DISSOCIATIVE EXCITATION OF SIH₄ BY COLLISIONS WITH METASTABLE ARGON ATOMS

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The excitation transfer from Ar^* to SiH₄ has been studied by observing UV and visible emission in a flowing afterglow and beam apparatus. The emission rates of SiH($A^2\Delta$) and Si^{*} atoms have been determined. From the nascent rovibrational distribution of SiH(A), the fractions of the available energy deposited into vibration and rotation of SiH(A) were estimated to be 2.9% and 4.4%, respectively.

1. Introduction

The dissociation process of SiH4 has captured attention because of its importance in the fabrication of amorphous silicon films. Amorphous silicon films have been produced from SiH₄ using various types of discharge plasma sources and a mercury photosensitized technique [1]. Toyoshima et al. [2] has recently employed energy transfer from metastable $Ar({}^{3}P_{2})$ atoms to SiH₄ as a new valuable technique of the preparation of amorphous silicon films. Since optical emission from electronically excited products provides a useful means for the diagnostics of the discharge condition, UV and visible emission spectroscopy has been extensively applied to the study of silane discharges. During Ar* CVD Toyoshima et al. [2] measured an emission spectrum from the $Ar({}^{3}P_{2})/SiH_{4}$ reaction in the 200-800 nm region. It was found that the spectrum consisted entirely of the SiH(A $^{2}\Delta$ -X $^{2}\Pi_{r}$) system in the visible region. However, detailed studies on the excitation process such as measurements of excitation rate and rovibrational distribution have not been carried out.

In the present optical study, dissociative excitation of SiH₄ by collisions with metastable argon atoms has been investigated by using flowing afterglow (FA) and beam apparatus. In addition to the SiH(A-X) emission observed by Toyoshima et al. [2], a number of SiI atomic lines are identified. The emission rates and the corresponding emission cross sections are determined. The energy disposal to SiH(A) is estimated from its nascent rovibrational distribution.

2. Experimental

The FA and beam apparatus used in this study were essentially identical to those reported previously [3,4]. Ar* atoms were generated by a microwave discharge of high purity Ar in a discharge flow operated at 0.10-0.60 Torr. In the FA experiment, the sample gas (1/10 mixture of SiH₄/He) was injected from a nozzle about 10 cm downstream from the center of the discharge. The sample gas pressure was 0.5-1.0 mTorr. In the beam experiment, a part of the Ar discharge flow was expanded from a 2.0 mm diameter nozzle into a low-pressure chamber. The pressures of Ar and SiH₄ in the collision region were 1 and 0.05-0.1 mTorr, respectively. The effect of

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ionic active species, Ar^+ and Ar^{+M} (metastable ions), were examined by using an ion-collector grid placed between the discharge and reaction zone.

The emission spectrum was dispersed with a 1.0 m scanning monochromator equipped with a cooled Hamamatsu photonics R376 photomultiplier. The monochromator and the optical detection system were calibrated by using deuterium and halogen lamps.

3. Results and discussion

In fig. 1a is shown a typical FA spectrum produced by the Ar(${}^{3}P_{0,2}$), Ar⁺, Ar^{+M}/SiH₄ reactions. The spectrum consists of the SiH($A^2\Delta - X^2\Pi_r$) emission from v' = 0-2 and SiI lines; the spectral assignment was carried out by reference to reported tables [5,6]. When Ar⁺ and Ar⁺ ions were trapped by using the ion-collector grid, no appreciable change in the intensity was found for the SiH(A-X) emission, while the triplet and singlet SiI lines reduced their intensities by 20-40% and 50-60%, respectively, as shown in fig. 1b. On the basis of these facts, the active species for the production of SiH(A) are the metastable $Ar({}^{3}P_{0,2})$ atoms, but $Ar({}^{3}P_{0,2})$ and Ar^{+} (and/or Ar^{+M}) participate in Si* production. The dependence of the emission intensity of Si* produced through ionic reactions on the Ar carrier gas-pressure was similar to that of the CH(A² Δ -X² Π_r) emission produced through the Ar^{+M}/CH₃CN reaction [7], but it was different from that of the OCS⁺ ($\tilde{A}^2\Pi - \tilde{X}^2\Pi$) emission from the Ar⁺/OCS re-



Fig. 1. Emission spectra obtained from the (a) Ar^* , Ar^+ , $Ar^{+M}/$ SiH₄ and (b) Ar^*/SiH_4 reactions in the Ar afterglow. Lines marked • and × are SiI and stray ArI lines, respectively. The optical resolution is 4.7 Å (fwhm).

