

## CHAPTER 8

# Chemical Reactions in Plasma Deposition

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### I. Introduction and Overview

Glow-discharge deposition is the most complicated technique used for the production of hydrogenated amorphous silicon (a-Si:H). However, it is also the method that has produced the most efficient solar cells. The connection between deposition parameters and the properties of the film produced is indirect, as shown in Table I. Electrons in the discharge are accelerated by the electric field and undergo both elastic and inelastic collisions with the atoms and molecules present. The electron energy distribution is therefore determined by the types of atoms and molecules present in the discharge, their concentration, and the magnitude and frequency of the electric field. Inelastic collisions with atoms and molecules can ionize them, replacing electrons lost to the discharge. Inelastic collisions with molecules can raise them to unstable excited states that dissociate. In silane discharges  $\text{SiH}_n$  ( $n = 0-3$ ) free radicals and atomic hydrogen are produced as well as ions. Increasing the electric field increases both the number and average energy of the electrons.

The  $\text{SiH}_n$  species produced polymerize on the substrate to produce the

TABLE I  
THE EFFECT OF DEPOSITION PARAMETERS ON THE  
FILM GROWTH PROCESS<sup>a</sup>

Deposition parameters	Film growth process
Electrode geometry Voltage Frequency Gas composition Flow rate Pressure  Substrate temperature	Plasma Composition: Stable molecules Reactive fragments Electrons Ions Photons ↓ Flux of particles onto film ↓ Composition, structure, and morphology of film ↓ Optoelectronic properties of film

<sup>a</sup> Arrows in the diagram represent causal relationships.

a-Si:H film. Rapid hydrogen elimination occurs from activated species produced by the reaction of these  $\text{SiH}_n$  species with the film surface. Slower, thermally activated hydrogen elimination can also occur if the substrate temperature is high enough. Atomic hydrogen can break and hydrogenate Si-Si bonds as well as remove surface hydrogen from the film. Ion bombardment also removes hydrogen from the film, probably by providing activation energy for hydrogen elimination.

## II. Historical Background

One of the first efforts to understand the chemical reactions occurring in silane discharges was a study of the kinetics of silane decomposition in a dc discharge (Nolet, 1975). The first-order rate constant was found to depend approximately linearly on current and to decrease with increasing total pressure for a 10% silane in argon mixture. These results were interpreted in terms of the effects of pressure and current on the electron concentration and temperature, in a model in which the initial step involved an electron-molecule collision.

Brodsky (1977) pointed out that the films deposited from silane glow discharges contain hydrogen, and he discussed the effects of pressure on the type of film deposited. At low pressure, surface reactions predominate, whereas gas-phase polymerization is more important at higher pressures.

Turban *et al.* (1979) published a study of the kinetics of a-Si:H deposition

in a silane-helium rf discharge. They used a model of the deposition process in which electron-molecule collisions produce neutral free radicals. These are transported to the walls where they undergo surface polymerization. The electron concentration was measured by microwave interferometry as a function of power, and the deposition rate was measured as a function of power and position in the deposition system. The experimental results were explained by the model, and the silane reactivity was found to be an order of magnitude higher than that of methane.

In a paper presented at the Eighth International Conference on Amorphous and Liquid Semiconductors (Cambridge, MA, 1979), Knights (1980) discussed the nucleation and growth of a-Si:H films and proposed that his observation could be explained if the films grow from  $\text{SiH}_2$  and  $\text{SiH}_3$ . These species would be expected to have higher surface mobility than more unsaturated species such as atomic Si.

At the same conference, Griffith *et al.* (1980) reported that the optical emission spectra of silane rf glow discharges show the presence of the species Si, SiH, H,  $\text{H}_2$ , and some impurities. There was also a paper by Kocian (1980), who measured the electron concentration and energy distribution in a dc silane discharge at various conditions and discussed the changes in the properties of the deposited films.

Subsequently, several papers appeared reporting on the emission spectra measured during the plasma deposition of a-Si:H under a variety of conditions. Kampas and Griffith (1980) observed emission from SiO,  $\text{N}_2$ , and SiCl when oxygen, nitrogen, or chlorosilanes were present in the discharge and discussed the effects of these impurities on film properties. Perrin and Delafosse (1980) examined the emission from SiH in silane-hydrogen rf discharges and concluded that the rotational and vibrational temperatures of the emitting excited state of SiH are abnormally high.

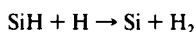
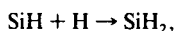
Taniguchi *et al.* (1980) examined the effect of a magnetic field on the emission spectra and films deposited from rf silane discharges. Emission from SiH, H, and  $\text{H}_2$  decreased with increasing magnetic field due to a decrease in the electron temperature. Infrared absorption studies of the deposited films showed increased monohydride concentration and decreased dihydride concentration with the application of the magnetic field. Hamasaki *et al.* (1980) reported that crystalline phosphorus-doped silicon could be deposited from a silane-hydrogen rf discharge at substrate temperatures below  $200^\circ\text{C}$  at low flow rates in the presence of a magnetic field. Under those conditions the emission from SiH is very weak compared to emission from H and  $\text{H}_2$ , and emission from doubly excited  $\text{H}_2$  states is absent. This was ascribed to reactive hydrogen attacking the film surface and increasing the surface mobility of silicon atoms.

Mass spectrometry was another technique used to study the chemical

reactions occurring during the plasma deposition of a-Si:H. Drevillon *et al.* (1980) examined the deposition and mass spectra from a low-pressure (< 5 mTorr) dc multipole silane discharge. The predominant ion was found to be  $\text{SiH}_3^+$  and the contribution of ions to the deposition was found to decrease rapidly with pressure, implying that for discharges around 100 mTorr pressure, neutral species in the plasma are responsible for the deposition. Haller (1980) examined the ions formed in rf silane discharges in the pressure range of 17–100 mTorr and found ions containing as many as seven silicon atoms whose concentration decreased by a constant ratio with an increasing number of silicon atoms. Turban *et al.* (1980) also observed ions with as many as seven silicon atoms in rf discharges in silane–hydrogen and silane–helium mixtures. Although they were not able to observe neutral-free radicals directly, they concluded that such radicals must be responsible for film deposition, since the ion flux is one to two orders of magnitude too low to explain the deposition rate. The mass spectrum of a  $\text{H}_2$  discharge showed that H can etch a-Si:H, and studies of silane–helium–deuterium discharges implied that atomic H or D in the plasma can be incorporated in the film. This was believed to be most important at high power or low flow rate.

The discovery by Scott *et al.* (1980) that the glow-discharge deposition of a-Si:H proceeds at a considerably higher rate from disilane than from monosilane led to their proposal that the film grows from  $\text{SiH}_2$ . They argued that glow-discharge processes are analogous to the thermal decomposition of the various silanes, which are known to produce  $\text{SiH}_2$  and to proceed at a higher rate for disilane than monosilane. In order to account for the fact that a-Si:H films prepared by glow discharge have a smaller hydrogen content than  $\text{SiH}_2$ , they proposed that a rapid surface reaction eliminates silane and molecular hydrogen.

