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Mechanism of surface reaction in the deposition process of *a*-Si:H by rf glow discharge

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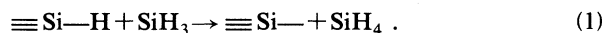
Hydrogenated amorphous Si (*a*-Si:H) films are deposited by the rf glow discharge of SiH_4. The mechanism of the surface reaction of the incident SiH_3 radical produced by the glow discharge to form the *a*-Si:H network was studied in this work. The hydrogen concentration was investigated by IR absorption in *a*-Si:H films deposited under various conditions of the substrate temperature T_s and the SiH_4 partial pressure P_s in the reactant gases. The hydrogen concentration in the films was divided into SiH and SiH_2 configurations by spectral deconvolution. While the SiH concentration S_1 was not influenced very much by variation of the deposition conditions, the SiH_2 concentration S_2 was remarkably influenced. S_2 increased with an increase in the deposition rate of the film at a different rate by the variation of T_s and P_s. The following reaction scheme of the radicals adsorbed on the growing surface is proposed to explain these changes in S_2 and S_1. The dehydrogenation and Si-Si bond formation into the network are made by two kinds of processes, the fast process and the slow process. The fast process occurs predominantly in high-rate depositions and incorporates SiH_2 into the network. The slow process occurs predominantly in low-rate depositions and incorporates some SiH. The fast process takes place by interactions of two adsorbed radicals and the slow process takes place at steplike sites after migration on the surface. The observed variations in S_2 with T_s and P_s are analyzed by this model and the rate constants of each process are determined. The activation energy in the slow process is obtained to be 0.3 eV, which is considered to be due to the migration of the SiH_3 radical on the growing surface. The data of the S_1 variation are also analyzed and the minimum concentration of H atom is found to be about 10 at. %, in agreement with experiments. Variation of the dangling-bond density with deposition condition is found to have similarities with that of S_1 and S_2. The features of the surface reaction mechanism are successfully explained by this model.

I. INTRODUCTION

Hydrogenated amorphous Si (*a*-Si:H) films are very important materials for semiconductor devices, where a large area is necessary, e.g., thin-film transistors (TFT's) which drive large-area liquid-crystal-display panels. The films are usually deposited at low temperatures by the radio frequency (rf) glow discharge of SiH_4 gas. Understanding the deposition mechanism is essential both for control of the deposition process and improvement of the film quality. Although many efforts have been made to clarify the deposition mechanism, there has been no definite clue to analyze the relationship between the deposition mechanism and the film properties, because the deposition mechanism from plasma is very complicated for *a*-Si:H. There is a large variation in the parameters of preparation conditions and also in the parameters of atomic and electronic structures. Among the various deposition methods, the conventional method for the undoped material is the capacitively coupled rf glow discharge of SiH_4 and H_2 gas mixture at a gas pressure between 1 and 0.1 Torr, and a substrate temperature between 250 and 300 °C.

It was shown recently by IR diode laser absorption spectroscopy[1,2] that the SiH_3 radical is the main precursor in the conventional SiH_4-H_2 plasma. The incident SiH_3 radicals are considered to be weakly adsorbed on the H-atom-terminated growing surface, which then from Si—Si bonds constituting an *a*-Si:H network during migration on the surface. The sticking probability for SiH_3 radicals incident on the growing surface was experimentally determined.[3] The monolayer coverage of the growing surface by hydrogen during deposition at temperatures below 380 °C was experimentally confirmed.[4,5] In previous studies of the surface reaction,[3,6,7] attention has been paid only to the Si—Si bond formation in the growing surface. In order to form a Si—Si bond in this situation, a dangling bond on the growing surface seems necessary. The reason for this is that the Si—H bond is stronger than the Si—Si bond,[8] and a simple substitutional reaction of a $\equiv$Si—H bond by a SiH_3 radical to a $\equiv$Si—SiH_3 bond seems unlikely to take place,[6] where $\equiv$Si represents the Si atom at the surface which is bonded into the network.

The abstraction reaction producing a surface dangling bond was reported to occur more easily by H atoms than by alklyl radicals.[9] Since the lifetime of H atoms is shorter than SiH_3 in the plasma due to a reaction with SiH_4 producing SiH_3+H_2,[10] the H-atom density in the gas phase near the surface is considered to be much smaller than the SiH_3. Therefore, it has been postulated[6,7] that two SiH_3 radicals are necessary to make a Si—Si bond. The first SiH_3 radical arriving at the H-terminated growing surface abstracts the H atom to become SiH_4, and leaves a dangling bond on the growing surface:



$$\equiv\text{Si—H}+\text{SiH}_3\rightarrow\equiv\text{Si—}+\text{SiH}_4\ . \tag{1}$$

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The second incident SiH_3 radical reacts with this dangling bond, leading to growth by the formation of a Si—Si bond:

$$\equiv Si— + SiH_3 \rightarrow \equiv Si—SiH_3 \ . \quad (2)$$

The above model is reasonable with respect to the energy balance of the reaction.

The hydrogen-atom content in *a*-Si:H films deposited at a substrate temperature T_s of 250 °C, where films of good electronic quality are usually deposited, is about 20 at. %.[11] A large number of H atoms in the SiH_3 radicals have to be released when the Si—Si bonds are formed during the surface reaction. It is known[11] that films deposited at lower temperatures contain a larger number of H atoms. It has been considered[5] that a conversion of pair of Si—H bonds into an Si-Si bond accompanying a formation of a H_2 molecule releases excess H atoms from the network. However, this rebonding will occur and become an exothermic reaction when the Si atoms are free to reach a position satisfying the short-range order. It was found experimentally[5] that the hydrogen-rich surface layer of multiply H-bonded Si atoms is one monolayer during deposition at the 240 °C substrate temperature, although it extends to about 5 ML thick on a room-temperature substrate. Once a Si-Si network with cross linking is formed by the surface reaction, it is considered to be difficult to release H atoms retained in the network beneath the surface under the conventional deposition conditions. Therefore, the above-postulated reaction mechanism does not explain the dependence of the H-atom concentrations in the deposited films upon the deposition conditions described in this paper.

It has been reported that the growing surface in the steady state is not uniform, but has about 10-Å roughness after coalescence of nuclei by time-resolved ellipsometry.[12] The roughness depends on the deposition condition. The above 10-Å roughness is the minimum value under the condition producing films of good electronic quality. This result is also not explained by the above mechanism. Therefore, further experimental studies are necessary to establish the reaction mechanism to explain the dehydrogenation reaction as well as the Si—Si bond formation on the growing surface.

The hydrogen concentration in the film is detected by IR absorption. The hydrogen atoms in *a*-Si:H are divided into two configurations, i.e., SiH and SiH_2, which have different IR-absorption frequencies. It is believed that the probability that H atoms in SiH_3 radicals are incorporated into the *a*-Si:H network as either SiH or SiH_2 is determined by the dehydrogenation reaction when the Si—Si bond is formed.