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action [8]. Therefore, Ar^{+M} was found to be the dominant ionic active species for the Si* production: the available energies of Ar^{+M} are 16.4-20.3 eV for the $Ar^{+M} \rightarrow Ar^{+}$ excitation transfer and 17.9-22.2 eV for the $Ar^{+M} \rightarrow Ar^{*}$ charge transfer [9]. In order to examine the effect of ArI resonance lines emitted from the discharge source, a hollow-cathode discharge source with a bent light trap was used. The observed spectrum was the same as that obtained using the microwave discharge source without a light trap, indicating that the ArI resonance lines are not responsible for the production of the emitting excited states. Since the first ionization potential of SiH_4 (²T₂, 11.60 eV [10-12]) is close to the electronic energy of Ar*(${}^{3}P_{2}$, 11.55 eV; ${}^{3}P_{0}$, 11.75 eV), Ar*/SiH₄ Penning ionization and subsequent ionelectron recombination processes may result in neutral excited fragments. In order to examine the effect of such secondary reactions, emission spectra from the Ar(${}^{3}P_{0,2}$)/SiH₄ reaction have been observed under single-collision conditions by using the beam apparatus. Although the emission intensity was too weak to detect all Si* lines found in the FA experiment, the relative intensity of the dominant Si* lines and the SiH(A-X) band was similar to that in the FA experiment. It is thus concluded that the SiH(A)and Si* emissions are excited by the following primary reactions:

$$Ar^{*}+SiH_{4}$$

$$\rightarrow SiH(A^{2}\Delta)+H_{2}(X^{1}\Sigma_{g}^{+})+H(1^{2}S)+Ar(^{1}S),$$
(1)
$$\rightarrow Si^{*}(triplet states)+2H_{2}(X^{1}\Sigma_{g}^{+})+Ar(^{1}S),$$
(2a)
$$\rightarrow Si^{*}(singlet states)+2H_{2}(X^{1}\Sigma_{g}^{+})+Ar(^{1}S).$$

(2b)

The SiI lines measured with a better spectral resolution to resolve fine structure are shown in fig. 2. The identified transitions and their calculated threshold energies are given in table 1. No contribution from cascade transition is found for the observed SiI atomic lines.

The Ar(${}^{3}P_{0}$)/Ar(${}^{3}P_{2}$) ratio under operating conditions was evaluated to be about 0.01 from the intensity distribution of the N₂(C-B, v' = 0-3) emission [15]. We therefore assumed that the



Fig. 2. SiI lines produced from the Ar^*/SiH_4 reaction in the Ar afterglow. The optical resolution is 1.2 Å (fwhm).

contribution of $Ar({}^{3}P_{0})$ is negligible. The emission rate constants were estimated by using the following reaction as a reference [15]:

$$Ar({}^{3}P_{2}) + N_{2} \xrightarrow{\kappa_{3}} N_{2}(C {}^{3}\Pi_{u}, v' = 0) + Ar({}^{1}S) ,$$

$$k_{3} = 2.75 \times 10^{-11} \text{ cm}^{3} \text{ s}^{-1} .$$
(3)

By comparing the emission intensity of N₂(C-B, v'=0) with each emission band measured under the identical experimental conditions, $k_{\rm em}$ values have been determined. The results are given in table 1 along with the corresponding emission cross sections estimated from the relation $\sigma_{\rm em} = k_{\rm em}/\langle v \rangle$, where $\langle v \rangle = (8kT/\pi\mu)^{1/2}$ is the mean Boltzmann speed at 300 K. The emission cross section for SiH(A) is larger than that for the total production of Si* by a