At the Tetrahedrally Bonded Amorphous Semiconductor Conference (Carefree, Arizona, 1981) Kampas and Griffith (1981a,b) presented a model of the glow-discharge deposition of a-Si:H in which  $\text{SiH}_2$  inserts into a Si–H bond on the growing film surface, producing an activated group that can eliminate  $\text{H}_2$  to produce a divalent silicon. This divalent silicon can then insert into a nearby Si–H bond to cross-link the structure. At the same conference Hirose *et al.* (1981) reported on the optical emission spectra and deposited film properties from silane–hydrogen rf glow discharges as a function of flow rate. They found that the Si and SiH emission intensities increased with flow rate, as did the deposition rate and the monohydride concentration in the films. However, the dihydride concentration decreased. These results were interpreted in terms of the reactions



occurring on the film surface. Dalal *et al.* (1981) presented a model of the deposition of a-Si:(H,F) from  $\text{SiF}_4$  and  $\text{H}_2$  that explained many of the properties of that material in terms of reactive-ion etching occurring during deposition. Reimer and Knights (1981) presented data obtained by nuclear magnetic resonance on the concentration and distribution of hydrogen in a-Si:H films prepared under a variety of deposition conditions. They found a positive correlation between deposition rate and hydrogen content that they explained in terms of increased strain in the lattice producing more hydrogenated structures. They also found that cathode films have a lower concentration of polysilane regions. This was explained in terms of "scouring" of the film surface by silicon-containing ions (also see Reimer *et al.*, 1981).

A paper by Kampas and Griffith (1981c) on the emission spectrum of the silane discharge showed that the emitting excited states of Si and SiH are produced directly by the electron impact decomposition of the silane molecule, explaining the high rotational and vibrational temperatures observed for SiH by Perrin and Delafosse (1980).

Stable molecule and ion concentrations in  $\text{SiH}_4$ - $\text{SiD}_4$ -He and  $\text{SiH}_4$ - $\text{H}_2$ - $\text{D}_2$  rf glow discharges were measured by Turban *et al.* (1981, 1982) using mass spectrometry. The data were explained using known reactions between  $\text{SiH}_2$ ,  $\text{SiH}_3$ , and H occurring in the discharge. A picture of the deposition mechanism was proposed in which chemisorbed  $\text{SiH}_2$  and  $\text{SiH}_3$  are incorporated into the growing film with some  $\text{H}_2$  elimination, and H can either be incorporated in the film or etch it. A paper by the same group (Catherine *et al.*, 1981) on the reactions in the deposition of a-SiC:H from  $\text{SiH}_4$ - $\text{CH}_4$  mixtures concluded that the two gases break down independently to make  $\text{SiH}_2$ ,  $\text{SiH}_3$ ,  $\text{CH}_2$ , and  $\text{CH}_3$ , which react to grow the film and make disilane and various hydrocarbons.

At the Ninth International Conference on Amorphous and Liquid Semiconductors (Grenoble, France, July 2-8, 1981) Matsuda *et al.* (1981) presented a simplified model of the glow-discharge deposition of a-Si:H and a-Si:(H,F) based on the strengths of the bonds between the atoms in the reactive species that occur in the plasma. Using results from a cross-field deposition system, Hotta *et al.* (1981) reported on the effect of the substrate potential on the optical emission spectrum of the discharge and the properties of deposited films. The emission spectrum only from the plasma near the substrate was affected by the bias voltage. The dark conductivity and photoconductivity, hydrogen bonding structure, and doping efficiency of the films were all found to depend on substrate potential. Vepřek *et al.* (1981) discussed the deposition of amorphous and microcrystalline silicon films from silane-hydrogen discharges in terms of the departure of the system from chemical equilibrium, the forward reaction being deposition and the reverse reaction etching of the film by atomic hydrogen. The film is

amorphous when the system is far from equilibrium and microcrystalline when the deposition is near partial chemical equilibrium (also see Wagner and Vepřek, 1982).

Optical spectroscopy continued to be a useful technique for studying the glow-discharge deposition of a-Si:H. Knights *et al.* (1982) reported on the spectrum of a silane discharge in the infrared. Emission and absorption were observed for both SiH<sub>4</sub> and SiH molecules. Vibrational and rotational temperatures of 2000 and 485° K were deduced for SiH and 850 and 300° K for SiH<sub>4</sub>. The species SiH<sub>2</sub> and SiH<sub>3</sub> were not observed, probably because the lower symmetry of those molecules splits the lines into more components, decreasing their intensities. In a separate publication, Perrin and Schmitt (1982) reported the cross sections for production of excited Si, Si<sup>+</sup>, SiH, SiH<sup>+</sup>, and H by electron impact excitation of silane in the energy range 17–68 eV. Tachibana *et al.* (1982) measured the time dependence of the optical absorption of atomic Si in a pulsed rf silane–argon discharge in order to obtain the Si concentration and diffusion constant. They concluded that 70% of the deposition in their system is due to atomic Si.

Drawing an analogy with the gas-phase reaction of atomic H with Si<sub>2</sub>H<sub>6</sub>, Kampas (1982) proposed that H can remove a bonded H to produce a dangling bond, break a Si–Si bond to produce a dangling bond, or passivate a dangling bond during the deposition of a-Si:H by glow discharge or reactive sputtering. This explains qualitatively the change in the substrate temperature dependence of the film hydrogen content when H<sub>2</sub> is present in the discharge.

A study of the neutral and ion chemistry in ethylene–silane discharges by Catherine *et al.* (1982) showed that the major neutral species produced by electron impact dissociation of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>3</sub> and C<sub>2</sub>H<sub>2</sub>. This result and the results obtained by the same group on silane–methane discharges (Catherine *et al.*, 1981) are in agreement with the results of a study of the infrared spectra of a-SiC:H films produced by glow discharge, which concluded that material produced from silane–methane mixtures contains CH<sub>3</sub> groups, whereas material produced from silane–ethylene mixtures contains C<sub>2</sub>H<sub>3</sub> groups (Tawada *et al.*, 1982).

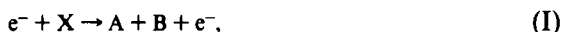
Recently, Perrin *et al.* (1982) have measured the electron impact dissociation cross sections of silane and disilane from their ionization energies to 100 eV. The most probable decomposition mechanism of disilane involves formation of monosilane and other fragments.