In this paper, we propose a mechanism for the Si—Si bond formation and dehydrogenation reaction on the growing surface. Hydrogenated *a*-Si films were deposited by rf glow discharge of SiH_4 gas diluted with H_2 at a different substrate temperature T_s or under a different partial pressure P_s of SiH_4. IR absorption of these films was investigated. The hydrogen concentrations of SiH and SiH_2 configurations were determined from the integrated absorption intensity by spectral deconvolution. It was found that the SiH_2 concentration S_2 is much larger than the SiH concentration S_1 in most of these films, and that variations of S_1 and S_2 concentrations with variations of T_s and P_s are quite different. Different mechanisms are considered to be working in the incorporation of the SiH and SiH_2. The deposition mechanism has to be able to explain these variations in H concentrations with variations of deposition conditions. Since the variation of the S_2 concentration is larger than that of S_1, the mechanism of SiH_2 incorporation is first considered in this paper and then S_1 is analyzed similarly.

In the film formation process, the first-order (monomolecular) reaction rate on the surface varies with T_s. The incident flux density of SiH_3 varies with P_s, and influences the second-order (bimolecular) reaction rate. These changes are considered to produce changes in the hydrogen concentrations. A mechanism of the surface reaction is devised based on this idea to explain the experimental variations in the H concentrations. There are two kinds of surface reaction processes; the fast process dominates at fast deposition rates, and the slow process dominates at slow deposition rates. These two processes differ in the dehydrogenation of the adsorbed radicals. The fast process involves interactions between radicals, and the slow process involves surface diffusion of the adsorbed radicals to steplike sites. Numerical values of the reaction-rate constants are obtained by analyzing the experimental data to fit the theoretical relations.

Dangling-bond densities N_s were also measured in these films. The variation of N_s with the deposition condition has similarities to that of S_1 and S_2. This result suggests that the mechanism of dangling-bond formation is related to the dehydrogenation reaction in the network formation.

In this paper, the experimental procedure is described in Sec. II, and the experimental results in Sec. III. The mechanism of surface reaction is considered in Sec. IV; Sec. IV A describes basic considerations, and Sec. IV B deals with analysis of the experimental data. A discussion on the above model is made in Sec. V. The conclusion is provided in Sec. VI.

II. EXPERIMENTAL PROCEDURE

Hydrogenated *a*-Si films used in experiments were prepared by rf glow discharge of a SiH_4 and H_2 gas mixture in a capacitively coupled reactor.[13] The gas pressure was 0.5 Torr in the reaction chamber, and the rf power density was 0.07 W/cm^2. The substrate temperature T_s was kept constant during deposition. Two kinds of substrates were used for different purposes; crystalline Si for measurements of IR absorption, and fused quartz for measurements of electron-spin resonance (ESR).

Conditions for the series of depositions varying either the substrate temperature T_s or the SiH_4 partial pressure P_s were as follows. For the variation of P_s, the total gas flow rate $[SiH_4]+[H_2]$ was kept constant at 100 SCCM (where SCCM denotes cubic centimeter per minute at STP), and T_s was 250 °C. The SiH_4 partial pressure P_s was varied from 0.25 to 0.50 Torr by varying the SiH_4 flow rate from 50 to 100 SCCM. For the variation of T_s, the flow rate was fixed at 50 SCCM for each SiH_4 and H_2

gas, and T_s was varied from 120 to 360 °C. The condition common to the two series of depositions, i.e., $T_s = 250$ °C and $P_s = 0.25$ Torr, is called the standard condition of deposition. An additional deposition was made at the gas pressure 0.07 Torr with a SiH_4 gas flow rate of 5 SCCM at $T_s = 120$ °C in order to compare the films deposited at different gas pressures. The thickness of the samples was made more than 8000 Å to avoid errors due to a surface effect. The film thickness was measured by a Talystep. ESR experiments were made by an X-band apparatus in the dark at room temperature.

III. EXPERIMENTAL RESULTS

Deconvolution of the IR-absorption spectra for determining the H density was made under the assumption that (1) the peaks in the spectral region from 2000 to 2090 cm^{-1} are due to the stretching mode of the Si-H configuration having a peak at around 2000 cm^{-1}, and the Si-H_2 configuration having a peak at around 2090 cm^{-1}; and (2) the component spectrum has a Gaussian shape. As for the proportional constant converting the integrated absorption intensity to the atomic concentration, the values given by Langford *et al.*[14] were used: $A(\mathrm{SiH}) = 0.9 \times 10^{20}$ cm^{-2} and $A(\mathrm{SiH_2}) = 2.2 \times 10^{20}$ cm^{-2}.

Figures 1–3 show the results of deconvolution. The concentrations of Si-H and Si-H_2 thus obtained are shown for the variation of P_s in Fig. 1(a), and for the variation of T_s in Fig. 1(b). In almost all samples, the SiH_2 concentration S_2 is larger than the SiH concentration S_1. The large variation of the total H concentration under preparation conditions is mainly due to S_2. S_2 increases by increasing P_s, i.e., by decreasing the H_2 gas dilution. This dependence is in agreement with a previous report,[15] but is contrary to a simple expectation that the H concentration in the solid is proportional to the H concentration in the gas phase. S_1 varies in the opposite direction to S_2 with variations in the preparation conditions. S_1 decreases by increasing P_s and increases by increasing T_s. It is noted that the SiH concentration is nearly equal to that of SiH_2 in the present study under the condition usually employed to make an a-Si:H film of good electronic quality, i.e., $T_s = 250$ °C and the flow ratio $[H_2]/[SiH_4] = 1$. This condition is referred to as the standard condition in this paper.

Parsons, Tsu, and Lucovsky[16] reported nearly the same variations of the absorption coefficients at peaks of 2000 and 2100 cm^{-1} with variations in T_s. Their result has been considered to represent the concentration of S_1 and S_2. However, the proportional constant converting the absorption coefficient to the atomic density[14] has to be multiplied to represent the density, since the oscillator strength is different for each mode of vibration. The two absorption bands overlap, and their spectrum, peak ener-

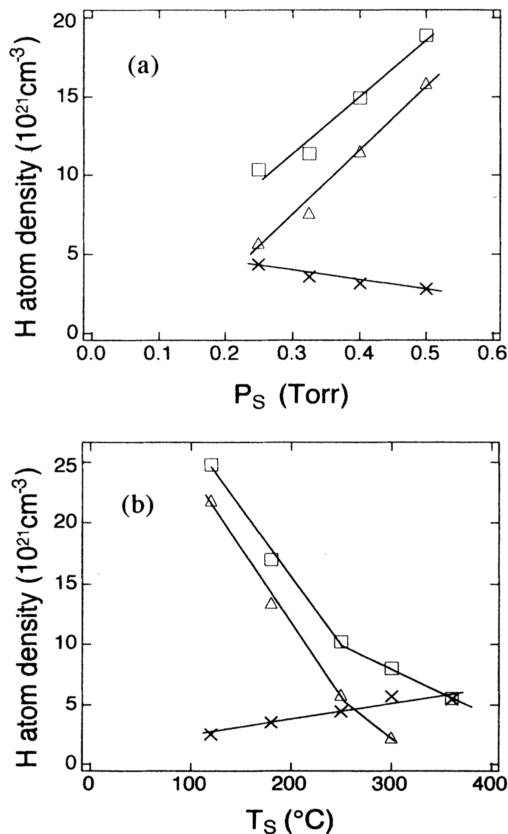


FIG. 1. H-atom densities in a-Si:H films. Films were (a) deposited by varying P_s and (b) deposited by varying T_s. Total H-atom density $(S_1 + S_2)$ (□), S_1 (×), and S_2 (△).