factor of 15. Processes (1) and (2) require three and four bonds to be broken, respectively, accompanied by elimination of molecular H₂. It has been known that elimination of H₂ is an unimportant exit channel in most reactions of metastable argon atoms with hydrogen-containing compounds, for example $H_2O(f_{H_2}=0)$ and $C_2H_6(f_{H_2}<0.04)$ [16]. Although the total quenching cross section of the $Ar({}^{3}P_{2})/SiH_{4}$ reaction has not been measured, it must be of the order of $\gtrsim 100 \text{ Å}^2$ on the basis of a linear correlation between total quenching cross sections and the long range attractive van der Waals coefficient C_6 [17]. From a comparison of this value and σ_{em} for process (1), an upper limit of $f_1 = 0.04$ for process (1) is deduced. The small branching fraction indicates that process (1) is a minor exit channel. It is expected that the major pathway $(f \ge 0.96)$ of the Ar $({}^{3}P_{2})/$ SiH₄ reaction is by other competing channels. The most probable channels are dissociation to $SiH_2 + H_2$ (2H) and SiH₃+H, because the Ar(${}^{3}P_{2}$)/SiH₄ reaction is an effective way of generating amorphous silicon films [2].

The calculated threshold energies of SiH(A), Si(³P^o) and Si(¹P^o) are 8.69, 9.12, and 9.27 eV, respectively. The appearance potential of SiH(A) has been observed at 10.5 ± 0.5 eV in the electron-impact excitation of SiH₄ [18,19] and at 9.43 ± 0.04 eV in the photoexcitation [20]. The SiI lines start at 11.5 ± 0.5 eV in the electron-impact excitation [18,19] and at ≈ 10.3 eV in the photoexcitation [20]. Since the energy of Ar(³P₂) is higher than these

Table 1

Emission rates and cross sections of excited fragments obtained from the $Ar({}^{3}P_{2})/SiH_{4}$ reaction. The labels refer to the markers for SiI lines in fig. 2

Label	Transit ion	Wavelength (nm)	Threshold energy (eV) ^{a)}	$k_{\rm em} (10^{-12}{\rm cm}^3{\rm s}^{-1})^{\rm b)}$	$\sigma_{\rm em}$ (Å ²) ^{b)}
	SiH(A ² Δ -X ² Π_r)	409.4-423.21	8.69	24	4.0
	SiI lines				
6	4s ¹ P°-→3p ^{2 1} D	288.2	0.27	0.23	0.038
	4s ¹ P°→3p ^{2 1} S	390.5	9.27	0.011	0.0019
5	$3d^{1}P^{\circ} \rightarrow 3p^{2}S^{1}S$	263.1	10.81	0.0069	0.0012
3	$3d^{1}D^{\circ} \rightarrow 3p^{2}D^{1}D$	243.5	10.06	0.095	0.016
4 4	$4s {}^{3}P^{\circ} \rightarrow 3p^{2} {}^{3}P$ $4s {}^{3}P^{\circ} \rightarrow 3p^{2} {}^{1}D$	251.4-252.9 250.7-251.9	9.11-9.14	0.95	0.16
1	$3p^{3}D^{o} \rightarrow 3p^{2} ^{3}P$	220.8-221.9	9.80	0.28	0.047
2	$3d {}^{3}F^{\circ} \rightarrow 3p^{2} {}^{1}D$	229.1	10.38	0.016	0.0027

^{a)} Calculated from refs. [6,13,14]. ^{b)} Uncertainty $\pm 10\%$.

values, the observation of SiH(A) and SiI lines by the Ar* impact is consistent with the previous findings in the electron and photon-impact excitation [18-20]. The calculated threshold energy of the observed SiI atomic lines ranges from 9.12 to 10.81 eV. A wide energy distribution of Si* may suggest that the entrance potential of Ar*/SiH₄ is attractive, then the probability of intersections with a number of product surfaces is enhanced.

