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Translational Energy Distributions and Emission Cross Sections of the Excited Hydrogen Atom Produced in e-SiH_4 Collisions

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The translational energy distributions of H* (n=3, 4) produced in e–SiH_4 collisions were obtained by measuring the Doppler profiles of the Balmer-α and β lines with a Fabry–Perot interferometer. There are three major components in the translational energy distributions of H* (n=3,4). The first component lies in the 0—3 eV region, the second one peaks at 2—3 eV, and the third one lies at above 4 eV. Thus, dissociation of SiH_4 for the formation of H* (n=3,4) should proceed through three different groups of Rydberg states. The emission cross sections were determined separately for H* (n=3,4) with the translational energy of 0—2, 2—4, 4—6, 6—8, and 8—10 eV, respectively.

The study of electron–silane (SiH_4) interaction has received considerable attention due to its importance to plasma diagnostics in semiconductor technology. The mechanism and cross sections of electron-impact dissociation of SiH_4 are needed for understanding and simulating deposition processes of amorphous silicon films.

High resolution spectroscopy on electron–molecule collision processes is a powerful tool for such studies.[1] The translational energy distribution of fragments,[1,2] the emission cross section of certain fragments produced in a specified dissociation process[1,3] and the symmetry of dissociation processes[1,4] have been obtained with this technique. Reactivity of an excited species may depend on the translational energy it has. Thus, the emission cross section of an excited species should be more useful for a simulation of a plasma, if it is determined separately for species with different translational energies.

Perrin et al.[5–8] investigated the dissociation dynamics of SiH_4 and determined the emission cross section of fragments such as H*, Si*, Si+*, SiH*, and SiH+*. The translational energy distributions of H* (n=4) were obtained with the use of a grating spectrometer and three groups of H* (n=4) were found in the translational energy distribution; their peaks lay at about 0.3 eV, 2.5 eV and a higher energy.[7] The excitation functions of H* (n=3,4) were determined and three major thresholds were found for the formation of H* (n=3,4).[6,9,10] Cooper et al.[11] obtained absolute oscillator strengths for photoabsorption, photoionization, and ionic photofragmentation, and photofragmentation branching ratios of silane, and concluded that the $(3a_1)^{-1}$ state is a many-body state and plays an important role for the formation of H^+.

We have measured high-resolution spectra of the Balmer-α and β lines with a Fabry–Perot interferometer and obtained the translational energy distributions of H* (n=3,4). We have also determined the emission cross sections for the excited hydrogen atom of certain translational energy with an expectation that such values are useful for an understanding and simulation of plasma. To our best knowledge, this is the first attempt to determine the emission cross section separately for species with different translational energies.

Experimental

The experimental apparatus was described in detail in the previous papers.[12,13] In brief, the stainless-steel collision chamber has an electron gun and a gas cell. The sample gas (10.1% SiH_4 in He; obtained from Seitetsu Kagaku) was collided with the electron beam. The typical electron-beam current was 10—100 μA and the typical operating pressure was $1—4\times10^{-5}$ Torr (uncorrected, 1 Torr=133.322 Pa) at the wall of the collision chamber.

The optical radiation was measured perpendicularly with the electron beam with a Spex 1269 monochromator when the broad band spectra were obtained. The Doppler profile of the Balmer lines was measured at 55° (magic angle) with respect to the electron beam with a Mizoziri Fabry–Perot interferometer. The optical resolution was 0.010 nm for the Balmer-α line and 0.007 nm for the Balmer-β line. A DIF-C filter ($\Delta\lambda_{1/2}$=1.0 nm: Vac. Opt. Co. Jpn.) was used for separating the Balmer-α line and another DIF-C filter ($\Delta\lambda_{1/2}$= 1.3 nm) for the Balmer-β line. The photons were counted with a Hamamatsu R585 or R649 photomultiplier.

The relative emission cross sections of the excited hydrogen atom with each translational energy were determined from its translational energy distributions, and the summed totals were normalized to those measured by Sato and Goto[9] in order to make the relative values absolute.

