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Estimation of negative ions in VHF SiH_4/H_2 plasma

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The characteristics of a VHF SiH_4/H_2 plasma (frequency: 60 MHz) at high pressures were examined as a function of silane concentration with a heated Langmuir probe. Anomalous reductions in electron saturation current were observed, suggesting the existence of many negative ions. An estimation of the concentration of negative ions was attempted using the sheath theory including negative ions. It was found that there exist H^- and $SiH_3{}^-$ ions as dominant negative ions in the VHF SiH_4/H_2 plasma. In addition, the measured floating potential agreed with the theoretical value.

1. Introduction

Microcrystalline silicon has been widely investigated using VHF SiH_4/H_2 plasmas in order to reduce the production cost of silicon thin-film solar cells. Now, the solar cell industry requires a deposition rate higher than 1 nm/s. Kondo et al.[1] have proposed a high pressure depletion method that provides higher deposition rates. This method is achieved by a narrow-gap discharge at high pressures. Microcrystalline silicon is deposited by introducing a small amount of SiH_4 gas into H_2 plasmas. As is well known, negative ions are produced in a SiH_4 plasma.[2,3] The cross section of electron attachment is much lower than that of ionization. However, negative ions are confined in a plasma without diffusing to electrodes, leading to a high negative ion density. Thus, in solar cell development, it is important to investigate the parameters of a SiH_4/H_2 plasma at high pressures. In fact, Takatsuka et al.[4] succeeded in obtaining a deposition rate of 2.5 nm/s by reducing the discharge gap d (< 10 mm). We have performed the experiments on the characteristics of a VHF SiH_4/H_2 plasma produced by such a narrow-gap discharge, where the discharge gap is narrower than 10 mm.

Negative ions are usually measured with a quadrupole mass spectrometer[2] and a laser photodetachment technique.[5] However, the quadrupole mass spectrometer does not provide correct information about negative ions in a plasma produced inside the discharge electrodes at high pressures because of short mean free paths of negative ions. On the other hand, the Langmuir probe provides the local values of the plasma parameters. Thus, we have estimated the negative ion concentration α from the reduction in electron saturation current:[6]

$$\alpha = \frac{n_-}{n_+} = 1 - \frac{I_{es}}{I_{es0}}, \tag{1}$$

where n_- and n_+ are the densities of negative and positive ions, and I_{es} and I_{es0} are the electron saturation currents with and without negative ions, respectively. On the other hand, it has been reported that there are many negative ions (H^- ions) in a H_2 plasma,[7] so that two negative ion species, H^- and $SiH_3{}^-$ ions, are discussed in this experiment because the negative ion currents due to higher-order silane ions are neglected compared with those of H^- and $SiH_3{}^-$ ions.

As is well known, the floating potential V_w is the potential at which the ion current is equal to the electron current (the probe current $I = 0$). When there are negative ions in a plasma, the floating potential V_w is modified as[8]

$$V_w \approx -\frac{\kappa T_e}{2e} \ln\left(\frac{2M_+}{\pi m}\right) - \frac{\kappa T_e}{e} \ln(1-\alpha), \tag{2}$$

where the plasma potential is defined as 0 V. Here, κ and e are the Boltzmann constant and electron charge, and m and M_+ are the masses of electrons and positive ions, respectively. Note that Eq. (2) shows that V_w is independent of negative ion species. In this study, we examined the characteristics of a VHF SiH_4/H_2 plasma at high pressures using a Langmuir probe and attempted to estimate the negative ion density in the VHF SiH_4/H_2 plasma using Eq. (2). In addition, the experimental results were compared with the results obtained on the basis of the sheath theory including negative ions.

