

Mechanism of Silicon Film Deposition in the RF Plasma Reduction of Silicon Tetrachloride

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Plasma-chemical reduction of SiCl₄ in mixtures with H₂ and Ar has been studied by optical emission spectroscopy (OES) and laser interferometry techniques. It has been found that the Ar:H₂ ratio strongly affects the plasma composition as well as the deposition (τ_D) and etch (τ_E) rates of Si:H, Cl films and that the electron impact dissociation is the most important channel for the production of SiCl_x species, which are the precursors of the film growth. Chemisorption of SiCl_x and the reactive surface reaction $\text{SiCl}_x + \text{H} \rightarrow \text{-SiCl}_{(x-1)} + \text{HCl}$ are important steps in the deposition process. The suggested deposition model gives $\tau_D \propto [\text{SiCl}_x][\text{H}]$, in agreement with the experimental data. Etching of Si:H, Cl films occurs at high Ar:H₂ ratio when Cl atoms in the gas phase become appreciable and increases with increasing Cl concentration. The etch rate is controlled by the Cl atom chemisorption step.

KEY WORDS: Silicon deposition; etching; SiCl₄; optical emission; laser interferometry; surface processes.

1. INTRODUCTION

Radiofrequency plasma deposition is a well-established technique for producing undoped and doped silicon films for photovoltaic devices. The starting material is generally silane⁽¹⁾ or silicon tetrafluoride,⁽²⁾ diluted with argon and hydrogen, and the resulting material is amorphous silicon, which contains a variable percentage of hydrogen or hydrogen and fluorine, respectively. A material which contains chlorine and hydrogen (Si:H, Cl) can be obtained using silicon tetrachloride diluted in H₂ or Ar as plasma feed.⁽³⁻⁶⁾ Some studies are in progress, with the aim to better understand the chemical processes involved in these systems. In particular, the open

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questions are: identity of the film growth precursors, the effectiveness of etching processes which can occur together with the deposition, and the effect of the gas phase and surface chemistry on the material properties. The answers to the above questions are strictly related to the suitability of the utilized diagnostic techniques. So far, mass spectrometry (MS) and optical emission spectroscopy (OES) techniques have been extensively utilized to obtain informations on the species present in the plasma phase, in order to understand the processes involved in the plasma deposition.⁽⁷⁻¹⁰⁾ A lot of work has been done in this direction, in particular for the deposition of Si:H films from silane.⁽¹¹⁾ Nevertheless, different conclusions, concerning both the discharge processes and their correlation to the film properties, have been reported. Hamasaki *et al.*⁽¹²⁾ have studied, by OES, the plasma deposition of *a*-Si:H in a glow discharge confined by a magnetic field, and they found that the gas phase and/or the heterogeneous processes of the type $\text{SiH} \rightarrow \text{Si} + \text{H}$ and $\text{SiH} + \text{H} \rightarrow \text{SiH}_2$ play an important role in the growth process and on the hydrogen content in the material. A recent work⁽¹³⁾ reports that the deposition rate is a linear function of the flux density of low-energy ions impinging on the surface. In the same work it is also reported that the main reaction channel for the silane decomposition in the gas phase is the electron-impact-induced dissociation of SiH_4 into SiH_2 and H_2 .

The important role of ions in the deposition of silicon films has been emphasized by Manory *et al.*,⁽⁸⁾ who studied the dissociation of silicon tetrachloride in a microwave discharge. More recently, Mayo *et al.*⁽¹⁴⁾ have found that, in the dissociation of silicon tetrachloride, the occurrence of ion-molecule or radical-molecule reactions depend on the argon/hydrogen ratio in the plasma mixture.

In a previous paper⁽¹⁵⁾ we have found that the chemical and structural characteristics of Si:H, Cl films, prepared by the glow-discharge decomposition of silicon tetrachloride mixed with hydrogen, are affected by the addition of Ar to the feed.

The aim of the present paper is twofold:

1. To illustrate the importance of optical emission spectroscopy and laser interferometry for the study of the film deposition in a glow discharge fed with silicon tetrachloride.
2. To present data, even though on a qualitative basis, on the kinetics of film deposition and, in particular, on the processes which occur both in the gas phase and at the solid surface.

We have studied the influence of argon addition to $\text{SiCl}_4\text{-H}_2$ mixtures on the deposition rate and on the concentration of the emitting species

present in the plasma phase, and the occurrence of the etching process under particular feeding conditions.