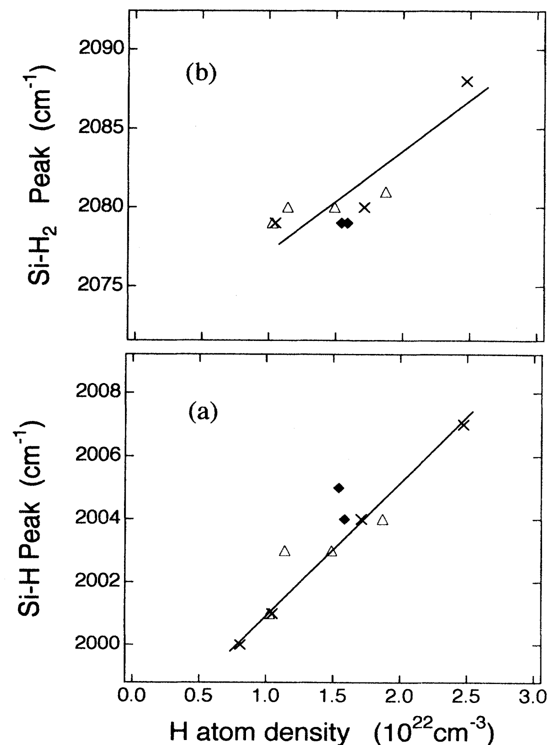


FIG. 2. Frequency shifts of Si-H stretching mode with total H-atom densities. (a) SiH peak. (b) SiH_2 peak. Films deposited at various T_s (×), films deposited at various P_s (△), and films deposited at low pressure (◆).

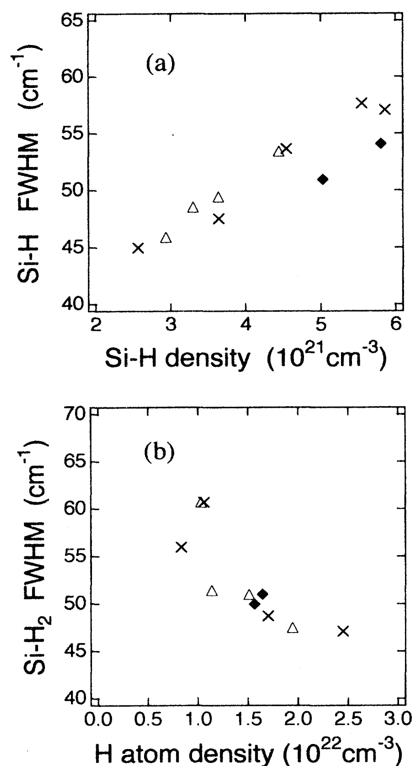


FIG. 3. Spectral width FWHM of Si-H stretching mode against H densities. (a) SiH FWHM vs SiH density, and (b) SiH_2 FWHM vs total H-atom density. Films deposited at various T_s (×), films deposited at various P_s (△), and films deposited at low pressure (♦).

gy, and width may change with the concentration. Hence the integrated absorption intensity obtained by spectral decomposition employed in this paper is more accurate for obtaining each concentration than the absorption coefficient at the fixed peak position.

As for the above results of the S_1 and S_2 vs T_s relation, it should be mentioned that exactly the same temperature dependence of the H concentrations in a-Si:H films was independently reported by nuclear-magnetic-resonance (NMR) measurements.[17] In the NMR spectrum, there is a narrow component due to the dispersed H atoms $[H]_n$ and a broad component due to the clustered H atoms $[H]_b$. It is considered that $[H]_n$ corresponds to the dispersed SiH concentration, and that $[H]_b$ corresponds to the sum of SiH_2 and clustered SiH concentrations.[18] Exactly the same assignments apply to the IR absorption. The absorption at 2000 cm^{-1} is assigned to the stretching mode of isolated SiH, and the absorption at 2100 cm^{-1} is assigned to that of SiH_2 and clustered SiH.[14] The proportional constant A is considered to be different for the SiH_2 and the clustered SiH. However, the temperature dependence of $[H]_n$ and $[H]_b$ is the same as that of the isolated SiH and SiH_2 concentrations, respectively, if one ignores clustered SiH. It is known that a-Si:H has microvoids, on whose internal surface H is believed to cluster. Hence the clustered SiH concentration seems to be small compared with the isolated SiH concentration in the present samples. Reliability is thus assured for the above S_1 and S_2 determinations.

The peak shift of the spectrum is shown for the SiH peak in Fig. 2(a) and for the SiH_2 peak in Fig. 2(b) as functions of the total H-atom density. These two peaks exhibit peak shifts of nearly the same amount with the total H-atom density. The observed peak shift of SiH is about 7 cm^{-1} for the total H-atom density 2.4×10^{22} cm^{-3}, which is a little small but nearly equal to a value calculated according to the Lucovsky model given for films deposited by remote plasma-enhanced chemical vapor deposition (RPECVD).[19] The distinguishing feature of RPECVD is the small H concentrations, especially the SiH_2 concentration in the deposited film compared with the conventional glow discharge. The absorption at 2090 cm^{-1} is not detected in the film deposited at T_s higher than 200 °C.[16] According to the Lucovsky model of the frequency shift with composition, a small difference may arise by a partition of H atoms between SiH and SiH_2 for the same total H concentration. The SiH_2 peak is located at rather small wave numbers 2079–2088 cm^{-1}, as shown in Fig. 2(b) by the spectral deconvolution of the two overlapped Gaussian spectra.

The spectrum widths [full width at half maximum (FWHM)] are shown for the SiH peak in Fig. 3(a) against the SiH density, and for the SiH_2 peak in Fig. 3(b) against the total H-atom density. It is interesting to note that the width of the SiH spectrum increases with the SiH density, as shown in Fig. 3(a), but decreases with the total H-atom density similarly to the SiH_2 width, as shown in Fig. 3(b), since the densities of SiH and the total H atom vary in opposite directions with deposition conditions. These spectral widths are much smaller than the reported widths of 60–120 cm^{-1} of the SiH mode.[19] A cause of this discrepancy may be the neglect of an unresolved small contribution of the SiH_2 mode in RPECVD films. In Figs. 2 and 3, experimental data for films deposited under the lower gas pressure are also shown to be in agreement with data for films deposited at the higher gas pressure.