At the Solar Energy Research Institute Amorphous Materials Subcontractors Review Meeting (Alexandria, Va., 1982), the results of two mass spectrometric studies of silane discharges were presented. Gallagher detected neutral free radicals and found the SiH<sub>3</sub> was the most common product (Robertson *et al.*, 1983). Longeway measured the effect of NO, a

$\text{SiH}_3$  scavenger, on the production of higher silanes by the discharge (Longeway *et al.*, 1983). He concluded that  $\text{SiH}_3$  is produced at a rate nine times higher than that of  $\text{SiH}_2$  and noted that there was no film deposition under conditions of complete  $\text{SiH}_3$  scavenging.

### III. Primary Processes in the Discharge

An inelastic collision between an electron and a molecule can raise the molecule to a higher rotational, vibrational, or electronic state. Excited electronic states of molecules are often unstable because an electron has been removed from a bonding orbital and transferred to an antibonding orbital. The excited molecule may decompose, ionize, or both:



The rates of these reactions are given by Bell (1974):

$$R_i = n_e k_i [X], \quad (1)$$

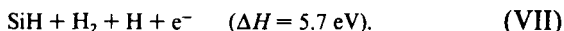
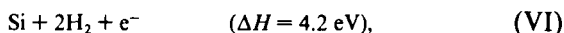
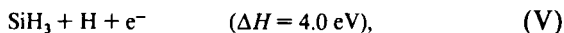
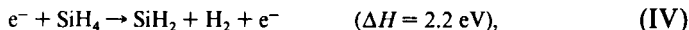
where  $n_e$  is the electron concentration,  $k_i$  is the rate constant for the reaction, and  $[X]$  is the concentration of  $X$ . The rate constant is given by

$$k_i = (2/m_e)^{1/2} \int E^{1/2} f(E) \sigma_i(E) dE, \quad (2)$$

where  $m_e$  is the electron mass,  $f(E)$  is the normalized electron energy distribution, and  $\sigma_i(E)$  is the cross section for the reaction as a function of energy. The electron energy distribution is not necessarily Maxwellian, although it is often assumed to be for simplicity. Typical values for  $n_e$  are  $1 \times 10^9 - 1 \times 10^{12} \text{ cm}^{-3}$ ; the average electron energy is usually several electron volts.

#### 1. DISSOCIATION

Enthalpies of formation of the various  $\text{SiH}_n$  ( $n = 0-3$ ) fragments are known, so it is possible to calculate the energy required to produce them (Turban, 1981):



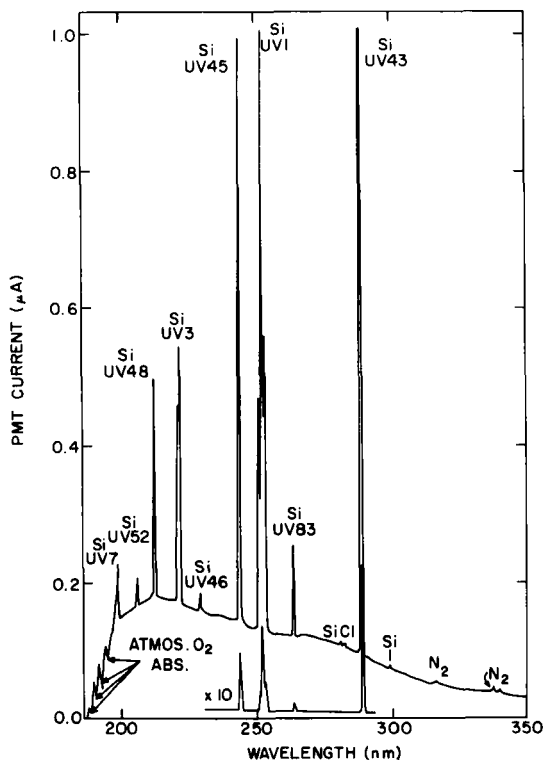
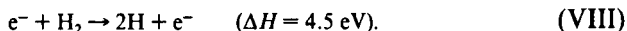


FIG. 1. Optical emission spectrum of a pure silane, rf glow discharge from 180 to 350 nm. The emission from SiCl at 280 nm is due to the impurity  $\text{SiH}_3\text{Cl}$  in the silane. The atomic Si lines are labeled using the notation of Moore (1967).

Another important reaction is the dissociation of  $\text{H}_2$ , which is a product of the deposition process and is sometimes used to dilute the silane:



Furthermore, there are reactions similar to reactions (IV), (VI), and (VII) in which  $2\text{H}$  is produced instead of  $\text{H}_2$ . These require 4.5 eV more energy for each  $\text{H}_2$  dissociated.

As discussed earlier, the rates of the primary reactions depend on the electron concentration and energy distribution. Some information about how these factors depend on deposition conditions can be obtained using optical emission spectroscopy, since the emitting excited states of some of the species observed are formed by dissociation of silane (Kampas and Griffith, 1981c, Perrin and Schmitt, 1982) as shown below:



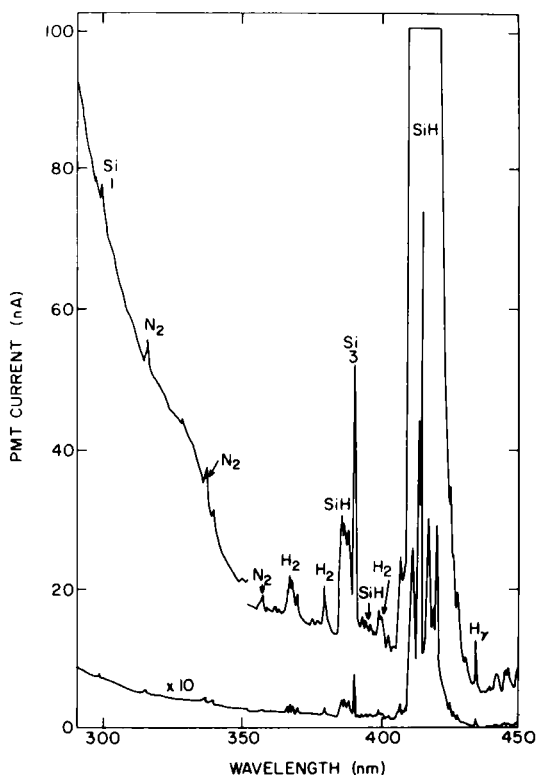
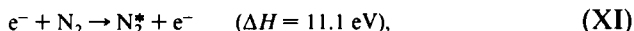


FIG. 2. Optical emission spectrum of a pure silane discharge from 300 to 450 nm.



An emission spectrum of a silane discharge is shown in Figs. 1–3.