2. Experimental methods

Figure 1 shows a schematic of the experimental apparatus consisting of a stainless steel vacuum vessel (height, 420 mm, width, 1350 mm, and depth, 470 mm), a multirod electrode[9] of $1200 \times 115\,mm^2$, and a VHF power supply. The multirod electrode consisted of 5 stainless steel rods. The distance between the multirod electrode and the glass substrate was shorter than 10 mm, where a punched electrode (stainless steel disk plate) of $1200 \times 115\,mm^2$ was used as the substrate holder to examine plasma uniformity. Recently, we have developed a new power feeding method[9] to avoid abnormal VHF discharges. VHF powers were supplied to the feeding point on the multirod and punched electrodes through an impedance matching box, where the frequency of the VHF power source was 60 MHz and the power was up to 450 W. The VHF power was divided using a power divider consisting of two outputs with a 180° phase difference, and the output powers were fed to the multirod and punched electrodes through semirigid coaxial cables. The matching box was adjusted in such a way that the reflected powers became almost zero. Thus, we succeeded in realizing a stable VHF discharge between the multirod and punched electrodes. In addition, to produce a large-area VHF plasma at high pressures, as shown in Fig. 1, the control of VHF discharge regions was attempted by loading a variable capacitance to the discharge electrode, and we succeeded in controlling VHF discharge regions. The forward and reflected VHF power in front of the vacuum chamber was measured with

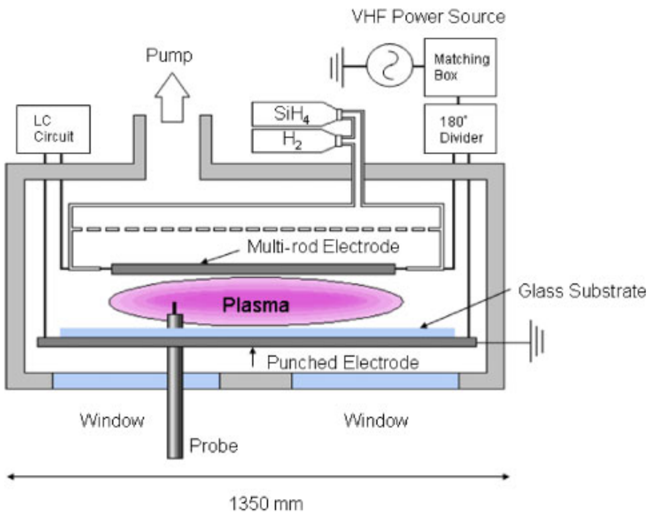

Fig. 1. (Color online) Schematic of the experimental apparatus.

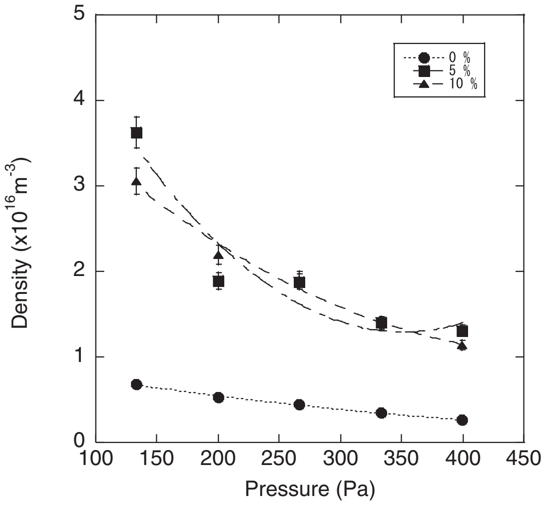

Fig. 2. Dependence of the plasma density on the pressure for different silane gas concentrations $[SiH_4]/([SiH_4] + [H_2])$. Here, the VHF power was 450 W.