The dependence of the deposition rate R on P_s and T_s is shown in Fig. 4. R increases linearly with P_s when T_s is kept constant. When an energy transfer from the H atom to the SiH_4 molecule can be neglected in the plasma of present H_2/SiH_4 gas ratios, the incident SiH_3 flux density is proportional to P_s. The observed P_s dependence of the deposition rate is in agreement with the SiH_3 flux density dependence reported previously.[20] This result suggests that only SiH_3 radicals derived from SiH_4 contribute to the growth of an a-Si:H network proportionally to its flux density. Although H-atom density in the gas phase surrounding the growing surface is considered to be increased by the dilution of the raw SiH_4 gas, it does not make a significant contribution to the growth, in agreement with the discussion in Sec. I. R has been reported to be independent of T_s.[3] However, R was found in our experiment to increase with decreasing T_s. As discussed in detail below, the cause of this increase is interpreted to be due to an increase of H concentration in the

film with decreasing T_s for the constant sticking probability, since the total atom density is nearly constant in an a-Si:H film of various H concentrations.[14]

The dangling-bond densities N_s determined by the ESR experiment are shown in Fig. 5 for variations in P_s and T_s. While N_s is about 3×10^{16} cm^{-3} for the film deposited under the standard condition, $[H_2]/[SiH_4]=1$ and $T_s=250\,°C$, it increases exponentially either with decreasing T_s or with increasing P_s. The same dependence of N_s on T_s was reported previously.[17] While the scale of N_s in Figs. 5(a) and 5(b) is logarithmic and the scale of H-atom densities in Figs. 1(a) and 1(b) is linear, the ranges of P_s and T_s for the variation in either N_s and the H-atom densities are the same in the corresponding figures. Here the large density of the SiH_2 is considered to have a dominant effect at temperatures below 250 °C, and a minimum value of N_s at temperatures above 250 °C in Fig. 5(b) is assumed to be a residual value related to the SiH density. Although N_s is smaller than the SiH_2 and SiH densities by several orders of magnitude, these results suggest a correlation of the cause of dangling-bond formation with the process of the SiH_2 and SiH incorporation.

IV. MECHANISM OF SURFACE REACTION

A. Basic consideration

The SiH_2 densities S_2 in the film obtained as a function of P_s and T_s as shown in Fig. 1 are replotted against the deposition rate R in Fig. 6. The S_2 density increases in both cases with increasing R, but quantitatively at a different rate depending on whether P_s or T_s is varied. This result makes us recognize that S_2 is determined by the common mechanism of the surface reaction in both cases. Different parameters involved in the surface reaction are influenced by P_s and T_s. Since the dehydrogenation reaction is an essential part of the surface reaction,

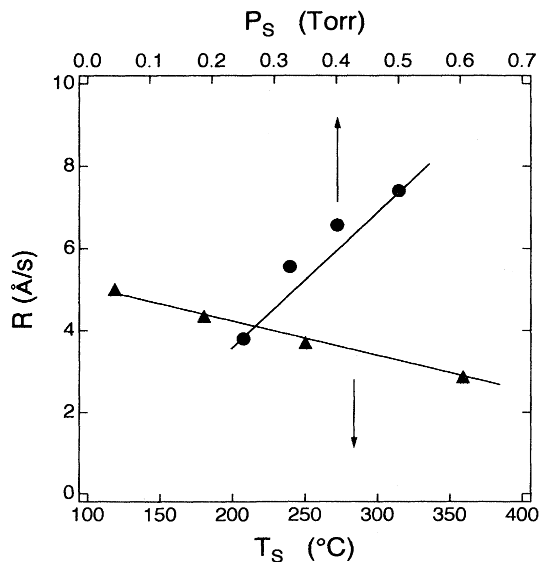


FIG. 4. Dependence of deposition rate R on substrate temperature T_s (▲) and SiH_4 partial pressure P_s (●).

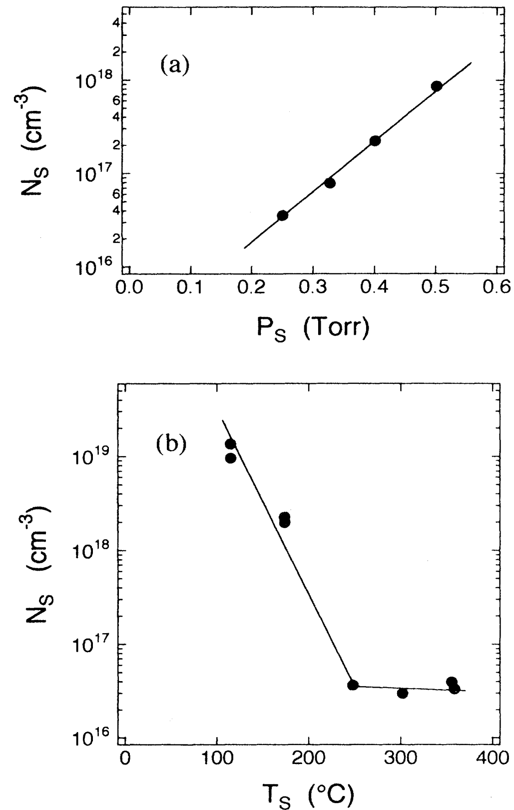


FIG. 5. Variation of Si dangling-bond density N_s with deposition conditions. (a) Films deposited varying P_s and (b) films deposited varying T_s.

the incorporated S_2 is the product of the surface reaction. The surface reaction is considered in this section by analyzing S_2 density as a clue.

At first the experimental data described in Sec. III are compared with Ref. 1 to confirm that the SiH_3 radical is the dominant precursor in the present deposition. This is done because the rf glow discharge is a nonlinear phenomenon, and other kinds of precursors may take part under different conditions; e.g., it was reported[20] that Si_2H_4 may participate in the reaction on the surface in the diode discharge system. Important parameters in the standard condition of the present experiment are compared with those of Ref. 1 in Table I. The main differences of the present parameters from Ref. 1 are (1)

TABLE I. Comparison of glow discharge deposition parameters.