Results and Discussion

Doppler Profiles and Translational Energy Distribution. The silane molecule produces lines of H*, Si*, and Si+*, and bands of SiH* and SiH+*.[5,6,9] We have separated the Balmer lines of H* (n=3,4) and measured their Doppler profiles with the use of a high-resolution Fabry–Perot interferometer, as shown in Fig. 1. The electron energy was 25—100 eV; however, no reliable profile of H* (n=3) was obtained at 25 eV due to poor signal-to-noise ratio. The Doppler profiles are dependent on the electron energy. It

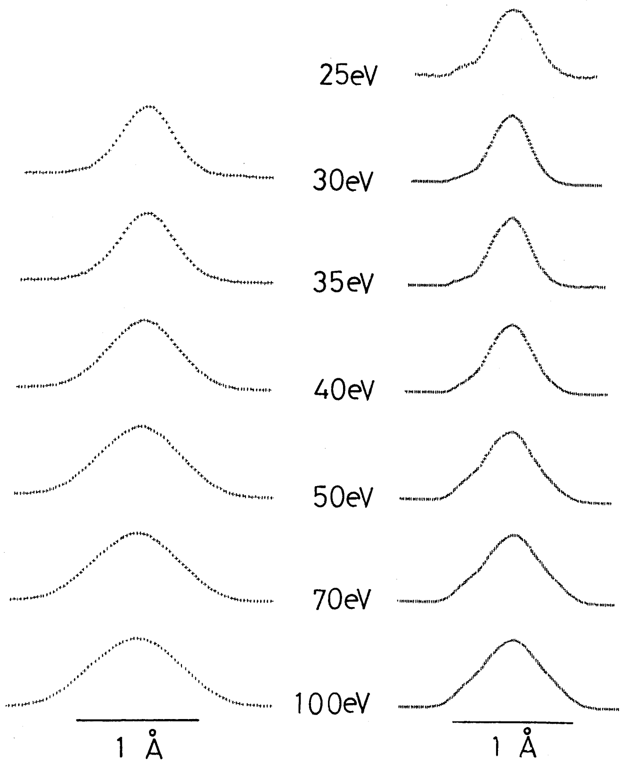

Fig. 1. Doppler profiles of the excited hydrogen atom (n=3, 4) produced in e-SiH_4 collisions. Observation angle: 55° with respect to the electron beam. (left) H*(n=3), (right) H*(n=4).

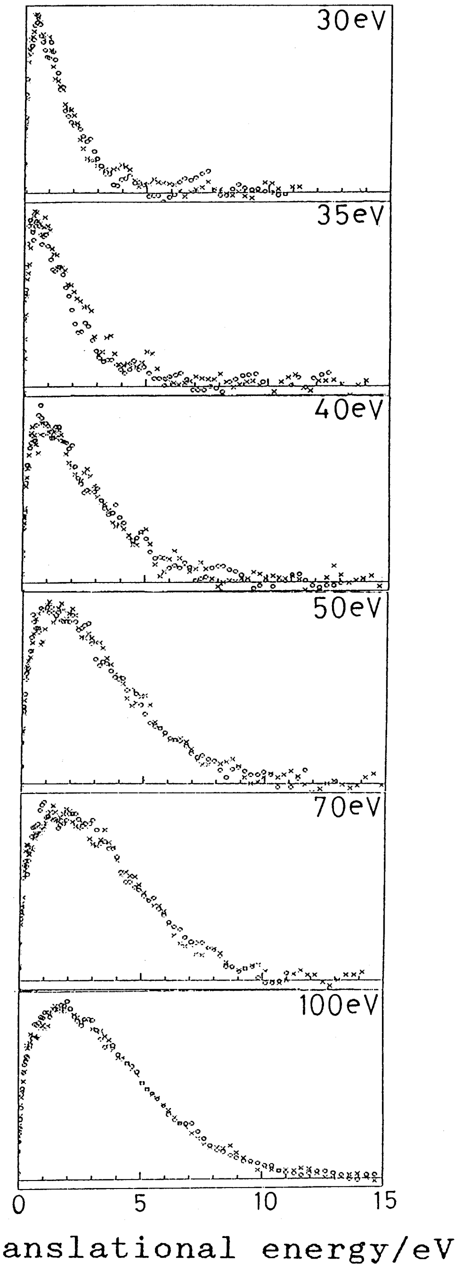

Fig. 2. Translational energy distributions of H*(n=3) produced in e-SiH_4 collisions. The translational energy distribution obtained from the longer wavelength side of the Doppler profile is shown as ○, and that obtained from the shorter wavelength side as ×. The two distributions agree with each other within experimental errors.

becomes wider at higher electron energies. There are two helium lines and one unidentified line (probably molecular origin) on the shorter wavelength (left) side of the Balmer-β line; they are clear on the spectrum taken with the Spex monochromator. Thus, the longer wavelength (right) side of the profile was used for the determination of the translational energy distribution of H* (n=4).

The translational enenrgy distribution of an excited species can be obtained by differentiating the Doppler profile obtained at 55° (magic angle),[14] so that any effect due to anisotropy should be negligible. The differentiation was carried out by smoothing the profile curve by a least square procedure using a 5-point cubic convolute.[15] The translational energy distributions of H* (n=3,4) are shown in Figs. 2 and 3. The distribution at 25 eV is noisier due to weak signals.