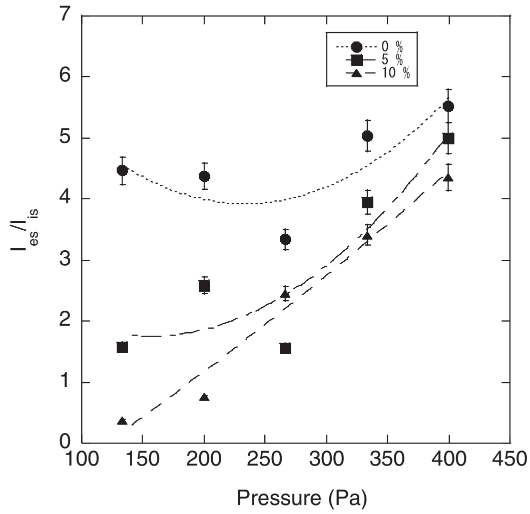

Fig. 3. Current ratio I_{es}/I_{is} as a function of pressure for different silane gas concentrations $[SiH_4]/([SiH_4] + [H_2])$, where I_{es} and I_{is} are the saturation currents of electrons and ions, respectively. Here, the VHF power was 450 W.

power meters to examine the characteristics of the balanced power feeding method developed here. The gas used was SiH_4 diluted with H_2 and the pressures ranged from 133.3 to 466.55 Pa. The gas flow rate of SiH_4/H_2 was 50 sccm. The plasma parameters were measured with a heated Langmuir probe, which was placed at a certain distance from the multirod electrode. To reduce the disturbance of the Langmuir probe, a tungsten wire of 0.3 mm diameter was used as the heated Langmuir probe. Before measuring VHF SiH_4/H_2 plasma parameters, the current range not disturbing plasma generation due to heating was confirmed, and calibration of the surface area of the heated Langmuir probe was performed by measuring argon and hydrogen plasmas using a conventional Langmuir probe. The plasma potential was determined by finding the intersection of the straight line used to estimate the electron temperature and by linear extrapolation of the electron saturation current on the semi-logarithmic plot of the probe *I*–*V* curves.

3. Results and discussion

First, we measured the plasma parameters as a function of pressure for different silane gas concentrations $[SiH_4]/([SiH_4] + [H_2])$, where the VHF power was 450 W. Figure 2 shows that the plasma density decreases with increasing pressure. Here, the plasma density was estimated from the ion saturation current, and dominant ions were assumed to be H^+ for the silane gas concentration of 0% and $SiH_3{}^+$ for 5 and 10%.[10] Figure 2 also indicates that the density of the SiH_4/H_2 plasma is higher than that of the pure hydrogen plasma, which is due to less diffusion loss. Then, the current ratio, I_{es}/I_{is}, was calculated from the *I*–*V* curves as a function of pressure, where I_{es} and I_{is} are the saturation currents of electrons and ions, respectively. Figure 3 shows that the current ratio I_{es}/I_{is} is much lower than the theoretical values calculated on the basis of the Bohm sheath theory ($I_{es}/I_{is} \sim 28$ when the dominant ions are H^+),[11] suggesting the existence of negative ions even in the H_2 plasma. Therefore, Eq. (1) is not useful for estimating the negative ion concentration in this experiment. Figure 3 also demonstrates that when the silane gas concentration is increased, I_{es}/I_{is} decreases, that is, more negative ions are produced with increasing silane gas concentration.

As is well known, the electron temperature is an important parameter in plasma-enhanced chemical vapor deposition (PECVD), and the characteristics of VHF plasma are affected by the generation of negative ions. Figure 4 shows that when the pressure is increased, T_e is doubled at high pressures. Generally, the electron temperature of a VHF plasma is lower than that of a RF plasma (frequency, 13.56 MHz). On the other hand, when negative ions are generated in a plasma, T_e tends to increase.