2. EXPERIMENTAL

The deposition is performed in a tubular plasma reactor (Pyrex tube, 10 cm diameter), coupled to a radio frequency generator (35 MHz) by means of two external annular electrodes. The substrates for the samples are placed on a stainless steel holder, which is temperature controlled (positioned in correspondence with the lower electrode). The substrate material is chosen according to the technique utilized for the characterization of the film (Corning glass, crystalline silicon, sapphire, stainless steel, molybdenum).

The feeding system consists of flow meters equipped with NRS valves (Matheson) and a thermoregulated reservoir with liquid SiCl_4 ; the vapor is transported by various mixtures of H_2 and Ar bubbling into the liquid. A rotary (Fomblin charged) and a diffusive pump are utilized for dynamic and static vacuum, respectively. The value of the base pressure before each run is less than 10^{-5} torr. An axonometric scheme of the reactor used for this study is shown in Fig. 1, where laser interferometric and optical spectroscopic systems are also shown.

Laser interferometry gives *in situ* measurements of the deposition and etch rate and consists of a He-Ne 1 mW laser and a photodiode detector.⁽¹⁶⁾ Figure 2 shows a typical output obtained during the film growth; the deposition rate values are calculated from the interference fringes, as reported in Ref. 16. The constant periodicity of the output is an indication of a constant deposition rate, and the appearance of the interference system, as soon as the discharge is on, points to the absence of any induction time in the deposition process. The growing films slightly absorb at the laser wavelength (6328 Å), causing the observed decrease of the fringe amplitude.

The gas-phase analysis is performed by optical emission spectroscopy (OES), which detects the emission of excited species in the plasma through a sapphire window set on the reactor side wall. According to the required resolution, a 1-m or a 25-cm monochromator is used.

In this investigation both deposition and etching experiments have been performed with the described apparatus. The deposition has been carried out in typical conditions which lead to undoped and doped material; in the last case, controlled amounts of PH_3 and B_2H_6 have been added to the feed; in order to obtain *n*- and *p*-doped samples. Some parameters have been kept constant in all the experiments: total flow rate $\Phi_T = 60$ sccm, total power $W \approx 10$ watts, substrate temperature $T_S = 300^\circ\text{C}$, $R_{\text{SiCl}_4} = \Phi_{\text{SiCl}_4} / \Phi_T = 0.05$.

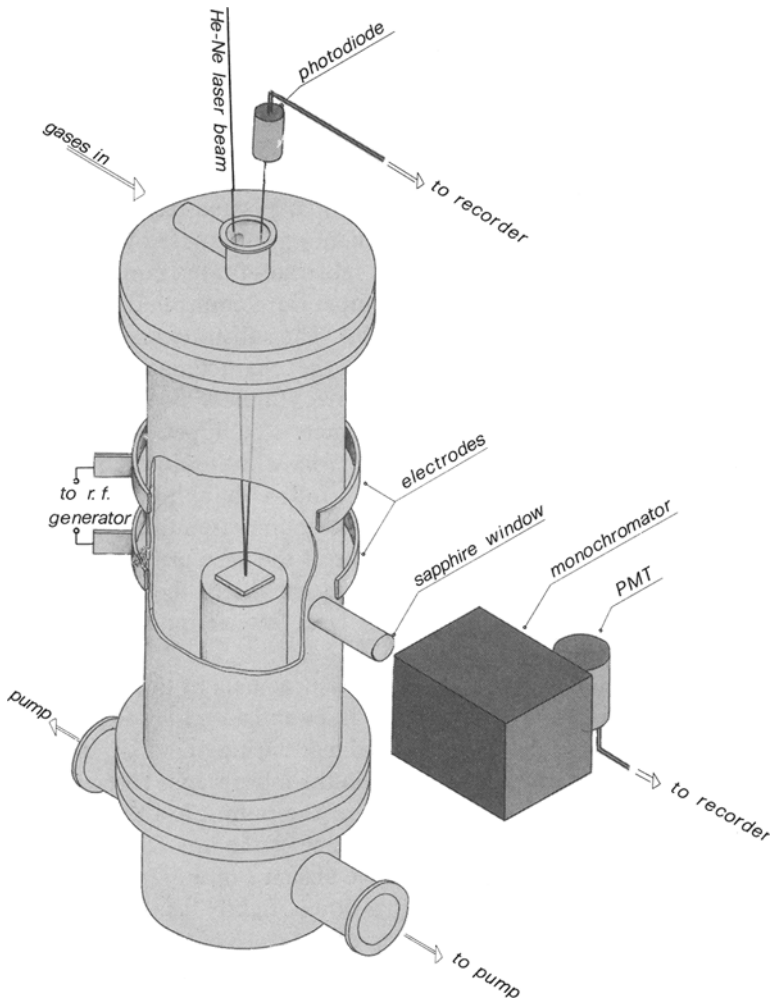


Fig. 1. Axonometric scheme of the plasma reactor equipped with laser interferometer and optical spectrometer.