	Ref. 1	This paper	Unit
Gas pressure SiH_4/H_2	50/30	250/250	mTorr
Total gas flow	16	100	SCCM
rf power density	400	70	mW/cm^2
Electrode spacing	3	2.5	cm
Deposition rate	1.8	5.0	Å/s
Substrate temperature	without heating	250	°C

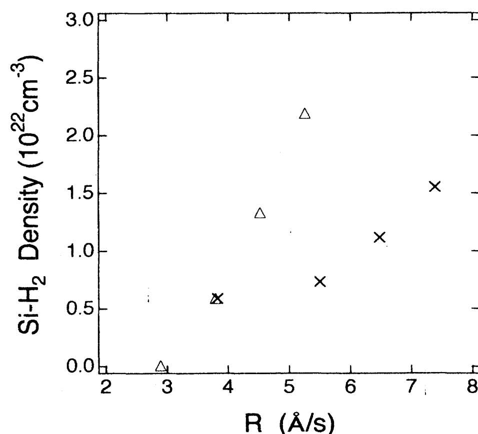


FIG. 6. SiH_2 densities against deposition rate R. Films deposited varying P_s (×) and films deposited varying T_s (△).

the SiH_4 partial pressure and the total gas flow are larger by a factor of 5–6, (2) the rf power density is smaller by a factor of approximately 6, and (3) the deposition rate is larger by a factor of approximately 3. In Ref. 1 the deposition rate for a substrate without heating was reported. According to the dependence of the deposition rate for the substrate temperature T_s shown in Fig. 4, the deposition rate in the present experiment is considered to be larger by a factor of approximately 4 at the same T_s. The deposition rate is proportional to the SiH_4 partial pressure in Fig. 4, but its dependence on the rf power density is unknown. A change of precursor from SiH_3 to others, for example, SiH_2, is considered to accompany a decrease of more than an order of magnitude in the deposition rate.[2] Therefore, it can be concluded that the two experimental results nearly coincide quantitatively, and that the main precursor for the deposition is also the SiH_3 radical in the present experiment.

According to the model used in previous studies,[3,5,7,20] the adsorbed SiH_3 radical migrates on the surface and forms a Si—Si bond to the network when it encounters a dangling bond. There is no specific correlation between the deposition rate and the SiH_2 concentration in the film. It has generally been considered that Si—Si bond formation during deposition between a pair of Si—H bonds bonded to the network releases a H_2 molecule,[5] and that the faster the deposition rate is the larger the H density incorporated into the network. However, it seems to be difficult to form a Si—Si bond between randomly bonded Si—H bonds with a small activation energy satisfying the requirement for the short-range order.

Figure 6 shows that the SiH_2 concentration S_2 increases several times compared with the standard condition up to a concentration comparable to that of the Si atoms, when the deposition rate R is increased. This variation of S_2 with R depends on whether R is varied by T_s or P_s. The dependence of the SiH concentration S_1 on T_s and P_s is opposite to that of S_2, as shown in Fig. 1, and S_1 decreases with increasing R. The dangling-bond density suspected to be left after release of H atoms into the network also decreases with the deposition conditions parallel to S_2, as shown in Fig. 5.

The migration velocity of the adsorbed SiH_3 is remarkably dependent on T_s due to its small activation energy. It is reasonable that the migration is the reason S_2 and S_1 are differently dependent on T_s and P_s. The destination of this migration is an issue which will help explain the experimental results. The adsorbed SiH_3 radical is considered to migrate to a favorable site where a Si—Si bond is formed easily from a pair of Si—H bonds without incorporation of the SiH_2 into the network. When the density of the adsorbed radical is increased, a bimolecular process is likely to take place during the migration. If the two relevant Si—H bonds are free to change their relative positions when they are loosely bounded by small energies, e.g., two adsorbed SiH_3 radicals, it would be possible to form a Si—Si bond by releasing a H_2 molecule.

The process which dominates at the slow deposition rate is called the slow process. When the deposition is made at a fast rate the Si—Si bond-making process proceeds accompanied by incorporation of the SiH_2 into the network. The process which dominates at the fast deposition rate is called the fast process. This fast process does not lead to incorporation of the SiH, the concentration of which depends differently on the deposition parameters T_s and P_s. Therefore, the fast and slow growth mechanisms, whether retaining the SiH_2 configuration or not, respectively, are expected to be correlated with the atomic processes considered above.

The two atomic processes above compete with each other, and a process having a short reaction time becomes the dominant process. Migration to the favorable site takes time, but this time becomes shorter when the substrate temperature is higher. The reaction time of the bimolecular process is inversely proportional to the square of the reactant concentration, which becomes larger when the migration velocity is slower and the incident flux density of reactant is higher. Therefore, the process of monomolecular migration corresponds to the slow process, which is dominant under the condition of high T_s and low P_s. The bimolecular process corresponds to the fast process, which is dominant under the condition of low T_s and high P_s.

As for the necessity of the dangling bond at the site where the Si—Si bond is formed in the network by the adsorbed SiH_3, it is considered as follows. If multiple Si—Si bonds are formed at the site of bond formation, the presence of a dangling bond is favorable but not a prerequisite regardless of the monomolecular or bimolecular processes. By the aid of exothermic reaction of the first Si—Si bond and H_2 molecule formation, the adsorbed state of the SiH_3 radical on the H-terminated Si surface is possibly converted to a Si—Si bond surmounting the endothermic reaction energy.

The observed increase in the deposition rate with decreasing T_s is calculated to be equal to the increase in the volume due to the increase in the H concentration shown in Fig. 1. The total atomic density of a-Si:H, Si, and H has been reported to be nearly constant independent of the H concentration.[14] This result is consistent with the

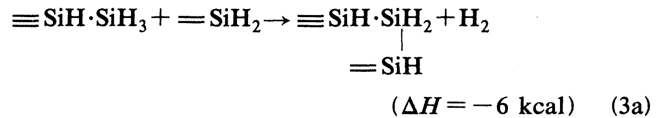
report that the sticking probability of the SiH_3 radical is constant independent of temperature below 350 °C.[3]

The step on the growing surface is well known as the site for the crystal growth by the slow and nearly in-equilibrium process. Although the growing surface is not as flat in amorphous material as in crystal, a steplike site can also be conceivable in amorphous material where the additive atom makes multiple bonds to the host network at the same time. The observed roughness of about 10 Å in the growing surface[12] is considered to be composed of this kind of step. During migration the radical is supposed to interact with another radical, when the density of the adsorbed radical is high. Due to this interaction the adsorbed radicals on the flat surface may have a chance to bond with each other and to the host network. A similar situation also occurs during crystal growth, when nucleation is made on a flat surface at high supersaturation of the growing material.

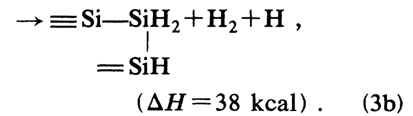
For the bonding reaction to take place spontaneously from the adsorbed state, the reaction has to be exothermic, i.e., the enthalpy change ΔH by the reaction has to be negative. The enthalpy change can be roughly estimated from the bond energies involved in the reaction. The following bond energies are given by Pauling:[8] Si—H bond, 70 kcal/mol; Si-Si bond, 42 kcal/mol; and H-H bond, 104 kcal/mol. The adsorption energy of $\equiv SiH \cdot SiH_3$ is estimated to be about 10 kcal/mol, since the desorption of the SiH_3 occurs at temperature above 350 °C.[3]

Although the structure of a real growing surface is supposed to be quite complex, a simplified scheme for the surface reaction is illustrated in Fig. 7 which satisfies the above considerations. The top horizontal flow is the slow process leading to the dehydrogenation at a steplike site, and the bottom flow is an example of the fast process leading to SiH_2 incorporation.