Then, we attempted to estimate the negative ion concentration, n_-/n_+, as a function of pressure using Eq. (2). Figure 5 shows a typical result for different silane gas concentrations, showing that when SiH_4 gas is introduced to the H_2 plasma, n_-/n_+ tends to increase although the data spread widely. However, the density difference between H^- and $SiH_3{}^-$ ions is at most 20%, that is, many H^- ions exist even in the SiH_4/H_2 plasma. In addition, Fig. 4 indicates that the negative ion density at 5% silane is higher than that at 10% silane. Recently, there has been a tendency to adopt

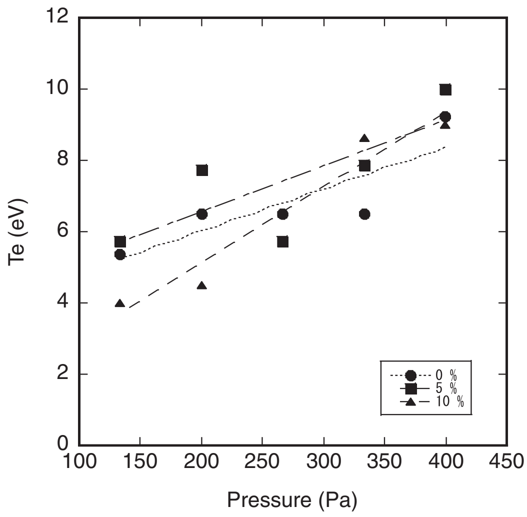

Fig. 4. Dependence of the electron temperature T_e on the pressure for different silane gas concentrations $[SiH_4]/([SiH_4] + [H_2])$. Here, the VHF power was 450 W.

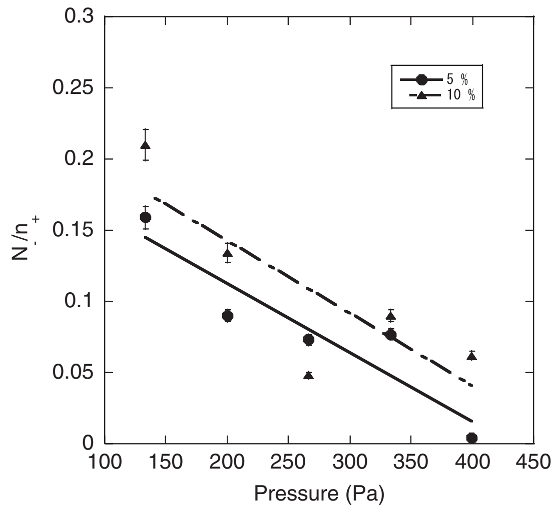

Fig. 6. Dependence of the SiH_3^- ion density normalized to n_+, N_-/n_+, on the pressure for different silane gas concentrations $[SiH_4]/([SiH_4] + [H_2])$. Here, the VHF power was 450 W.

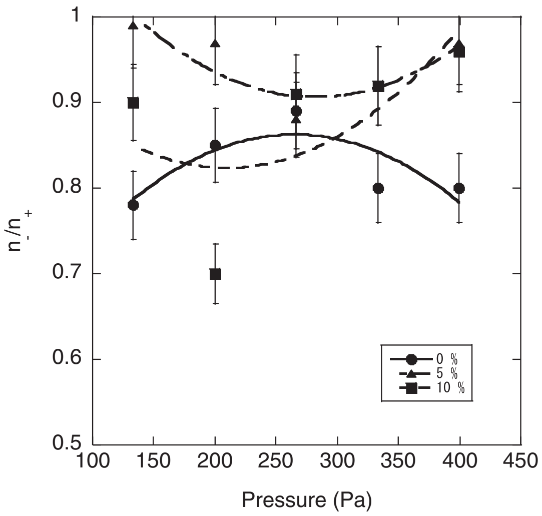

Fig. 5. Dependence of the negative ion concentration n_-/n_+ on the pressure for different silane gas concentrations $[SiH_4]/([SiH_4] + [H_2])$ at 450 W.

low silane gas concentrations such as 3–5%, resulting in the high conversion efficiency of silicon thin-film solar cells. The contribution of negative ions to the conversion efficiency of solar cells is a future work.