The fact that the  $\text{Si}^*$  and the  $\text{SiH}^*$  observed in the silane glow discharge are produced primarily by reactions (IX) and (X) rather than by excitation of ground state Si and SiH was deduced from a study of the rf power dependences of the emission intensities from Si, SiH, H,  $\text{H}_2$ , and  $\text{N}_2$  in a silane discharge containing a small fixed concentration of  $\text{N}_2$  (Kampas and Griffith, 1981c). Log–log plots of the emission intensities from Si, SiH, H, and  $\text{H}_2$  versus the emission intensity from  $\text{N}_2$  gave straight lines with slopes of 0.84, 0.78, 1.92, and 1.85, respectively (see Fig. 4). Since the formation of  $\text{N}_2^*$  is a one-electron process,



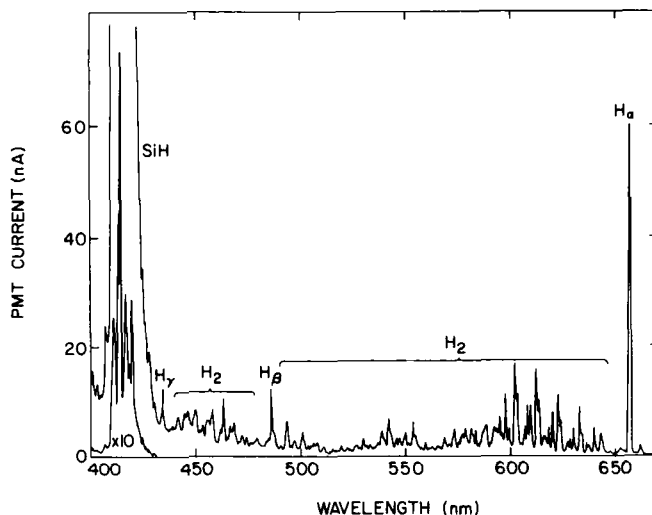
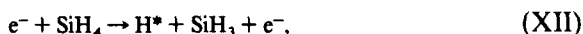


FIG. 3. Optical emission spectrum of a pure silane discharge from 400 to 650 nm.

formation of  $\text{Si}^*$  and  $\text{SiH}^*$  had to be one-electron processes also to account for the slopes of 0.84 and 0.78. The slopes were found to be larger for species with larger excitation energy because the electron energy distribution shifts to higher energy with increasing power.

Since the slopes corresponding to the emission intensities from  $\text{H}_2^*$  and  $\text{H}^*$  were near 2, it was concluded that both of these species arise from excitation from the ground state. However, Perrin and Schmitt (1982) have concluded that  $\text{H}^*$  can be formed from  $\text{SiH}_4$  or  $\text{H}_2$ :



However, emission from  $\text{H}_2^*$  is a result of excitation of ground state  $\text{H}_2$ . Emission from  $\text{H}^*$  and  $\text{SiH}^*$  is not a measure of the concentration of H and SiH but rather a measure of the concentration of  $\text{H}_2$  and  $\text{SiH}_4$ .

Although the optical emission does not give information about the ground state concentrations of species other than  $\text{H}_2$ , it is useful for studying how electron concentration and energy distribution change with deposition conditions, as illustrated earlier. Emission spectroscopy has shown that the average electron energy increases with rf power. Emission spectroscopy has also demonstrated that electron concentration decreases and average electron energy increases with increasing silane concentration in argon-silane discharges at fixed power and total pressure. This explains why the deposition rate of a-Si:H from argon-silane mixtures is not proportional to the silane fraction (Kampas, 1983).

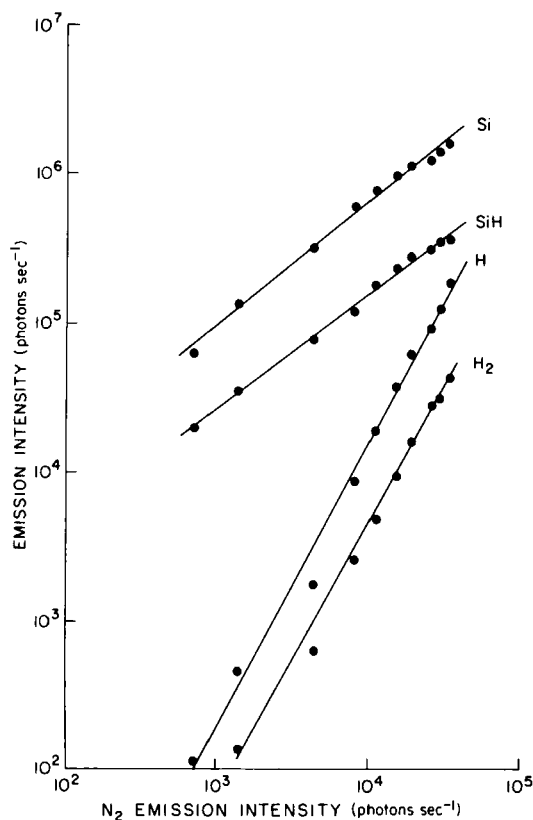
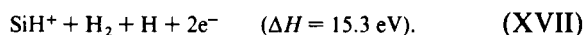
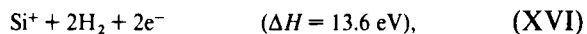
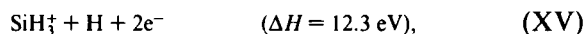


FIG. 4. Log-log plot of emission intensity of Si, SiH, H, and H<sub>2</sub> versus N<sub>2</sub> emission intensity as the rf power level is varied in a silane discharge with a small amount of added N<sub>2</sub>.

## 2. IONIZATION

The appearance potentials of the positive ions formed from the ionization of silane and disilane [reactions (XIV)–(XVII)] have been measured by Potzinger and Lampe (1969) and the ionization cross sections have been measured approximately by Turban *et al.* (1982). The SiH<sub>4</sub><sup>+</sup> ion is unstable and, therefore, not observed (Gordon, 1978).



Turban *et al.* (1982) have calculated the rate constants for these reactions as

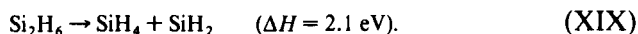
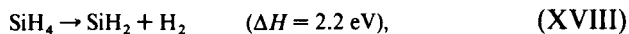
a function of average electron energy, assuming a Maxwellian electron energy distribution.

#### IV. Secondary Reactions

From the previous discussion it is clear that the species formed by the electron impact dissociation of silane are  $\text{SiH}_n$  ( $n = 0-3$ ),  $\text{H}$ ,  $\text{H}_2$ , and  $\text{SiH}_n^+$  ( $n = 0-3$ ). Of these  $\text{SiH}_2$  and  $\text{SiH}_3$  are probably formed in the largest quantities. With the exception of  $\text{H}_2$ , all of the species are very reactive. Their gas phase chemistry will be discussed in some detail in order to understand what reactions they might undergo in the plasma, and as a guide to the reactions involved in film growth.

#### 3. NEUTRAL REACTIONS

The absorption spectrum of the  $\text{SiH}_2$  molecule has been observed in a pulsed silane-hydrogen discharge and shows that the molecule is bent and has a singlet ground state (Dubois, 1968). Its chemistry is fairly well established because it can be produced by the pyrolysis of monosilane (Newman *et al.*, 1979) and by the pyrolysis of disilane (Bowrey and Purnell, 1971):



The pyrolysis of trisilane produced  $\text{SiH}_3\text{SiH}$  as well as  $\text{SiH}_2$  (Vanderwielen *et al.*, 1975).