The total pressure has been kept constant at $P=1$ torr, except for etching runs of undoped Si:H, Cl films, in which it has been varied between 0.5 and 2.0 torr.

The deposition runs have been carried out by varying the H_2/Ar ratio in the $SiCl_4-H_2-Ar$ mixture for undoped material and the dopant concentration in the gas feed for doped material (see Table I).

Etching of undoped and doped predeposited samples has been carried out without H_2 in the gas feeding mixture. As for the deposition, both the

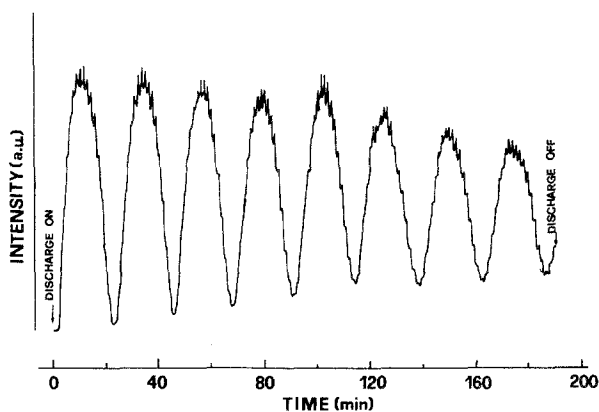


Fig. 2. Laser interferometric trace obtained during the growth of a typical Si:H, Cl film.

Table I. Experimental Conditions for the Deposition of Undoped and Doped Si:H, Cl Films from SiCl₄:H₂:Ar Mixtures^a

Type of sample	$\chi_{Ar} \left(= \frac{\Phi_{Ar}}{\Phi_{H_2} + \Phi_{Ar}} \right)$	Dopant	$R_{dop} \left(= \frac{\Phi_{dop}}{\Phi_T} \right) (\times 10^3)$
Undoped	0-1	—	—
Doped	0.25	B ₂ H ₆ , PH ₃	0.01-7.0

^a See text for the unlisted parameters.

etch rate and the intensity of the emitting species have been measured during the etching experiments. The effect of chlorine atom concentration on the etch rate of undoped material has been evaluated by varying the total discharge pressure (see Table II).

Table II. Experimental Conditions for the Deposition and Subsequent Etching of Undoped and Doped Si:H, Cl Films^a

Type of sample	Deposition				Etching	
	Gas mixture	χ_{Ar}	Dopant	R_{dop} (%)	Gas mixture	Pressure (torr)
Undoped	SiCl ₄ :H ₂ :Ar	0.25	—	—	SiCl ₄ :Ar	0.5-2.0
Doped	SiCl ₄ :H ₂ :Ar	0.25	PH ₃ , B ₂ H ₆	0.02	SiCl ₄ :Ar	1.0

^a See text for the unlisted parameters.

3. RESULTS

3.1. Optical Emission Spectroscopy (OES)

The existence of the various reactive species in the plasma phase was indicated by the analysis of the optical emission.

Figure 3 shows a typical emission spectrum observed for a $\text{SiCl}_4\text{-H}_2\text{-Ar}$ plasma mixture with $\chi_{\text{Ar}} = 0.9$. The main observed emission lines and bands, which have been assigned to some electronic excited states⁽¹⁷⁾ of H, H_2 , Ar, Cl, Si, SiCl, and SiCl_2 , are summarized in Table III.

Emission from two different electronic transitions ($B'^2\Delta \rightarrow X^2\Pi$ and $B^2\Sigma^+ \rightarrow X^2\Pi$) of SiCl have been identified. The state $X^2\Pi$ is the electronic ground state of SiCl, and $B'^2\Delta$ and $B^2\Sigma^+$ are the electronic excited states, the energy levels of which are 4.4 and 4.2 eV, respectively. Rotational-vibrational details of these electronic transitions are shown in Fig. 4 for two different $\text{SiCl}_4\text{:H}_2\text{:Ar}$ gas compositions. The observed strong continuum at 330 nm, which is superimposed on the broad H_2 continuum, is not reported in the literature. We have assigned this continuum to an electronic excited state of SiCl_2 , which radiatively dissociates into SiCl and Cl. This assignment has been suggested by the experimental observation (see Fig. 4) that two different ways of formation of $\text{SiCl}(B'^2\Delta)$ exist. In fact, since the energy levels of $\text{SiCl}(B'^2\Delta)$ and $\text{SiCl}(B^2\Sigma^+)$ are almost equal, the ratio of the emission intensities should be constant at different gas compositions, if the electron impact is the only process responsible for excitation. This is not the case observed in our experiments, pointing to an

