, total gas flow rate and H_2/SiH_4 gas flow ratio. In addition, the parametric effects on T_{rot} were similar to that on the electron temperature analyzed through Si/SiH emission intensity ratio.

ACKNOWLEDGMENTS

This work was partly supported by the Ministry of Knowledge Economy under Contract No. 2008NPV12J032100. The authors thank Mr. Y. S. Lee in Korea Advanced Institute of Science and Technology for his technical supports and discussions.

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