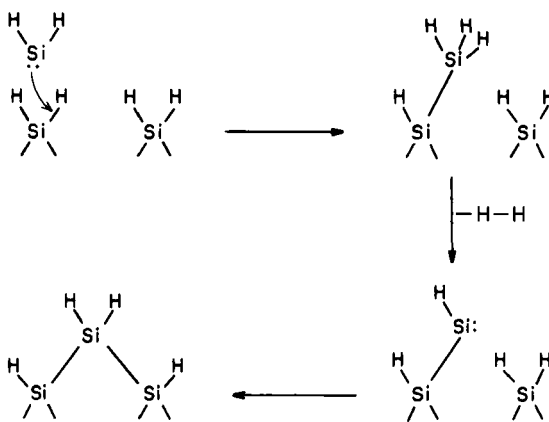
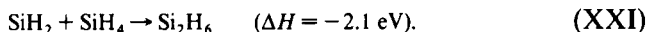
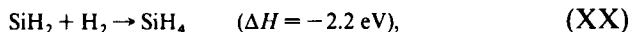


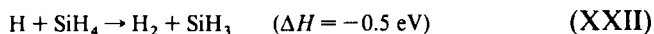
FIG. 5. Proposed mechanism of  $\text{SiH}_2$  reaction with growing  $\text{a-Si:H}$  film and subsequent hydrogen elimination and cross-linking.

The reverse of reactions (XVIII) and (XIX) is also known:

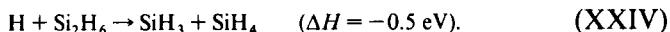
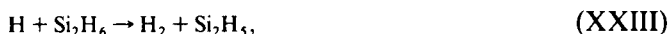


(John and Purnell, 1973). Reaction (XXI) is an example of a well-characterized insertion reaction into a Si-H bond as shown in Fig. 5.

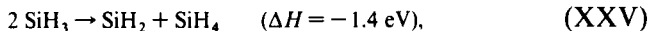
The  $\text{SiH}_3$  radical has a doublet ground state and is pyramidal in shape, according to electron spin resonance (Morehouse *et al.*, 1966). It is rapidly formed by the reaction of atomic hydrogen with silane (Austin and Lampe, 1977):



There is a similar reaction between atomic hydrogen and disilane as well as a reaction in which atomic hydrogen splits the Si-Si bond in disilane (Pollock *et al.*, 1973):



The  $\text{SiH}_3$  radical can react with itself in two ways: disproportionation or the formation of an activated disilane molecule (Reiman *et al.*, 1977).

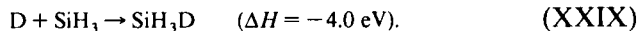


The notation  $\text{Si}_2\text{H}_6^{**}$  indicates a disilane molecule with an internal energy of 3.2 eV (Perkins *et al.*, 1979). This molecule breaks up [reaction (XXVII)] unless deactivated by a collision [reaction (XVIII)] (Reiman *et al.*, 1977):



Reaction (XXV) can be distinguished from the sequence reaction (XXVI) and reaction (XXVII) by isotopic labeling.

It is also worth noting that  $\text{SiH}_3$  can react with atomic hydrogen (or deuterium) (Mihelcic *et al.*, 1974):



The reactions of atomic Si and SiH are less well understood. Atomic Si is known to react with a number of molecules such as  $\text{H}_2$ ,  $\text{CH}_4$ , and  $\text{SiCl}_4$  (Husain and Norris, 1978). The reaction of Si with  $\text{H}_2$  goes as follows:



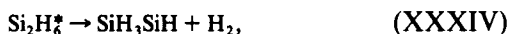
A mass spectrometric study of the photolysis of silane by 8.4-eV photons

provides a model for the reactions that might occur in glow-discharge deposition from silane (Perkins *et al.*, 1979). The results were interpreted in terms of the formation of  $\text{SiH}_2$ ,  $\text{SiH}_3$ , and  $\text{H}$  in the primary photolytic step:



However, it was noted that production of  $\text{Si}$  and  $\text{SiH}$  is possible energetically. The analysis of the data gave quantum yields of 0.83 and 0.17 for the production of  $\text{SiH}_2$  and  $\text{SiH}_3$ , respectively.

An important result was that disilane and trisilane were formed simultaneously. Addition of  $\text{NO}$ , which suppresses any pathways involving species with unpaired spin such as  $\text{SiH}_3$ , reduced the disilane yield to 0.53 of its initial value and reduced the trisilane yield to 0.07 of its initial value. In order to explain the prompt formation of trisilane in the presence of  $\text{NO}$ , the following reaction sequence was proposed (Perkins *et al.*, 1979):



The species  $\text{Si}_2\text{H}_6^*$  is a disilane molecule with an internal energy of 2.1 eV. Reaction (XXIV) was estimated to be slightly exothermic. The small trisilane yield from this mechanism (7% of the total) was ascribed to competition between the reaction (XXXIV) and deactivation of  $\text{Si}_2\text{H}_6^*$ :

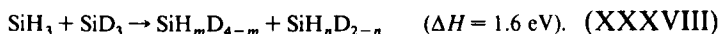


Gaspar (1981) has criticized reaction (XXXIV) on the grounds that trisilane formation could also be explained by the generation of  $\text{Si}$  or  $\text{SiH}$  in the primary photolysis step. Perkins *et al.* also proposed the reaction



where  $\text{Si}_2\text{H}_6^{**}$  is formed from two  $\text{SiH}_3$  molecules as described earlier [reaction (XXVI)]. They concluded that most of the  $\text{Si}_2\text{H}_6^{**}$  molecules decomposed according to reaction (XXXVII) under the conditions of the measurement (silane-helium mixture, 2 Torr silane partial pressure, 42 Torr total pressure).

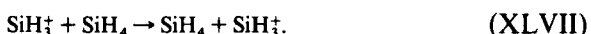
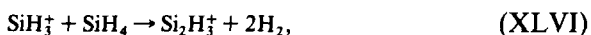
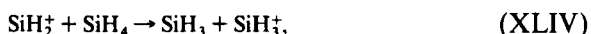
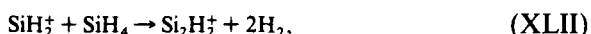
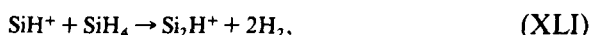
In their mass spectrometric studies of silane discharges, Turban *et al.* (1981, 1982) found  $\text{Si}_2\text{H}_6$  in  $\text{SiH}_4$ -He discharges and  $\text{SiH}_2\text{D}_2$ ,  $\text{SiHD}_3$ , and all partially deuterated disilanes in  $\text{SiH}_4$ - $\text{SiD}_4$ -He discharges. The formation of the partially deuterated silanes was ascribed to the reaction (XXIX) and to a reaction analogous to (XXV):



Disilane formation in the discharge occurred through the reaction (XXI), since the pressure was not high enough for stabilization of  $\text{Si}_2\text{H}_6^{**}$  formed from  $\text{SiH}_3$  as in reaction (XXXVI).