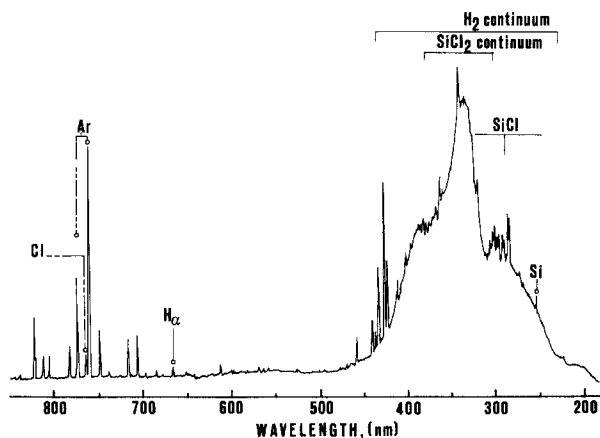
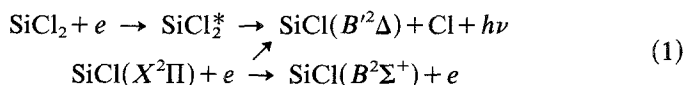


Fig. 3. Optical emission spectrum from r.f. discharge in $\text{SiCl}_4\text{-H}_2\text{-Ar}$ mixture, $\kappa_{\text{Ar}} = 0.9$.

Table III. Principal Spectral Systems Observed in SiCl₄-H₂-Ar Discharges

Species	Emission wavelength (nm)	Transition	Energy of emitting state above ground state (eV)
Si	251-253	UV1 $4s^3P^0-3p^2^1D$	4.9
Si	288	UV43 $4s^1P^0-3p^2^1D$	5.1
SiCl	281-282	$B'^2\Delta-X^2\Pi$	4.4
SiCl	287-288	$B^2\Sigma^+-X^2\Pi$	4.2
SiCl	292-294	The same	The same
SiCl	297-299	The same	The same
SiCl ₂	Continuum 310-400	—	—
N ₂	316	(SPS) $C^3\Pi u-B^3\Pi g$	11.1
N ₂	337	The same	The same
N ₂	358	The same	The same
H	434	H γ $5d^2D-2p^2P^0$	13.0
H	486	H β $4d^2D-2p^2P^0$	12.7
H	656	H α $3d^2D-2p^2P^0$	12.0
H ₂	Continuum 160-500	$2s^3\Sigma_g^-2p^3\Sigma_u$	11.9
H ₂	Many lines	$3d^1\Sigma-2p^1\Sigma$ etc.	14.0
Cl	755	$4p^4S^0-4s^4P$	10.6
Ar	750	$4p'(1/2)-4s'(1/2)^0$	13.7
Ar	764	$4p(1\frac{1}{2})-4s(1\frac{1}{2})^0$	13.2

additional contribution to the formation of SiCl($B'^2\Delta$) state. We can depict the processes which give SiCl($B'^2\Delta$) and SiCl($B^2\Sigma^+$) as follows:



This scheme shows how the SiCl($B'^2\Delta$) state can be correlated to the SiCl ground state by the direct electron impact and to the SiCl₂ excited state by the dissociation process.

In order to correlate the emission intensity of excited species to their concentration in the ground state, we have normalized each peak height to that of argon at 750 nm.

This "actinometric" technique, which is extensively utilized in plasma etching systems,⁽¹⁸⁾ represents a useful tool for evaluating the trends of active emitting species.

More investigations on this technique are, however, needed in order to better define the validity limits in our system.

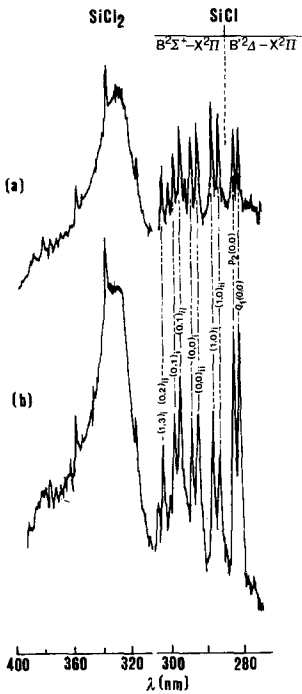


Fig. 4. Emission spectrum of SiCl_2 and SiCl species in the region 280–400 nm, for two different $\text{SiCl}_4:\text{H}_2:\text{Ar}$ ratios: (a) 5:85:10; (b) 5:14:81.

