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DIRECT OBSERVATION, BY THE MATRIX ISOLATION TECHNIQUE, OF NITRIC OXIDE EFFECTS IN LOW-PRESSURE SILANE DISCHARGES

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Hydrogenated silicon radicals produced in a 0.2 mTorr silane multipole dc plasma are compared to those observed in 0.2 mTorr silane + 0.3 mTorr nitric oxide plasma. The detection of plasma radicals has been performed by the solid Ar matrix isolation technique, associated with IR absorption spectroscopy. This study presents evidence for the IR absorption line assignments. When NO is added to the silane plasma, the concentration of silyl relative to silylene radicals increases while the silane and disilane decrease. The results are discussed in terms of plasma–surface chemical reactions; due to the low pressure of silane and nitric oxide, no gas phase radical reactions can occur.

1. Introduction

The development of high quality hydrogenated amorphous silicon (a-Si:H) films is necessary for many applications in the semiconductor industry such as solar cells, thin films transistors, image sensors, etc. Each application requires specific properties depending upon the nature and the concentration of defects which are directly influenced by the preparation method.

One of the most used techniques to grow a-Si:H films with interesting semiconducting properties is the plasma-enhanced chemical vapor deposition (PECVD), where silane is dissociated in a dc or rf glow discharge. In this dissociation, the ions and radicals generated by electron impact on silane, contribute to the condensation of the amorphous film on a substrate. For gas pressures $p < 1$ mTorr, the relative Si atom flux going to the substrate in an ionized form is predominant, while at higher pressures, as for example at $p > 20$ mTorr, which is used in the industrial reactors, it becomes smaller than 10% [1]. At these pressures, the main precursors of the growing film are the silylene (SiH_2) and the silyl (SiH_3) radicals produced in the plasma gas phase [2]. The quality of the film depends on the branching ratio SiH_3/SiH_2, so it is necessary to study the plasma chemistry of these radicals, and how they are incorporated in the a-Si:H film. In rf discharges the branching ratio depends on the pressure and the discharge power deposition. At 300 mW cm^{-1} power deposition and moderate pressure (<0.5 Torr) for example, it is about 5 [3]. In dc discharges at 40–80 mTorr silane, SiH_3 is the dominant monosilicon radical [2]. In spite of numerous experimental investigations the details of these processes remain controversial (see refs. [2,3], and references therein).

The mechanisms of silane and disilane decomposition in static dc glow discharges at 0.25–0.75 Torr, have been studied by mass spectrometry, using the scavenging properties of nitric oxide (NO) toward the monosilicon radicals [4,5]. The addition of NO, at 2–30% mole fraction, in a static silane glow discharge, produces the complete inhibition of SiH_x solid deposition, and decreases the yield of disilane and trisilane formation. In the case of a disilane plasma, the introduction of NO reduces the formation of trisilane and tetrasilane, as well as the growing of the a-Si:H film.

The first observations of scavenging effects of nitric oxide were reported on mercury-photosensitized decomposition of methylsilane and silane [6]. The addition of a small amount of NO leads to the suppression of disilane formation, and to an increase in the yield of H_2 and N_2.

The study of the vacuum ultraviolet photolysis of methylsilane has shown that silyl radicals (SiH_3) can effectively be scavenged by relatively small concentrations of nitric oxide [7].

Karamatos and Lampe [8] studied also the mercury-photosensitized reactions of silane and methylsilane with a few percent of NO, by mass spectrometric analysis. The working pressures are 5–20 Torr. The authors demonstrated the inhibition of disilane formation by NO. As, in their pressure range, Si_2H_6 is supposed to be formed mainly by the reaction

$$SiH_3 + SiH_3 \rightarrow Si_2H_6\,,$$

the observed inhibition of Si_2H_6 is attributed to the fact that SiH_3 radicals are scavenged by NO.

The situation is quite different when 147 nm radiation from a Xe lamp is used to photolyse SiH_4 in He, at a partial pressure 1–8 Torr, as reported in ref. [9]. The presence of NO reduces considerably the trisilane formation, but not the disilane. Other reactive intermediates than SiH_3 are needed for the description of the mechanism, and SiH_2 is considered unreactive toward NO. The quantum yield for depletion of silane is increased from 4.4 to 7, while N_2O and SiH_3OSiH_3 are the main produced species.

The present paper reports direct observations of the effects of NO, when it is added to a low pressure (0.2 mTorr) silane multipolar dc discharge. In this discharge, the plasma is essentially sustained by fast primary electrons, and the dominant chemical processes occur between the plasma and the walls of the chamber, and not in the gas phase volume. A direct study of plasma radicals is performed by the matrix isolation technique, which has proven to be an efficient way to concentrate, stabilize and study, by infrared absorption spectroscopy, the neutral species generated in the plasma [10]. The effects of NO will also help to assign some IR absorption lines to hydrogenated monosilicon radicals.