#### 4. ION-MOLECULE REACTIONS

Ion-molecule reactions are faster than radical-molecule reactions. This explains why ions containing as many as seven silicon atoms are found in silane discharges (Haller, 1980; Turban *et al.*, 1980), whereas the largest stable neutral molecule found in the silane discharge is trisilane. Henis *et al.* (1972) have studied the reactions of  $\text{SiH}_n^+$  ( $n = 0-3$ ) with  $\text{SiH}_4$ :



The  $\text{H}^-$  transfer reaction (XLVII) was established by using isotopically labeled ions.

Reaction (XLIV) is the reason that  $\text{SiH}_3^+$  is the ion with the highest concentration in the silane discharge (Drevillon *et al.*, 1980; Haller, 1980; Turban *et al.*, 1980) even though  $\text{SiH}_2^+$  is the main product of the ionization of silane (Turban *et al.*, 1982). The higher silane ions are the result of sequential reactions (Haller, 1980; Turban *et al.*, 1980, 1982).

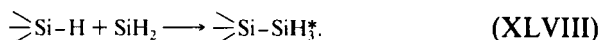
#### V. Film Growth Reactions

Reactive species in the plasma include both radicals:  $\text{SiH}_n$  ( $n = 0-3$ ), atomic H, and ions:  $\text{Si}_x\text{H}_y^+$ , and  $\text{H}^+$ . The ion flux onto the surface of the growing film is too small to account for the rate of film growth (Turban *et al.*, 1980), which strongly suggests that the silicon-containing species responsible for film growth are the neutral silane fragments  $\text{SiH}_n$ . Recent results have indicated that  $\text{SiH}_3$  is the neutral free radical produced in the largest quantity in silane discharges (Robertson *et al.*, 1983) and that the a-Si:H film can be deposited from it (Longeway *et al.*, 1983).

The reactions that might be expected to occur between  $\text{SiH}_2$  or  $\text{SiH}_3$  and the growing film surface can be described, based on the gas-phase chemistry

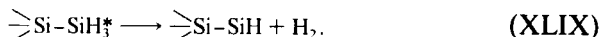
of these species. The thermal decomposition of silane and disilane produces  $\text{SiH}_2$  only via reactions (XVIII) and (XIX). Therefore, the film growth reactions for a-Si:H produced by chemical vapor deposition (CVD) are also applicable to the reactions of  $\text{SiH}_2$  in glow-discharge deposition.

The first step in the reaction of a chemisorbed  $\text{SiH}_2$  with the growing amorphous film surface should be the addition of the  $\text{SiH}_2$  across a Si-H bond on the film surface, in analogy to reaction (XXXIII).



The asterisk indicates that the surface complex has approximately 2 eV internal energy.

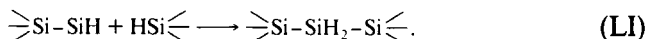
The processes that occur after the initial insertion have been the subject of some speculation. It is clear that there is rapid elimination of  $\text{H}_2$  because films grown by CVD and glow discharge have much smaller hydrogen content than the  $\text{SiH}_2$  molecule. The author has proposed that  $\text{H}_2$  be eliminated immediately (Kampas and Griffith, 1981a,b) in analogy to reaction (XXXIV), which was proposed by Perkins *et al.* (1979) to explain the results of their mass spectrometric study of silane photolysis:



The reaction competes with deactivation of the excited complex:



The divalent silicon atom formed as a result of the  $\text{H}_2$  elimination in reaction (XLIX) next attacks an adjacent Si-H bond, in this model:



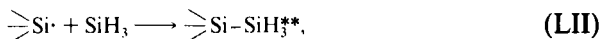
The entire sequence of reactions is shown in Fig. 5.

Scott has proposed a similar scheme in which  $\text{H}_2$  or  $\text{SiH}_4$  can be eliminated in fast surface reactions (Scott *et al.*, 1981) as shown in Fig. 6. These concerted reactions involve atoms attached to two different silicon atoms. Heating polysilane  $(\text{SiH}_2)_n$  in a vacuum is known to produce various silanes as well as hydrogen (Schwarz and Heinrich, 1935). Furthermore, there is some evidence that hydrogen evolution from already deposited films involves hydrogens on different silicon atoms rather than two hydrogens on the same silicon atom (John *et al.*, 1980).

As far as their overall effect on the film hydrogen content is concerned, the two models cannot be easily distinguished. Therefore, the mechanism of hydrogen elimination following  $\text{SiH}_2$  insertion must be regarded as an open question.

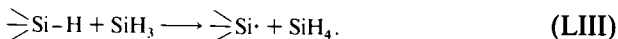


The species  $\text{SiH}_3$  has an unpaired spin and should react with unpaired spins on the growing film surface (dangling bonds)



where  $\text{>Si-SiH}_3^*$  has an internal energy of about 3 eV.

Reaction (LII) has been written in analogy to reaction (XXVI). Hydrogen elimination and deactivation reactions for  $\text{>Si-SiH}_3^*$  can be written that are similar to the reactions of  $\text{>Si-SiH}_3^*$  [(XLIX) and (L)]. Another possible reaction of  $\text{SiH}_3$  with the a-Si:H film surface is hydrogen abstraction, resulting in a dangling bond:



A film can grow from  $\text{SiH}_3$  alone, according to the reactions (LII) and (LIII). Perkins *et al.* (1979) have concluded that the deposition on the walls of their photolysis chamber is due to species with unpaired spins such as  $\text{SiH}_3$  and not divalent silicon species that are too reactive to reach the walls. Brodsky and Haller (1980) and Knights (1981) have deposited a-Si:H films by reacting atomic H with  $\text{SiH}_4$ , which produces  $\text{SiH}_3$  [reaction (XXII)]. Longeway has shown that NO, which scavenges  $\text{SiH}_3$ , prevents film deposition in a dc discharge at a silane pressure of 0.5 Torr (Longeway *et al.*, 1983).