3.2. Deposition of Undoped and Doped Si:H, Cl Films

In Fig. 5 the deposition rate of undoped films (r_D) is reported as a function of the progressive substitution of H_2 with Ar, at constant SiCl_4 molar fraction (see Table I). In the same figure the normalized intensities of the emitting species have been reported, according to the actinometric technique, in terms of $I_x/I_{\text{Ar}} \cdot \chi_{\text{Ar}}$, where χ_{Ar} represents the molar fraction of Ar in the feeding mixture.

Inspection of this figure shows that:

1. The deposition rate as well as the intensity profiles are strongly dependent on the Ar addition.
2. A nondeposition region is present at high Ar addition; in that zone the chlorine atom concentration becomes significant and increases with the Ar: H_2 ratio.

Deposition rates have been measured also during the growth of doped samples. Their trends as a function of PH_3 and B_2H_6 addition in the gas feed are reported in Fig. 6. Two opposite behaviors of the deposition rate are observed for phosphorus and boron-doped material. Since the addition of dopants does not lead to a variation of the emission intensity of Ar, we

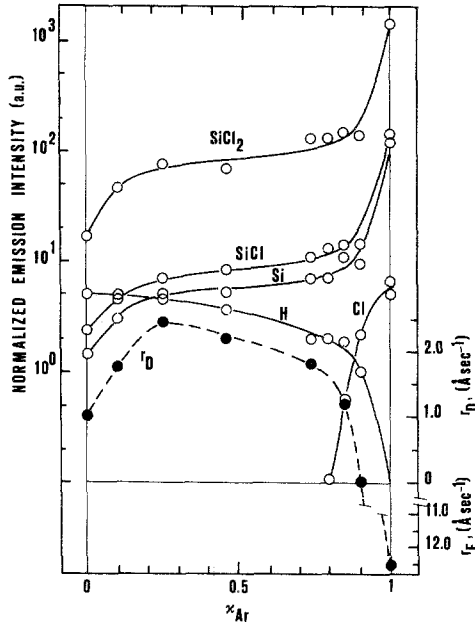


Fig. 5. Intensity of the emitting species (○) normalized to Ar peak at 750 nm vs. H_2 -Ar mixture composition, χ_{Ar} . Values of the deposition r_D and etch rate, r_E (●) refer to the right-hand scale (see Table I for other parameters).

can assume that the electron density and likely the energy distribution function do not change appreciably. Therefore the observed effect of the dopant addition on the deposition rate should be mainly related to the different influence of n - and p -type material on the growth mechanism (see Section 4.2).

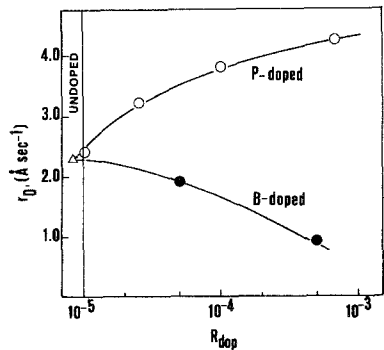


Fig. 6. Deposition rate r_D of doped (○, ●) and undoped (△) samples vs. PH_3 and B_2H_6 addition, R_{dop} (see Table I for other parameters).

3.3. Etching of Undoped and Doped Si:H, Cl Films

The predominant role of the etching process in the nondeposition region, at high Ar concentration (see Fig. 5), has been confirmed by submitting fresh predeposited samples to SiCl_4 -Ar discharges.

The etching rate was measured with the same laser interferometric technique utilized during deposition. In Fig. 7 the typical interferometric output is shown for a deposition and subsequent etching run of an undoped sample. The switch from deposition to etching condition was made by substituting H_2 with an equivalent Ar flow, keeping constant all the other parameters (see Table II).

The Si:H, Cl films submitted to etch experiments have been grown under experimental conditions leading to the highest deposition rate, $r_D = 2.4 \text{ \AA sec}^{-1}$ (i.e., the maximum of Fig. 5). The high value of etch rate obtained ($r_E = 12.5 \text{ \AA sec}^{-1}$), as shown in Fig. 7, has been reported in the etching region of Fig. 5, at $\chi_{\text{Ar}} = 1.0$.