2. Experimental

The main experimental details have been already described [10]. The discharge is generated in a multipole magnetic confinement chamber by accelerated electrons emitted by a hot filament. The accelerating bias has been adjusted to $V_d = 80$ V, the discharge current was $I_d = 0.4$ A, and the total pressure p was 0.2 mTorr for pure silane discharges, and 0.5 mTorr for the gas mixture: 0.2 mTorr SiH_4 + 0.3 mTorr NO. The temperature of the chamber walls is about 200°C. A 6 mm diameter effusion hole, allows the plasma neutrals to be trapped on a He-cooled CsBr window. Pure Ar is codeposited to ensure the isolation of the species coming from the plasma. In order to avoid radical formation within the matrix due to positive ions, the plasma chamber was biased at −20 V with respect to the cryostat. Typical mole ratio Ar/SiH_4 of the polycrystalline film obtained at 20 K on the cold window is 1000. The thickness of the cold sample is 300–800 μm, according to the duration of the experiment. Then the sample is cooled to 10 K, and IR spectra are recorded from 400 to 4000 cm^{-1} with a Perkin–Elmer 580 spectrometer. The resolution is 1 cm^{-1}, and the wavenumber accuracy is ± 0.5 cm^{-1}, obtained by calibration with H_2O lines. The sample is annealed during 30 min at 30 K. In this process, which allows some migration of the species, new lines corresponding to polymers may appear. It is interesting to mention that a specific feature of this technique is the possibility of different trapping sites in the matrix for one molecular species, which may create multiplet structures, and that the trapping site symmetry may induce lifting of degeneracy, resulting also in a multiplet structure [11].

3. Results

Figs. 1 and 2 show typical IR absorption spectra obtained in the stretching and bending regions of silane. In each figure, five spectra are presented. The corresponding experimental conditions are given in the caption to fig. 1.

The main absorption lines are listed in table 1.

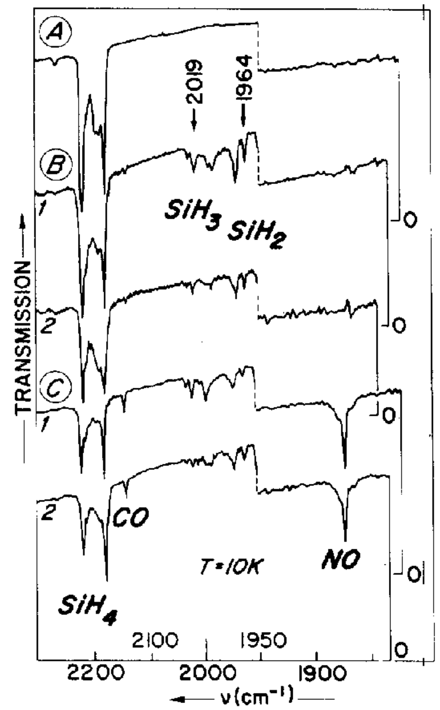

Fig. 1. IR absorption spectra in the stretching range recorded at 10 K. (A) $SiH_4/Ar = 1/1000$. Deposition time at 19 K 3 h. Sample thickness: 800 μm. (B) Plasma: 0.2 mTorr SiH_4; $V_d = 80$ V, $I_d = 0.5$ A. $SiH_4/Ar = 1/700$. Deposition time at 19 K 4 h. Sample thickness: 800 μm. (1) Before annealing, (2) after annealing: 30 min at 30 K. (C) Plasma of 0.2 mTorr SiH_4 + 0.30 mTorr NO; $V_d = 120$ V, $I_d = 0.4$ A. $SiH_4/Ar = 1/700$. Deposition time at 19 K: 1 h 20 min. Sample thickness: 300 μm. (1) Before annealing, (2) after annealing: 30 min at 30 K.

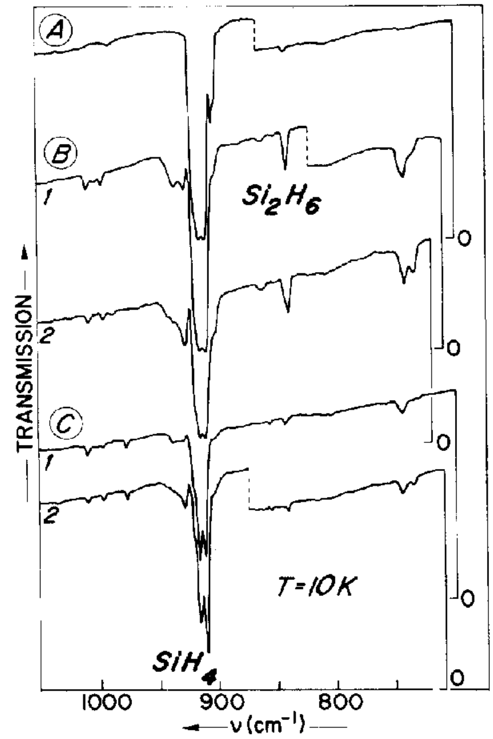

Fig. 2. IR absorption spectra in the bending range. (A, B, C) Same as in fig. 1.