At incident electron energies of 25 and 30 eV, there is a clear peak in the translational energy distribution at about 0.5 eV, as shown in Figs. 2 and 3. This component is located in the 0—3 eV region and is dominant at electron energies of 25—35 eV. Another component starts to appear on the distribution at an incident energy of 40 eV. This component has a peak at 2—3 eV becomes more intense at higher incident energies. The third one appears on the distribution at above 50 eV; this component lies in the 4—10 eV region of the translational energy. Thus, there are three major components on the translational energy distributions of H* (n=3,4) as Perrin and Schmitt observed.[7] This finding indicates that there should be at least three major dissociation processes for the formation of the excited hydrogen atom from silane.

Both of the translational energy distributions of H*

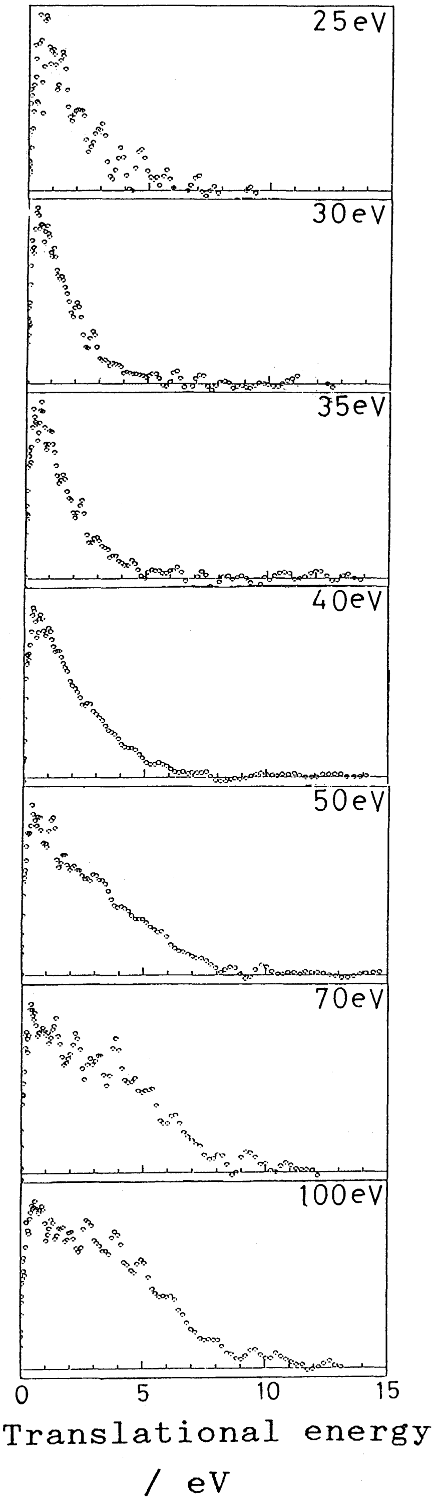

Fig. 3. Translational energy distributions of H*(n=4) produced in e–SiH_4 collisions. The translational energy distribution was obtained from the longer wavelength side of the Doppler profile.

(n=3) and H* (n=4) have three components and they are qualitatively similar. Relative intensity of the three component is, however, different; the second component of H* (n=3) is relatively more intense than that of H* (n=4).

There are three thresholds on the excitation function of H* produced in e–SiH_4 collisions; they lie at about 19 eV, 23 eV, and 35—40 eV.[6,9,10] However, these thresholds and the translational energy distribution do not show one-to-one correspondence. The first and second thresholds can be correlated with the first component of the translational energy distributions. The second component appears at 40 eV and becomes dominant at higher electron energies; the threshold of this component should be slightly below 40 eV. The difference in the relative intensity of the second component of H* (n=3) and H* (n=4) may correspond to the difference of their excitation function; the one for H* (n=3) has a steeper rise at about 40 eV.[9] The threshold of the third component is not clear.

Dissociation Process of Silane. Perrin and Schmitt[7] described that the formation of H* (n=4) proceeds via dissociative superexcited Rydberg states. Importance and contribution of such states were shown on various molecules.[1] The photoelectron spectrum of silane indicated that the $(3a_1)^{-1}$ state lies in the 17—40 eV region.[16] The dipole (e,e) spectrum also indicated that the $(3a_1)^{-1}$ state lies in the 16—40 eV region and that this state consists of the main state (threshold: 18 eV) and a many-body state (threshold: 24 eV); the appearance potential of H^+ was found at 24 eV, and H^+ should be produced through the $(3a_1)^{-1}$ state.[11] The formation of H^+ was correlated specifically with the many-body state of $(3a_1)^{-1}$.[11]

Since there is no onset of H^+ at about 19 eV in the dipole (e,e) spectrum, we can conclude that the threshold of H* (n=3,4) at 19 eV can be correlated with an optically-forbidden minor dissociation process; this process would be a triplet process. The major part of the first component of the translational energy distribution can be correlated with the threshold at 23 eV and the formation of H* (n=3,4) would proceed through Rydberg states converging to the many-body state of the $(3a_1)^{-1}$ state.