The appearance of chlorine atoms as the deposition rate starts to fall and the increase of their concentration in the etching region seem to indicate their effectiveness in the etching of Si:H, Cl samples. This has been confirmed by submitting a predeposited material to the etching action of SiCl_4 -Ar plasmas, in which Cl atom density has been varied by varying the total pressure (see Table II). The trend of the etch rate as a function of Cl atom density is reported in Fig. 8. Two points for phosphorus- and boron-doped material are also reported for a fixed value of Cl atom density. The

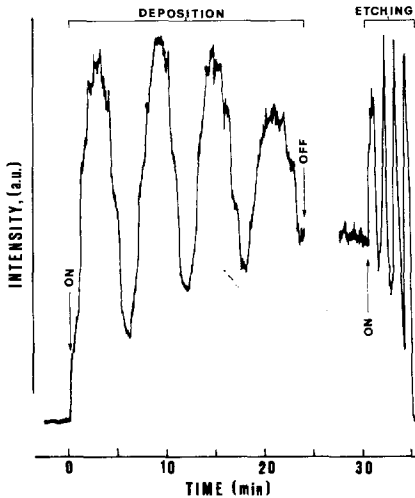


Fig. 7. Typical laser interferometric trace during the deposition and subsequent etching run.

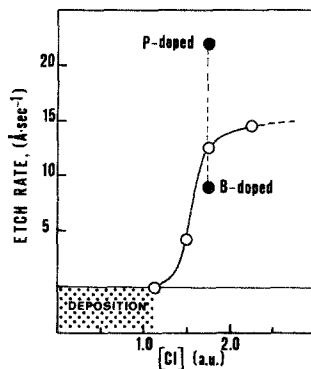


Fig. 8. Etch rate of Si:H, Cl films vs. chlorine atom density [Cl]. Filled circles refer to the etch rate of P- and B-doped samples.

p and *n* character of the surface must again be invoked to explain the different behavior of the doped materials with respect to etching.

4. DISCUSSION

4.1. Gas-Phase Processes

The OES measurements reported in Section 3.1 have shown typical emissions of SiCl₂, SiCl, Si, Cl, H, and Ar species, mainly due to electron impact excitation processes of the type

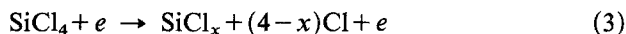


where M and M* are the generic species in the ground and excited state, respectively. Three types of processes leading to the formation of the above-mentioned species can be considered:

1. Collisions between neutral species and electrons
2. Collisions among neutral species
3. Collisions between charged and neutral species

All these processes have been reported to be important in the plasma-chemical reduction of silicon compounds, which leads to hydrogenated and/or halogenated silicon films.^(7,11)

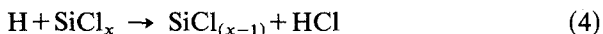
The results of Fig. 5 on the effect of Ar addition to SiCl₄-H₂ mixtures can be interpreted on the basis of the first two processes. We have not taken into account ion-involving reactions because we do not have evidence of their contribution to both gas-phase and surface processes. Direct electron impact is likely to be the main channel inducing dissociation of SiCl₄, under our experimental conditions:



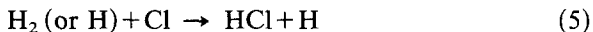
and therefore the electron density can play a fundamental role. The strong

decrease of SiCl_x density observed when a small percentage of H_2 is added to the SiCl_4 -Ar mixture can be attributed to a decrease of electron concentration with energy sufficient for process (3).

Theoretical and experimental studies^(19,14) have shown, in fact, that the addition of small percentages of a molecular gas to an argon plasma can cause a marked variation of the electron energy distribution function. On the other hand, Mayo *et al.*⁽¹⁴⁾ have found that the addition of H_2 to a SiCl_4 -Ar microwave plasma increases the SiCl_4 dissociation. This effect was attributed to the increasing occurrence of the reaction



We cannot exclude the presence of this bimolecular process in our system, but we think that its contribution is negligible in the zone of low H_2 concentration and may become significant with the further addition of H_2 . Hydrogen, however, has an important role, since the scavenging process



can reduce the Cl atom concentration and, therefore, can affect the deposition-etching equilibrium. The disappearance of Cl atoms with increasing H_2 addition is a clear confirmation of the importance of process (5).

Lee *et al.*⁽²⁰⁾ have found the presence of HSiCl emitting species in a SiH_2Cl_2 glow discharge. Its absence in our plasma system, together with the absence of emission from SiH usually found in SiH_4 systems,⁽⁹⁾ shows that the hydrogen incorporated in the Si:H, Cl films (up to 8 at.%)⁽¹⁵⁾ comes only from heterogeneous surface processes.