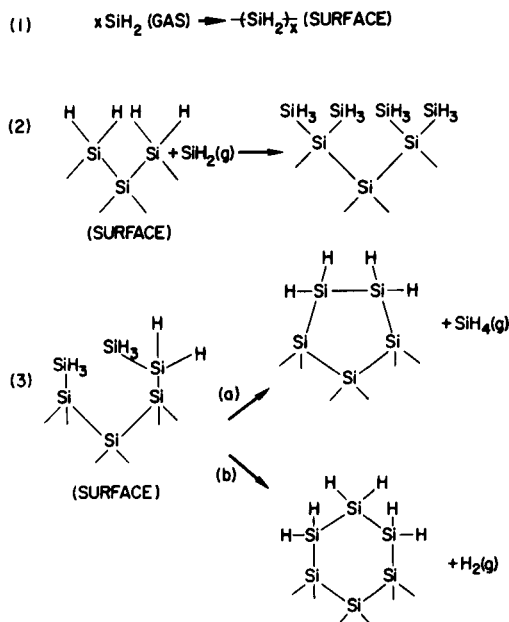


FIG. 6. Mechanism proposed by Scott *et al.* (1981) for growth of a-Si:H from  $\text{SiH}_2$ .

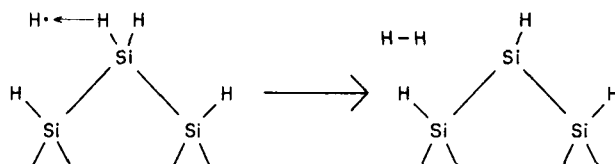


FIG. 7. Reaction of atomic H with a-Si:H, removing a H to produce a dangling bond.

That is probably too high a silane pressure for any  $\text{SiH}_2$  to reach the substrate.

The reactions of Si or SiH with the growing film surface are more a matter of speculation than in the case of  $\text{SiH}_2$  and  $\text{SiH}_3$ , whose gas-phase chemistry is better understood. However, it seems likely that activated groups result on the surface that may lead to hydrogen elimination. Films of a-Si:H deposited by reactive sputtering grow from Si and H (Moustakas *et al.*, 1981; Tiedje *et al.*, 1981). However, there has not been a complete study of the substrate temperature dependence of the film hydrogen content using this deposition method. Therefore, it is difficult to draw any conclusions about the possible mechanisms of hydrogen elimination. As far as glow-discharge deposition is concerned, Si and SiH probably react before reaching the substrate under most deposition conditions.

There is considerable evidence that atomic hydrogen in the plasma reacts with the growing film surface (see historical background section). The reactions of atomic hydrogen with silane and disilane [reactions (XXIII), (XXIV), and (XXIX)] can serve as a guide to the reactions at the film surface (Kampas, 1982). Atomic hydrogen is expected to remove hydrogen, leaving a dangling bond (see Fig. 7); break a Si-Si bond, leaving a dangling bond (Fig. 8); or passivate a dangling bond (Fig. 9). It is interesting to note that H can both create and passivate dangling bonds. Under conditions that produce a large flux of atomic hydrogen on the film surface in comparison to the flux of silicon containing species, etching of the film will become important. This occurs when all the bonds between a surface silicon atom and the silicons beneath it are broken. Weaker bonds will be more reactive toward H so that the Si atoms most likely to be etched away are those in positions that result in strained bonds. Therefore, the fact that microcrystal-

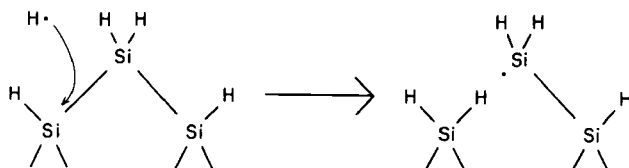


FIG. 8. Reaction of atomic H with a-Si:H, breaking a Si-Si bond.

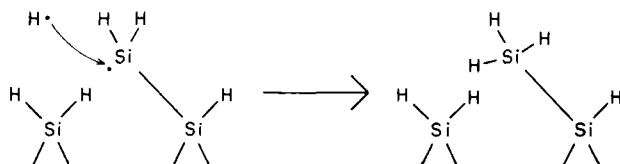


FIG. 9. Passivation of a dangling bond by atomic H.

line silicon, rather than amorphous silicon, is deposited at conditions of large silane dilution in hydrogen can be understood as being caused by etching away of surface atoms not fitting into the crystal structure.

Another factor that is known to affect the composition of the deposited a-Si:H film is ion bombardment. It is common practice in rf diode glow-discharge deposition to connect the rf "hot lead" to one electrode and connect the other electrode and the chamber to ground. This asymmetry results in the ungrounded electrode becoming negative with respect to ground (Chapman, 1980). The negative electrode is thus termed the cathode. Films grown on the cathode experience more ion bombardment than films grown on the grounded electrode (anode). Cathode films generally have less hydrogen than anode films; in addition, a smaller fraction of the hydrogen is in the form of dihydride groups or polysilane. Reimer and Knights (1981) have postulated that ion bombardment scours the growing film of polysilane regions (also see Reimer *et al.*, 1981).

## VI. Reactions Involved in Doping

The fact that it is possible to dope a-Si:H *n*- or *p*-type is essential to the usefulness of this material. However, the mechanisms involved in doping are mysterious. At one time it was thought that doping was impossible in an amorphous material, since the flexibility of the amorphous network would allow dopant atoms to have their normal coordination number rather than the electrically active coordination. Actually, the dopant atoms seem to have a variety of coordination numbers so that some fraction of them are active.

Phosphine ( $\text{PH}_3$ ) is normally used as an *n*-type dopant, although arsine ( $\text{AsH}_3$ ) has been used as well. Extended x-ray absorption fine structure (EXAFS) studies have shown that approximately 20% of the arsenic atoms are four-fold coordinated with silicon at doping concentrations of around 1% (Hayes *et al.*, 1977).

About the only guide to what the chemistry of *n*-type doping might be is a study of the 147-nm photolysis of phosphine-silane mixtures (Blazejowski and Lampe, 1981). The primary products of  $\text{PH}_3$  photolysis are PH,  $\text{PH}^*$ ,

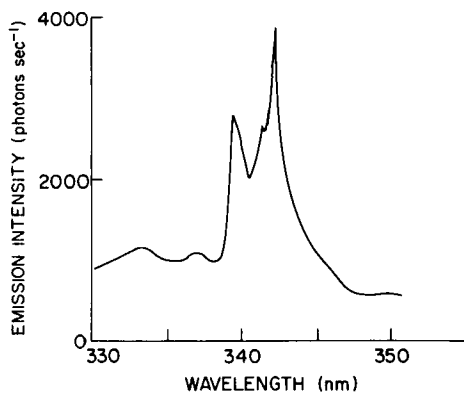
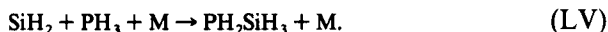
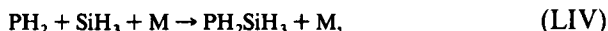


FIG. 10. Emission from PH ( $A^3\pi \rightarrow X^3\Sigma$  transition) in a 1%  $\text{PH}_3$  in  $\text{SiH}_4$  rf discharge.

and  $\text{PH}_2^*$ . This is in agreement with the emission spectrum (see Figs. 10 and 11) of an rf phosphine-silane mixture glow discharge that showed emission from PH and  $\text{PH}_2$  (Kampas and Griffith, 1981a). The only gaseous product of the photolysis containing both phosphorus and silicon was  $\text{PH}_2\text{SiH}_3$ . Its formation was ascribed to two reactions:



where M represents any third body.