An example of the bonding reaction at a steplike site $=SiH_2$, if it is divided into two steps, is as follows:

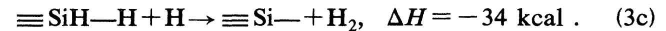


$$\equiv SiH \cdot SiH_3 + {=}SiH_2 \rightarrow \equiv SiH \cdot \underset{\displaystyle =SiH}{\underset{|}{Si}}H_2 + H_2 \quad (\Delta H = -6 \text{ kcal}) \qquad (3a)$$



$$\rightarrow \equiv Si\text{—}\underset{\displaystyle =SiH}{\underset{|}{Si}}H_2 + H_2 + H , \quad (\Delta H = 38 \text{ kcal}) . \qquad (3b)$$

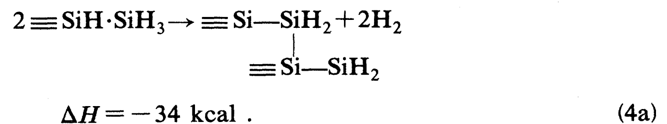
Here ΔH is the enthalpy change in each reaction. While ΔH is positive in reaction (3b), this reaction is considered to be coupled with an exothermic reaction of the H atom produced in reaction (3b) to form a H_2 molecule; for example, the reaction with a nearby terminating H atom is



$$\equiv SiH\text{—}H + H \rightarrow \equiv Si\text{—} + H_2, \quad \Delta H = -34 \text{ kcal} . \qquad (3c)$$

The total enthalpy change from (3a) to (3c) is negative. The dangling bond produced by reaction (3c) is also considered to be effective for the network formation by reaction (2). By these reactions two or three Si—Si bonds are formed, three or four H atoms are released, and the steplike site advances, forming a Si network with an appropriate short-range order.

The fast process is the Si—Si bond formation process, accompanying SiH_2 incorporation into the network by an interaction of two adsorbed radicals. There are many possible forms of the interaction. An easily conceivable example is two SiH_3 radicals adsorbed on nearest-neighbor sites of the flat growing surface. The reaction is



$$2 \equiv SiH \cdot SiH_3 \rightarrow \equiv Si\text{—}\underset{\displaystyle \equiv Si\text{—}SiH_2}{\underset{|}{Si}}H_2 + 2H_2$$
$$\Delta H = -34 \text{ kcal} . \qquad (4a)$$

By this reaction, two neighboring SiH_2 are produced parallel to the growing surface. Such a configuration

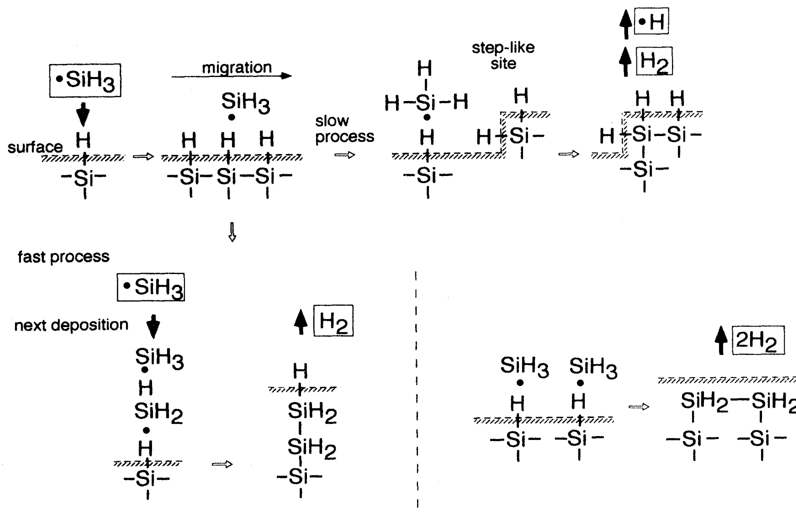
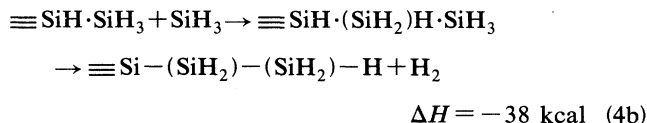


FIG. 7. Scheme of surface reactions. The horizontal flow is a slow process leading to dehydrogenation at a steplike site after surface migration. Vertical branching is an example of a fast process by interaction of radicals leading to SiH_2 incorporation. The solid arrow indicates the incidence or release of an atom or radical in a box.

may be considered to be rather unfavorable for the following reaction to reserve SiH_2.

Another configuration seems to be better for the fast process. When a second SiH_3 radical is incident and adsorbed on the first SiH_3 radical which is adsorbed on the surface, this atomic configuration is unstable. The reaction



$$\equiv SiH\cdot SiH_3 + SiH_3 \rightarrow \equiv SiH\cdot(SiH_2)H\cdot SiH_3$$
$$\rightarrow \equiv Si-(SiH_2)-(SiH_2)-H+H_2$$
$$\Delta H = -38 \text{ kcal} \quad \text{(4b)}$$

takes place. The resultant atomic configuration is two neighboring SiH_2 is arranged perpendicular to the growing surface. This configuration is a kind of steplike site but is rather favorable for the following reaction to reserve SiH_2. Here ΔH indicates the enthalpy difference between final and initial states. The probability of reaction (4a) seems to be larger than that of reaction (4b) by a factor of the number of available neighboring sites of interaction. It is not clear, however, whether the effective reaction for the fast process is (4a), (4b), or both (4a) and (4b). In Sec. IV B both reactions are assumed to be effective in the estimation of the reaction probability.

B. Analysis

The SiH_2 densities in the *a*-Si:H films are first analyzed in this section to derive the reaction-rate constant according to the surface reaction scheme described in the Sec. IV A. The SiH_2 density S_2 is considered to be decreased by the dehydrogenation reaction in the slow process during deposition from the initial value S_0. S_0 is the value of S_2 in the film where only the SiH_2 unit forms a Si-Si chain. The deposition proceeds simultaneously by both slow and fast processes. Denoting the probability of the slow process for an adsorbed radical by r_s, the average time τ_s necessary for the migration to a steplike site and release of H_2 is $1/r_s$. Denoting the probability of the fast process for an adsorbed radical by r_f, the average time τ_f necessary for the interaction with another SiH_3 radical to form Si—Si bonds incorporating a SiH_2 unit is $1/r_f$. The total probability of the two processes is (r_s+r_f). The SiH_2 concentration S_2 is S_0 when only the fast process occurs. Since the two processes occur simultaneously, the observed value S_2 is given by