Since some aspects of the gas-phase processes need further explanation, we are presently continuing our investigation by utilizing OES and mass spectrometric techniques.

4.2. Surface Processes

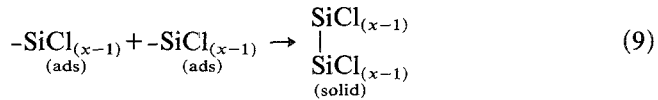
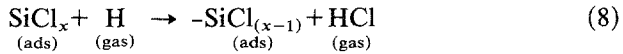
In a previous paper⁽²¹⁾ we have shown that the experimental dependence of the deposition rate on the dopant addition can be explained within the surface chemisorption theory. The results reported in Figs. 6 and 8 indicate that the chemisorption reactions are important for both deposition and etching processes. The chemisorption equilibria involved can be formulated as follows:



where SiCl_x can represent Si, SiCl, and SiCl_2 , as we cannot discriminate which silicon-containing species are involved in the growth process.

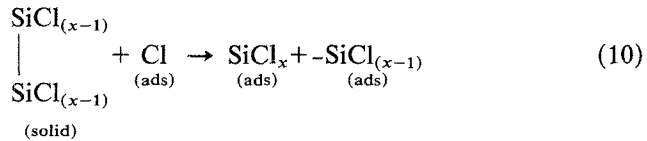
The importance of a chemisorption step has also been reported for *a*-Si:H deposition in SiH₄ plasma⁽²²⁾ and in Si₂H₆ photochemical dissociation systems.⁽²³⁾ These literature results show an increase of deposition rate with B₂H₆ doping and a decrease with PH₃ doping. The opposite behavior observed in our system (see Fig. 6) is certainly due to the chemisorption of different growth precursors on the solid surface.

Since the data of Fig. 5 show that the *r_D* trend is not strictly related to SiCl_{*x*} profiles and that *r_D* decreases up to zero in correspondence with a decrease in H atoms, a reactive process involving H atoms, besides chemisorption, must be considered in the formulation of a deposition model. Hydrogen atoms, in fact, can induce the formation of free-bond silicon species, which are involved in the reactive growth process. We can therefore propose the following scheme for the reactive surface processes:



The essential role of H atoms and surface free-bond silicon species on the deposition of Si:H, F films from SiF₄:H₂ plasmas has been also emphasized by Matsuda *et al.*⁽²⁴⁾ These workers propose, on the basis of thermodynamic considerations, a deposition model which involves surface reactive steps similar to the reactions (8) and (9).

Another surface process to be considered in the model is the etching action by Cl atoms:



where the adsorbed SiCl_{*x*} is rapidly desorbed according to equilibrium (6).

The deposition rate equation can therefore be written as

$$r_D = k_9 \cdot \Theta_{\text{SiCl}_{(x-1)}}^2 - k_{10} \cdot \Theta_{\text{Cl}} \quad (11)$$

where *k₉* and *k₁₀* are the rate constants for processes (9) and (10), respectively, and Θ represents the surface coverage for the indicated species. When *k₁₀* · Θ_{Cl} > *k₉* · Θ²_{SiCl_(*x*-1)}, *r_D* becomes negative, i.e., the etching process becomes predominant on deposition. This event occurs in the nondeposition region of Fig. 5 for χ_{Ar} ≥ 90%. In the region where 0 ≤ χ_{Ar} ≤ 80%, Cl atoms are absent and the deposition rate is controlled only by the surface concentration of free-bond silicon species. In this last case Eq. (11) can be

rewritten as

$$r_D = k_9 \cdot \Theta_{-\text{SiCl}_{(x-1)}}^2 \quad (12)$$

In the intermediate region ($80 < \chi_{Ar} < 90$) both terms of Eq. (11) are important. On the assumption that $k_9 \gg k_8$, a steady-state approximation for $-\text{SiCl}_{(x-1)}$ can be made:

$$\frac{d\Theta_{-\text{SiCl}_{(x-1)}}}{dt} = k_8 \cdot \Theta_{\text{SiCl}_x} \cdot p_H - 2k_9 \cdot \Theta_{-\text{SiCl}_{(x-1)}}^2 = 0 \quad (13)$$

$$k_8 \cdot \Theta_{\text{SiCl}_x} \cdot p_H = 2k_9 \cdot \Theta_{-\text{SiCl}_{(x-1)}}^2 \quad (14)$$

so that

$$r_D = \frac{1}{2} k_8 \cdot \Theta_{\text{SiCl}_x} \cdot p_H \quad (15)$$

The SiCl_x coverage Θ_{SiCl_x} , according to the Langmuir-Hinshelwood model,⁽²⁵⁾ is independent of the reactive processes and can be expressed by

$$\Theta_{\text{SiCl}_x} = \frac{K_6 \cdot p_{\text{SiCl}_x}}{1 + K_6 \cdot p_{\text{SiCl}_x}} \quad (16)$$

where K_6 is the equilibrium constant of the chemisorption process (6) and p_{SiCl_x} is the partial pressure of SiCl_x .