In the photodissociation, the singlet Si(4s ${}^{1}P^{\circ} \rightarrow$ $3p^{2}D$ line at 288.2 nm is dominant and the triplet Si(4s ${}^{3}P^{\circ} \rightarrow 3p^{2} {}^{3}P$) line at 251.6 nm was one order of magnitude weaker than the Si(4s $^{1}P^{0} \rightarrow 3p^{2} {}^{1}D$) line [21]. On the other hand, the emission cross section of the Si(4s ${}^{3}P^{0} \rightarrow 3p^{2} {}^{3}P$) line is about the same as that of the Si(4s ${}^{1}P^{0} \rightarrow 3p^{2} {}^{1}D$) line in the vicinity of the appearance potentials under the electron-impact excitation [18]. In the present Ar* impact study, it was found that the electronic distribution of Si* atomic states favors the lowest electronically excited triplet state and that the total emission cross section of the triplet levels is larger than that of the singlet levels by a factor of ≈ 4 . These differences can be explained by the spin-conservation rule. Since only $H_2(X^{1}\Sigma_{e}^{+})$ is energetically accessible as partners of Si excited states, singlet and triplet Si* levels must be produced through singlet and triplet excited states of precursor SiH^{*}₄. Possible candidates of the precursor states are triplet and singlet Rydberg excited states converging onto the first ionization potential, as observed in the electron energy-loss spectrum of SiH₄ [22]. A preferential formation of Si atoms in the triplet states implies that the spin conservation rule generally holds during the reaction. The observation of weak SiI lines in the singlet state indicates a violation of the spin-conservation rule. The formation of the singlet Si atoms is probably due to some strong perturbation in reaction intermediates. An enhancement of the singlet SiI lines in the Ar^{+M}/SiH₄ reaction is probably due to opening of a number of high energy spin-allowed processes leading to Si* singlet states.

Figs. 3a and 4a show expanded emission spectra of SiH(A-X) measured in the FA and beam experiments, respectively. The rovibrational distribution of SiH(A) was estimated by a computer simulation of the observed spectra assuming a single Boltzmann rotational distribution for each v'. The procedure



Fig. 3. The observed and calculated spectra of SiH(A ${}^{2}\Delta$ -X ${}^{2}\Pi_{r}$) obtained from the Ar*/SiH₄ reaction in the Ar afterglow. The optical resolution is 0.7 Å (fwhm).



Fig. 4. The observed and calculated spectra of SiH(A ${}^{2}\Delta$ -X ${}^{2}\Pi_{r}$) obtained from the Ar^{*}/SiH₄ reaction in the beam cell. The optical resolution is 2.9 Å (fwhm).

used for the spectral simulation was identical with that reported by Perrin and Delafosse [23]. In the simulation, we used Franck-Condon factors calcu-

Table 2						
Rovibrational	distribution	of	$SiH(A^{2}\Delta)$	produced	from	the
$Ar(^{3}P_{2})/SiH_{4}$	reaction at th	ern	nal energy			

		v'=0	v' = 1	<i>v'</i> = 2
beam	N _v T _r (K)	100 1600±200	60 ± 4 1400 ± 200	5±2 1000±300
FA ^{a)}	Ν _{ν΄} Τ _r (Κ)	$100 \\ 1300 \pm 100$	$\begin{array}{c} 60\pm3\\ 1100\pm100 \end{array}$	5±1 400±100

^{a)} Flowing afterglow at an Ar pressure of 0.3 Torr.

lated by Smith and Liszt [24] and a linear electronic-transition function of $R_e^2(\bar{r}) = 0.217 0.0962\bar{r}$ given by Carlson et al. [25]. The corresponding best fit spectra are shown in figs. 3b and 4b. The rovibrational distributions obtained are given in table 2. The vibrational distribution in the FA and beam experiments is similar, indicating that the vibrational relaxation by collisions with the buffer Ar gas is insignificant during the radiative lifetimes of SiH(A ² Δ : 400-600 ns for v' = 0, 1 and 140-160 ns for v' = 2 [25]). On the other hand, a comparison of the FA and beam data suggests that the SiH(A) radicals are rotationally relaxed by collisions with Ar in the FA experiment. By using the nascent rovibrational distribution obtained in the beam experiment, the average vibrational and rotational energies are estimated to be 0.088 and 0.13 eV, respectively. The available energy of reaction (1) for $Ar({}^{3}P_{2})$ was estimated to be 2.94 eV from the relation: $\langle E_{avi} \rangle =$ $-\Delta H_0^0 + 3RT$. The fractions of vibrational energy $\langle f_{\rm v} \rangle$ and rotational energy $\langle f_{\rm r} \rangle$ were evaluated to be 2.9% and 4.4%, respectively. This shows that a large amount of the available energy must be converted into the rovibrational energy of H₂ and the relative translational energy of products.

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