Here, we attempted to estimate the SiH_3^- ion density by assuming that the positive ion density does not change markedly when negative ions are produced. As can be understood easily, the SiH_3^- density normalized to n_+ $(= N_-/n_+)$ is expressed as

$$\frac{N_-}{n_+} = (1 - \beta)\left(1 - \frac{I_e}{I_{e0}}\right), \tag{3}$$

where β is the H^- ion density for 0%. Thus, we can estimate the SiH_3^- ion density normalized to n_+ from both β and I_e/I_{e0}. The result is shown in Fig. 6. Note that the $S_iH_3^-$ ion density decreases proportionally to pressure, which is consistent with Fig. 3. In addition, Fig. 6 indicates that the $S_iH_3^-$ ion density at 10% silane is higher than that at 5% silane. Kalache et al.[7] reported that when the vibrational temperature is increased, the H^- ion density drastically increases. We found that there are many H^- ions in the SiH_4/H_2 VHF plasma. Here, the discharge gap was very narrow, so the gas temperature was higher than that at the discharge gap of 34 mm, although it was not measured. There are many reports on H^- ions in low-pressure plasmas (collisionless plasmas) with a low electron temperature at approximately 1 eV, and it is believed that H^- ions are destroyed when the electron temperature is high. However, these were observed in low-pressure plasmas. A study of H^- ions in high-pressure regions (collisional plasmas) will be expected.

The floating potential is also an important parameter in PECVD because it corresponds to the ion bombardment energy. We measured the floating potential as a function of pressure at different silane gas concentrations. The results are plotted in Fig. 7. Here, the solid line indicates the theoretical values calculated from the sheath equation derived by Amemiya,[12] and Shindo and Horiike[13] numerically solved the sheath equation for applying negative ions to etching. The sheath equation and Bohm criterion voltage V_B are as follows:

$$\begin{aligned} n_e \exp\left(-\frac{eV}{kT_e}\right)\left(\frac{kT_e}{2\pi m}\right)^{1/2} + n_- \exp\left(-\frac{eV}{kT_-}\right)\left(\frac{kT_-}{2\pi M_-}\right)^{1/2} \\ = \left[\frac{2(kT_+ + eV_B)}{M_+}\right]^{1/2}\left[n_e \exp\left(-\frac{eV_B}{kT_e}\right) + n_- \exp\left(-\frac{eV_B}{kT_-}\right)\right], \end{aligned} \tag{4}$$

$$n_e \exp\left(-\frac{eV_B}{kT_e}\right)\left[\frac{1}{kT_e} - \frac{1}{2(kT_+ + eV_B)}\right] + n_- \exp\left(-\frac{eV_B}{kT_-}\right)\left[\frac{1}{kT_-} - \frac{1}{2(kT_+ + eV_B)}\right] = 0, \tag{5}$$