In low-pressure systems, the Langmuir isotherm equation (16) can be approximated by

$$\Theta_{\text{SiCl}_x} = K_6 \cdot p_{\text{SiCl}_x} \quad (17)$$

which gives a linear relationship between surface coverage and SiCl_x partial pressure. Under these conditions, the deposition rate equation becomes

$$r_D = \frac{1}{2} K_6 \cdot k_8 \cdot p_{\text{SiCl}_x} \cdot p_H \quad (18)$$

In Fig. 9 r_D values have been plotted as a function of the product of the relative emission intensities of H and SiCl_x species. The linear relationship shown in the figure for $0 \leq \chi_{Ar} \leq 0.8$ seems to confirm the validity of

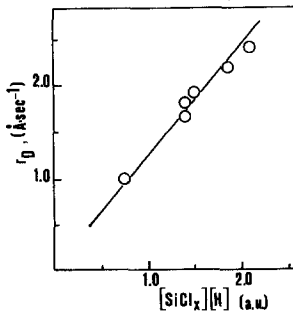


Fig. 9. Deposition rate r_D vs. product of SiCl_x and H densities, $[\text{SiCl}_x] \cdot [\text{H}]$, obtained from the data of Fig. 5 for $0 \leq \chi_{Ar} \leq 0.8$.

the model, at least in the zone in which Cl atoms are absent. On the contrary, in the presence of Cl atoms, the approximate equation (12) is not applicable and the analysis of the results is complicated by the competitive chemisorption of SiCl_x and Cl species. In this case all the terms of Eq. (11) have to be taken into account. The fact that r_E goes to zero (Fig. 8) even in the presence of Cl atoms is a clear indication of the competition between the deposition and etching processes and therefore of the contemporary occurrence of SiCl_x and Cl chemisorption. The dotted area of Fig. 8 is a region in which deposition should be expected, even in the absence of H atoms. We could not verify this event; however, literature results show that deposition of silicon films occurs in SiF_4 - SiF_2 -Ar r.f. discharges, without addition of H_2 , and that SiF_2 acts as a fluorine atom scavenger.⁽²⁶⁾ More recently, Avni *et al.*⁽²⁷⁾ have been able to obtain film deposition from SiCl_4 -Ar mixture. The presence of the "plateau" region in Fig. 8 is further evidence of a chemisorption-controlled etching mechanism. It can be due to the fact that chlorine atom surface coverage Θ_{Cl} reaches its saturation value according to the Langmuir isotherm law; therefore, the rate tends to become independent of the gas-phase Cl concentration. The strong dependence of the etch rate on the n and p character of the material (see the two points of Fig. 8) is indicative of the important role played by surface chemisorption. A similar doping effect has been found by Flamm *et al.*,⁽²⁸⁾ who attributed its origin to the ionic character of the silicon-halogen bond. Since the doping effect on the deposition rate (see Fig. 6) is in the same direction as that on the etch rate, the ionic character of Si-Cl bond can play an important role also in our case.

In the deposition mechanism discussed above, the effect of surface ionic bombardment has not been taken into account. Its role has been stressed by Vepřek *et al.*,^(13,29) who found a well-defined dependence of the deposition rate on the flux toward the surface. We cannot exclude the possibility that positive ions impinging on the surface may influence the chemisorption equilibrium and kinetic constants of the reactive steps involved in the growth and etch processes. However, under our conditions of low-ionization plasmas, the contribution of surface-positive ion interaction can be considered negligible, as the fitting of the experimental results by Eq. (18) shows in Fig. 9.

CONCLUSIONS

From this study the following remarks can be made:

1. In a SiCl_4 - H_2 -Ar glow discharge the gas-phase composition and the deposition rate are strongly affected by the Ar/ H_2 ratio. By

controlling this ratio one can shift from deposition to etching conditions.

2. There is strong evidence that chemisorption processes are important intermediate steps in the reactive processes occurring on the surface.
3. The deposition rate is linearly related to the product of H and SiCl_x concentration in the gas phase.

More accurate studies are necessary for a deeper insight into the kinetic mechanism in order to clarify the identity of the real growth precursors and the role played by ion bombardment.

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