$$S_2 = S_0 r_f/(r_f+r_s) = S_0\tau_s/(\tau_s+\tau_f) \ . \quad (5)$$

Equation (5) can be transformed to

$$S_2/(S_0-S_2) = \tau_s/\tau_f \ . \quad (6)$$

In the slow process, τ_s is estimated by setting half of the average distance between steps L equal to the diffusion length, $L^2 = D\tau_s$, where D is the surface diffusion constant. D is expressed as $D = D_0\exp(-\Delta E/kT)$, where D_0 is the preexponential factor, ΔE is the activation energy of diffusion, and kT is the thermal energy. In the fast process, τ_f is estimated as the reciprocal of the number of SiH_3 radicals n_f which stick to a surface area per unit time, where two SiH_3 radicals are able to produce a reaction, i.e., N_r times as large as the unit SiH_2 area. We can estimate n_f as N_r times the ratio of the deposition rate R to the unit-cell length d of an imaginary SiH_2 lattice:

$$\tau_f = (1/n_f) = (d/N_r R) \ . \quad (7)$$

Combining Eqs. (6) and (7), we obtain

$$S_2/(S_0-S_2) = (L^2 N_r R/dD_0)\exp(\Delta E/kT) \ . \quad (8)$$

Since the total atomic density N_t in *a*-Si:H is 5.3×10^{22} cm^{-3} approximately independent of the H concentration,[14] S_0 is equal to $2N_t/3 = 3.6\times10^{22}$ cm^{-3} for the atomic density ratio Si/H=1/2 and $d=(S_0/2)^{-1/3} = 3.8\times10^{-8}$ cm.

For the series of depositions varying T_s with a fixed P_s, Eq. (8) is transformed to

$$\ln\{S_2/(S_0-S_2)R\} = \ln(L^2 N_r/dD_0) + (\Delta E/kT) \ . \quad (9)$$

In Fig. 8, $\log_{10}\{S_2/(S_0-S_2)R\}$ is plotted against $1/T$. Experimental points align on a straight line. Equation (9) indicates that the gradient of the line gives the activation energy ΔE. L is assumed to be independent of temperature. The activation energy obtained from Fig. 8 is 0.30 eV. This value is close to but larger than the previously estimated value 0.2 eV.[20]

For the series of depositions produced by varying P_s with a fixed T_s, $S_2/(S_0-S_2)$ is plotted against the deposition rate R in Fig. 9 according to Eq. (8). A straight line through the origin of this figure can be drawn to represent the data, but the data points somewhat deviate from the line. This deviation is due to the deviation of P_s vs R data from the linear relation, as shown in Fig. 4. The gradient of the straight line gives the magnitude of $(L^2N_r/dD_0)\exp(\Delta E/kT)$ to be 7.5×10^6 s/cm. The magnitude of L is estimated to be 100 Å from an analysis of substrate-induced roughness during *a*-Si:H growth.[21] For an order-of-magnitude estimation, N_r can be set equal to 10, and the known values of d, ΔE, and kT are used. Then D_0 becomes 1×10^{-7} cm^2/s, which is equal to $a^2\nu$,[22] where a is the interatomic distance and ν is the

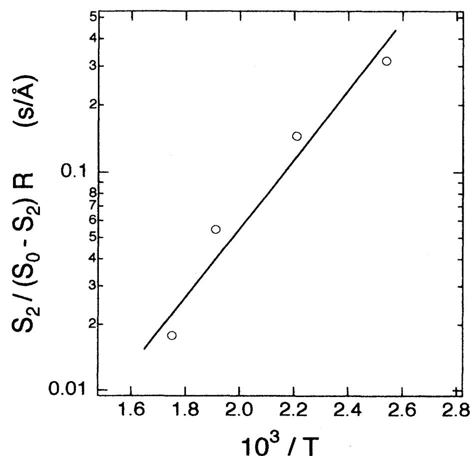


FIG. 8. Arrhenius plot of $S_2/(S_0-S_2)R$ to obtain the activation energy by the solid line.

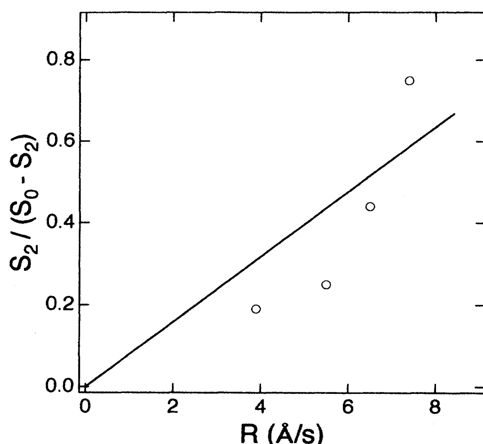


FIG. 9. Dependence of $S_2/(S_0-S_2)$ on deposition rate R to obtain the reaction-rate constant by the solid line.

jumping frequency. Since a^2 is about 10^{-15} cm^2, ν becomes 10^8 s^{-1}.

For this jumping frequency in the surface diffusion, the frequency ν_0 of optical mode vibration, about 10^{12} s^{-1}, is usually expected to be appropriate. However, a large difference was found in D_0 values from such an expectation for the surface diffusion of adsorbed atoms on metal by field-ion microscopy; e.g., $D_0=3.7\times10^{-7}$ cm^2/s for W atoms adsorbed on a W(211) surface and 1.5×10^{-2} cm^2/s for Re atoms adsorbed on W(100) surface.[22] The reason for this difference is that the entropy factor has to be multiplied to ν_0 for obtaining ν. By chemical thermodynamics,[23] the reaction-rate constant through an activated complex is proportional to $\exp(-\Delta G^*/kT)$, where $\Delta G^*=\Delta H^*-T\Delta S^*$, ΔG^* is the Gibbs free energy of activation, ΔH^* is the enthalpy of activation, and ΔS^* is the entropy of activation. In the present case, polyatomic SiH_3 makes a jump over the energy barrier ΔH^*. At this moment, four atoms in the radical have to move into the same direction simultaneously in the same phase of vibration. This situation causes $\Delta S^*$to have a large minus value. As a crude estimation, each H atom bonded to the Si atom has three freedoms of motion, and the three H atoms have to vibrate in phase with the Si atom. If the probability of in-phase motion for each freedom of motion is arbitrarily assumed to be $\frac{1}{2}$, the total probability is $\frac{1}{2}^9\simeq2\times10^{-3}$. Other contributions to the entropy term by motion of surface atoms are also conceivable. Therefore, the ratio ν/ν_0 seems to suggest that the model used in the analysis is reasonable.

The variations of the SiH concentration with T_s and P_s are of the opposite sign to those of the SiH_2 concentration as shown in Fig. 1. Since the mechanism of the SiH_2 incorporation can be explained by the fast process as above, the mechanism of the SiH incorporation is considered to be by the slow process. In reaction (3a), the H atom terminating Si atom at the steplike site is released by forming Si—Si bonds. It can easily be considered that all terminating H atoms are not released at steplike sites depending on the atomic configuration. At a steplike site, which is referred to here as a kinklike site, it seems difficult for an adsorbed SiH_3 radical to form three Si—Si bonds simultaneously with an appropriate short-range order. In other words, the retained H atom at a kinklike site terminates a possible defect in a-Si network.