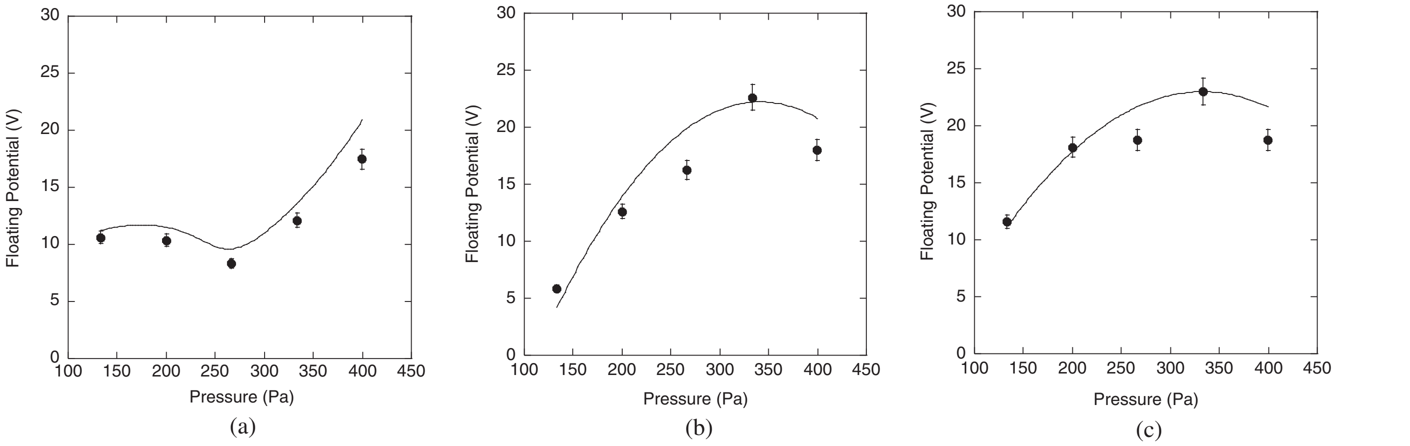

Fig. 7. Dependence of the floating potential on the pressure for different silane gas concentrations: (a) $[SiH_4]/([SiH_4] + [H_2]) = 0\%$, (b) $[SiH_4]/([SiH_4] + [H_2]) = 5\%$, and (c) $[SiH_4]/([SiH_4] + [H_2]) = 10\%$. Here, the solid curve indicates the theoretical values calculated from the sheath equation.

where n_e and V_B are the electron density and Bohm criterion voltage, and T_+ and T_- are the temperatures of positive and negative ions, respectively. In our calculation, we assumed H^+ and H^- ions as the positive and negative ion species for 0% silane. When a small amount of SiH_4 gas is introduced into the H_2 plasma,[14] the dominant ion species transition from H^+ ions to $SiH_3{}^+$ ions; thus, in our experiment, $M_+ = SiH_3{}^+$ was assumed for the silane concentrations of 5 and 10%. On the other hand, the reduced mass was used as M_-. In addition, $T_+ = T_- = 0.5\,\mathrm{eV}$ was assumed in all cases. As seen in Fig. 7, a good agreement between the experimental and theoretical values is obtained. This agreement suggests that the assumption for dominant ions is accurate.

According to the cross section for the dissociative attachment of electrons to silane, the cross section of $SiH_3{}^-$ ions is larger than those of $SiH_2{}^-$ and SiH^- ions.[15] Therefore, in this experiment, H^- and $SiH_3{}^-$ were assumed as dominant negative ions. As already described, lighter negative ions contribute to the negative ion currents passing through the probe. In addition, higher-order silane negative ions are strongly reduced in the VHF plasma.[16] Thus, it is concluded that two types of negative ions, H^- and $SiH_3{}^-$ ions, are produced in the VHF SiH_4/H_2 plasma, and that the H^- ion density is higher than the $SiH_3{}^-$ ion density at high pressures. These results are not understood well; thus, their quantitative explanation is a future subject.

As is well known, low-energy electrons contribute to the production of negative ions; thus electrons may have a Maxwellian distribution with two electron temperatures, leading to an apparently higher electron temperature. Thus, alternative methods for measuring the electron temperature are necessary for understanding a negative ion plasma. One suggested alternative method is the estimation of the electron temperature from the propagation velocity of the ion wave in a plasma.[17] However, this method is not useful at high pressures because of too many collisions. In our experiment, we measured the floating potential and compared it with the theoretical values. As shown in Fig. 7, the measured floating potentials were in agreement with the theoretical values, that is, it is concluded that the measured electron temperatures are those of bulk electrons.

4. Conclusions

We examined the characteristics of a VHF SiH_4/H_2 plasma at high pressures with a heated Langmuir probe. We found that there are two types of negative ions, H^- and $SiH_3{}^-$ ions, in the VHF SiH_4/H_2 plasma. We attempted to estimate the negative ion concentration using the floating potential theory developed by Amemiya. When the pressure was increased, the $SiH_3{}^-$ ion density decreased and the H^- ion density became higher than the $SiH_3{}^-$ ion density at high pressures. In addition, we found that the measured floating potentials were in agreement with the theoretical values calculated on the basis of the sheath theory including negative ions. In summary, our results will be useful for improving the conversion efficiency of silicon thin-film solar cells in the near future.

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