These reactions indicate what might happen on the surface of the growing film. However, not much has been done in this area at the present time.

Less is known about diborane than phosphine. The photolysis of diborane

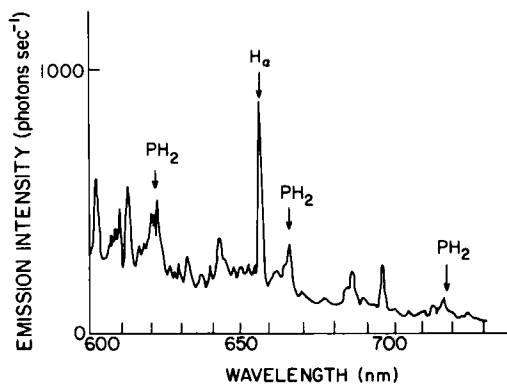


FIG. 11. Emission from  $\text{PH}_2$  ( $^2A_1 \rightarrow ^2B_1$  transition) in a 1%  $\text{PH}_3$  in  $\text{SiH}_4$  discharge. Peaks not labeled are due to  $\text{H}_2$ .

by photons of 185-nm light produces both  $B_2H_5$  and  $BH_3$  with a quantum yield of near 1 for  $B_2H_5$  and around 0.1 for  $BH_3$  (Kreve and Marcus, 1962). One might therefore expect that boron dimers are found in boron-doped a-Si:H. However, this remains controversial.

## VII. Deposition from Gases Other Than Silane

Hydrogenated amorphous silicon has been deposited from disilane as well as silane. This has the advantage of a higher deposition rate (Scott *et al.*, 1980). However, the reason for the higher rate has not been well established. Scott *et al.* have suggested that the glow-discharge decomposition is similar to thermal decomposition, as the thermal decomposition is faster for disilane than for monosilane. The increase in glow-discharge deposition rate varies, depending on the deposition system and conditions. Increases in deposition rate by factors of 20 (Scott *et al.*, 1980) and 5 (Delahoy *et al.*, 1982) have been reported. Perrin *et al.* (1982) have measured the electron impact dissociation cross sections for silane and disilane from their ionization energies to 100 eV. The maximum values, which occur at 60 eV, are

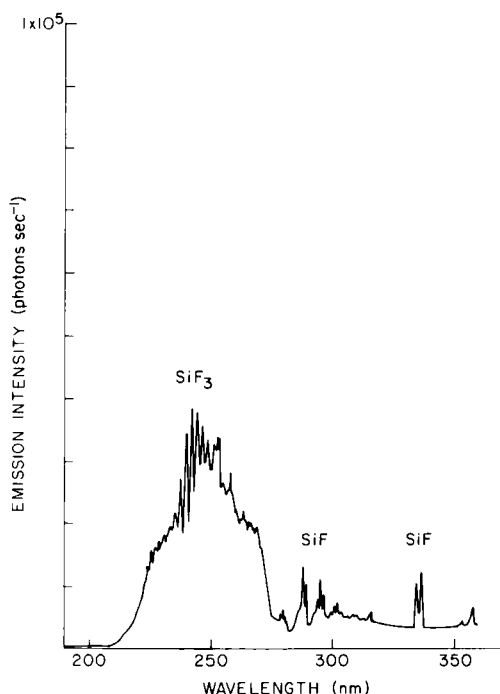


FIG. 12. Emission spectrum of  $SiF_4 + H_2$  discharge from 200 to 350 nm.

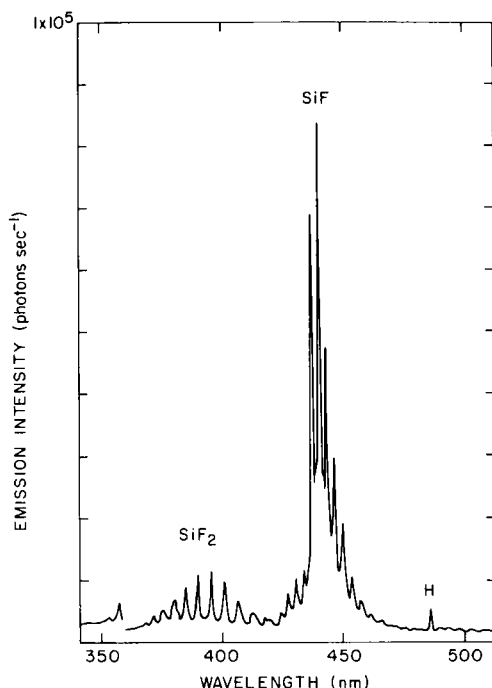


FIG. 13. Emission spectrum of a  $\text{SiF}_4 + \text{H}_2$  discharge from 350 to 500 nm. The break in the curve at 360 nm is due to insertion of an order filter.

$1.2 \times 10^{-15} \text{ cm}^2$  and  $2.6 \times 10^{-15} \text{ cm}^2$  for silane and disilane, respectively. Perrin *et al.* also estimate the thresholds for decomposition of silane and disilane to be 8 eV and 7 eV, respectively. The larger cross section and lower threshold for disilane may be sufficient to explain the higher deposition rate.

The alloy a-Si:(H,F) has been deposited from  $\text{SiF}_4 + \text{H}_2$  mixtures (Ovshinsky and Madan, 1978). Emission spectra from  $\text{SiF}_4$  discharges show the presence of  $\text{SiF}_n$  ( $n = 1-3$ ), but there is little or no deposition from  $\text{SiF}_4$  alone (see Figs. 12 and 13). Discharges containing  $\text{SiF}_4$  and  $\text{H}_2$  also show emission from H and  $\text{H}_2$ . The species  $\text{SiF}_2$  can be produced from Si and  $\text{SiF}_4$  at high temperature. However, pyrolysis of  $\text{SiF}_2$  produces a film with a high spin density (Janai *et al.*, 1981). It seems that deposition of a film with a low defect density requires hydrogen.

### VIII. Future Research

The most fundamental question about glow-discharge deposition of a-Si:H concerns the identity of the species that result in film growth.

Arguments have been made for Si, SiH, SiH<sub>2</sub>, SiH<sub>3</sub>, and various combinations of those. Mass spectrometry is just now beginning to give some answers to that question. One must also wonder if there are fundamental differences between material deposited from different silicon-hydrogen free radicals. The nature of defect formation processes is also a question with important technological ramifications. Finally, the mechanism of doping is almost completely mysterious. Presumably, the techniques applied to the question of the silicon-containing free precursors will be applied to the dopant precursors as well.

#### ACKNOWLEDGMENT

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