According to this model, the probability ratio m of the reaction at such kinklike sites in the total reactions by the slow process can be estimated from the ratio $S_1/(S_0-S_2)$. Since the total atomic density N_t in a-Si:H is independent of the H/Si atomic ratio, the following relation is satisfied:

$$[\mathrm{Si}]+2[\mathrm{SiH}]+3[\mathrm{SiH_2}]=N_t\ , \tag{10}$$

where $[SiH_x]$ represents the density of the Si atom which is bonded to x H atoms, and $(1+x)$ $[SiH_x]$ is the total atomic density of the SiH_x configuration. By this notation, S_1 is equal to [SiH], S_2 is equal to $2[SiH_2]$, and S_0 is $2N_t/3$. The probability ratio m is defined by

$$[\mathrm{SiH}]/([\mathrm{Si}]+[\mathrm{SiH}])=m\ .$$

Therefore, from Eq. (10) we have

$$S_1/(S_0-S_2)=3m/2(1+m)\ . \tag{11}$$

From the data of S_1 and S_2 shown in Fig. 1 for films deposited at various T_s's and under various P_s's, the value of $S_1/(S_0-S_2)$ is given by (0.15+0.03). For this value, m is obtained to be 0.1 by Eq. (11). This result means that the minimum H/Si atomic ratio is 0.1 in a-Si:H, if only the slow process occurs in the deposition. This result is reasonable for a-Si:H films which have been obtained so far, and indicates that the adopted model is suitable for the analysis.

V. DISCUSSION

The above analysis can explain the dependence of SiH and SiH_2 concentrations on temperature and partial pressure. The analysis gives a reasonable value for the activation energy of the adsorbed SiH_3 radical in the surface diffusion, and the SiH concentration by the slow process. Therefore, it is considered that this model represents the essential mechanism of surface reaction.

While there are many assumptions in the analysis, the most important issue is the apparent neglect of the desorption of the adsorbed SiH_3 radical before the Si—Si bond formation with the network. The desorption occurs by recombination of SiH_3 to stable molecules SiH_4 and Si_2H_6. It was reported[3] that the probability of recombination γ is $\frac{2}{3}$ of the adsorbed radical, and the probability of sticking s to the network is $\frac{1}{3}$. The formation of SiH_4 is by a monomolecular process, and the formation of Si_2H_6 is by a bimolecular process. Since it was reported[3] that both γ and s do not depend on T_s below 300 °C the desorption process is not taken into account and is simply replaced by the deposition rate in the present analysis. It is suspected that the probabilities of bimolecular and monomolecular processes depend differently on temperature. Therefore, it is interesting to investigate in detail the temperature dependence of γ and s for each SiH_4 and Si_2H_6.

While the distinction is made between the monomolec-

ular and bimolecular processes, an interaction between them can be considered. The example of the bimolecular process shown in Fig. 7 produces a steplike site favorable for the monomolecular reaction. When the H atom produced in the slow process shown in Fig. 7 forms a Si dangling bond as in reaction (3c), it may be effective to form a Si—Si bond, as shown by reaction (2).

Dangling-bond density is one of the most important material parameters in undoped *a*-Si:H. The mechanism of the dangling-bond formation has been reported by many authors.[24] Street and Winer proposed a thermal equilibrium for defect density in undoped *a*-Si:H.[25] The equilibrium defect density increases with temperature, and higher defect densities can be frozen in by quenching. Street proposed that atomic hydrogen in the plasma is a determining factor in the structure of the deposited *a*-Si:H by its chemical potential.[26] However, it was found in this work that an increase of H atoms in the reactant gas decreases the H content in the deposited *a*-Si:H film. The dangling-bond density N_s decreases with increasing temperature at temperatures below 250 °C, as shown in Fig. 5(b). These experimental results of as-deposited films at temperatures below 360 °C clearly contradict the assumption of thermal equilibrium. Although the assumption of thermal equilibrium may be appropriate for a growth of μc-Si or polycrystalline Si at higher temperatures, it seems not to be appropriate for *a*-Si:H deposition under the conditions of the present experiment.

As described at the end of Sec. III, it should be noted that the variation of the dangling-bond density N_s with the deposition condition shown in Fig. 5 is similar to those of S_1 and S_2 shown in Fig. 1. The magnitudes of S_1 and S_2 are of the order of $10^{22}-10^{21}$ cm^{-3}, and those of N_s are of the order of $10^{19}-10^{16}$ cm^{-3}. Therefore, the concentration ratio $N_s/[\mathrm{H}]$ is $10^{-3}-10^{-5}$. While it is very difficult to present concrete evidence of such small N_s values, it is interesting to investigate a correlation of the formation mechanism between the dangling bond and S_1 and S_2. In the deposition process, the Si atom on the growing surface is normally considered to be fourfold coordinated. The Si—Si bond of the network is formed by the dehydrogenation reaction. There should be an extra dehydrogenation process to form a dangling bond.

As a final comment in this discussion, experimental results were reported recently which are closely correlated with the present model. During rf glow discharge deposition of *a*-Si:H, a mechanical vibration of 2 MHz generated by piezoelectric device was applied on the substrate at a temperature of 120 °C.[27] By means of this ultrasonic (us) vibration, characteristics of the deposited films were improved. With increasing amplitude of the us vibration, IR absorption of SiH_2 decreases and that of SiH increases. The photoconductivity is also increased. An order-of-magnitude decrease in the gap state density is observed by the constant photocurrent method (CPM) spectrum. The us vibration is considered to promote the migration of adsorbed radicals: i.e., the slow process. These results are in good agreement with the proposed model.

VI. CONCLUSIONS

The following conclusions were obtained for the mechanism of surface reactions in the conventional deposition process of *a*-Si:H by rf glow discharge of SiH_4. These conclusions are based on investigations using the SiH and SiH_2 concentrations in the deposited films as a clue. The dehydrogenation reaction of the adsorbed SiH_3 radical occurs simultaneously with the Si—Si bond formation into the network. The incorporations of SiH and SiH_2 into the network are due to the different surface reactions. To explain the experimental results, the following scheme of the surface reaction is proposed. There are two kinds of processes for the adsorbed SiH_3 radicals: the fast process and the slow process. The fast process occurs predominantly in high-rate depositions and incorporates SiH_2 into the network. The slow process occurs predominantly in low-rate depositions and incorporates some SiH. The fast process takes place by interactions of two adsorbed radicals, and the slow process takes place at steplike sites after migration on the surface. The variation of the dangling-bond density with deposition condition was found to have similarities to that of H concentrations. Since the variation of the dangling-bond density cannot be explained by the thermal equilibrium process, a correlation is suggested in the processes between H-atom incorporation and dangling-bond formation.

The essential features of the surface reaction mechanism in the conventional glow discharge deposition of *a*-Si:H and the relationships among the important material parameters of the deposited films are successfully explained by this model.

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