The first component has larger translational energy than the second one in the case of methane. The Rydberg state converging to the $(2a_1)^{-1}$ state of methane was correlated with processes leading to the excited hydrogen atom with the translational energy of about 3 eV. While, the second component was slow. The contribution of curve crossing in the excited Rydberg states may be different between methane and silane and such difference can induce the observed difference in the translational energy distributions of H* (n=3,4) produced from the two molecules.

The second component in the translational energy distribution has the threshold at about 35 eV. There may be some doubly-excited Rydberg states such as $(2t_2)^{-2}(nR)^2$ (nR: a Rydberg orbital) in this energy region, which may play important roles for the formation of this component.

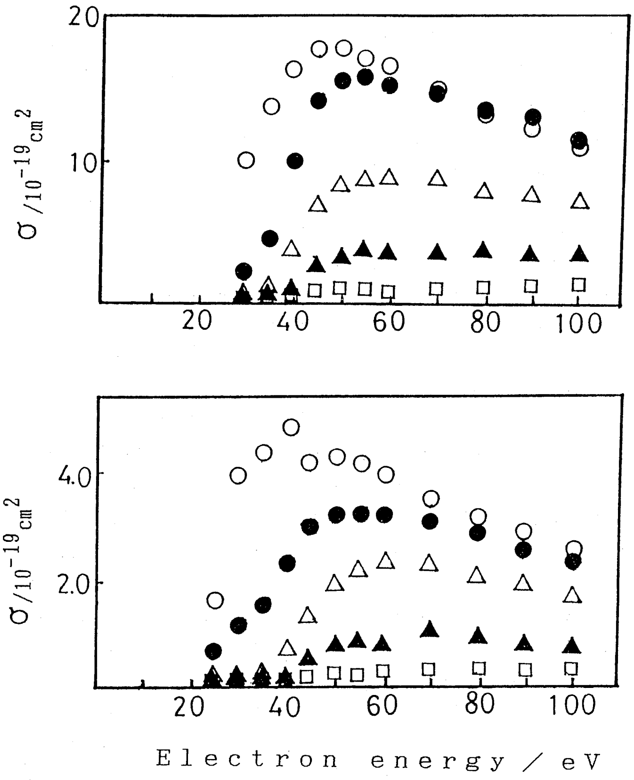

Fig. 4. Emission cross sections of $H^*(n=3, 4)$ with certain range of the translational energy distribution. (top) $H^*(n=3)$, (bottom) $H^*(n=4)$. ○: 0—2 eV, ●: 2—4 eV, △: 4—6 eV, ▲: 6—8 eV, □: 8—10 eV.

Emission Cross Sections. The total emission cross sections of H^* ($n=3,4$) were determined previously.[9] We have determined the emission cross sections of H^* ($n=3,4$) with certain translational energy separately by measuring their relative emission cross sections and by normalizing them to the total. No correction for collection efficiency was carried out, since such correction would be small for the Balmer-α and β lines.[17]

The emission cross sections of H^* ($n=3,4$) of translational energy of 0—2 eV(○), 2—4 eV(●), 4—6 eV(△), 6—8 eV(▲) and 8—10 eV(□) are shown in Fig. 4. The H^* ($n=3,4$) with translational energy above 10 eV is weak and was omitted in this Figure for clarity; its energy dependence is approximately identical with that of 8—10 eV. These results show that the first component is relatively more important for H^* ($n=4$). Whereas the rise of H^* ($n=3$) in the 2—4 eV region is steeper, and this finding indicates that the second component is more important for H^* ($n=3$). The emission cross sections at an electron energy of 100 eV are shown in Table 1.

Table 1. Emission Cross Sections of H^* ($n=3$, 4) Produced in e-SiH_4 Collisions at an Electron Energy of 100 eV

Translational energy/eV	H^* ($n=3$) 10^{-19} cm^2	H^* ($n=4$) 10^{-19} cm^2
Total[9]	36	7.5
0—2 eV	$10._{9}$	2.4
2—4 eV	$11._{2}$	2.2
4—6 eV	$7._{5}$	1.7
6—8 eV	$3._{8}$	0.7_{8}
8—10 eV	$1._{7}$	0.2_{7}
Above 10 eV	$1._{0}$	0.1_{5}

The chemical reactivity can depend on the translational energy of the species concerned. Such energy dependence is not yet discovered in plasma processing; however the partial emission cross section for each translational energy obtained here may be useful for its simulation.

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