3.1. Line assignments

Some of the assignments of the lines proposed in table 1 are straightforward. The IR spectrum of SiH_4 in solid Ar (figs. 1A and 2A) confirms the results reported in ref. [12], showing the effects of multiple trapping sites and some cluster bands corresponding to silane molecules trapped in neighbouring sites of the matrix. The assignment of the lines to Si_2H_6 will be presented in detail with the results of our studies of disilane plasma. It is in agreement with the observations reported in ref. [13].

3.1.1. CO and NO

The feature at 2139 cm^{-1} is due to CO trapped in solid Ar [14]. It has to be noted that in samples with NO (figs. 1C and 2C) a larger CO absorption is observed, probably due to oxidation of some contaminating molecules.

A reference spectrum, recorded with NO in solid

Table 1
Observed absorption lines with tentative assignments. P, polymer (molecules trapped in neighbouring sites); R1, monoradical; R2, diradical (increases irreversibly upon matrix annealing)

2264	SiH_4	995	SiH_2
2215	SiH_4	975	R1
2187	Si_2H_6+P	933	R1
2176	SiH_4	925	R2
2139	CO	913	SiH_4
2028	SiH_3	907	SiH_4
2019	SiH_3	860	R2
1996	SiH	837	Si_2H_6
1992	SiH_2	734	SiH_3+CH_3
1973	SiH_2	725	R2, HSiOH?
1964	SiH_2		
1954	SiH_3		
1875	NO		
1008	SiH_3		

Ar, shows that the 1875 cm^{-1} absorption belongs to NO. This corresponds to the 1880 cm^{-1} line observed in nitrogen matrix [15].

3.1.2. SiH_2

The new lines appearing in spectra B and C of figs. 1 and 2, are due to the neutral radicals created in the plasma. A silane UV photolysis experiment, performed in solid argon [16], shows similar features. Nevertheless, the proposed assignments, especially for silylene (SiH_2), are questionable, as it has been pointed out in ref. [17]. In their investigation of the reaction of silicon atoms with molecular hydrogen in an Ar matrix, the authors assign the 1992, 1972, 1963 and 996 cm^{-1} peaks unambiguously to the $2\nu_2$, ν_3, ν_1 and ν_2 modes of SiH_2 respectively. As a matter of fact, it will be seen in section 3.2 that the NO effect in the silane discharge shows clearly that these lines are correlated and belong to the same species.

3.1.3. SiH_3

The assignment of silyl radical (SiH_3) lines is not so clearly established. In a recent paper, Allen and Schaefer [18] report calculations concerning geometrical structures, force constants and vibrational spectra of $SiH_n (n<4)$ species, with a critical discussion of the literature data. Their calculated fundamental frequencies for SiH_3 are: $\nu_1=2150$ cm^{-1}, $\nu_2=773$ cm^{-1}, $\nu_3=2180$ cm^{-1} and $\nu_4=993$ cm^{-1}. On the other hand, the theoretical values proposed by Bunker and Olbrich [19] are: 2424, 778, 2106 and 976 cm^{-1}, respectively. Finally, Yamada and Hirota [20] using IR diode laser spectroscopy, observed the two inversion doubling components of the ν_2 mode at 727.94 and 721.05 cm^{-1}. As we will see in section 3.2, the NO effect leads to a correlation between the lines observed at 2029, 2019, 1952 and 1008 cm^{-1}. Taking into account the environmental effect, the following assignment could be proposed: 2029 and 2019 cm^{-1} for ν_3 with a lifting of degeneracy due to the matrix field, 1952 cm^{-1} for ν_1 and 1008 cm^{-1} for ν_4 modes of SiH_3. The absorption corresponding to the ν_2 mode of SiH_3 is probably included in the broad feature at 734 cm^{-1}. This line is also observed in GeH_4 plasmas [21], suggesting that it is not related to Si or Ge compounds, but probably to CH_3 from plasma contamination (a CH_3 bending mode is proposed at 730 cm^{-1} [22]). Furthermore, it is superimposed to a broader absorption near 725 cm^{-1}, which increases irreversibly upon annealing, and therefore could correspond to a diradical Si_2H_n or to HSiOH [23], due to the recombination of Si atoms with H_2O always present in the cold matrix, as observed in the 1600 cm^{-1} region.

3.1.4. SiH

The line observed at 1996 cm^{-1}, which does not show any correlation (see section 3.2) with the absorptions due to SiH_2 or SiH_3, could be assigned to SiH. This radical has been observed by IR laser-induced fluorescence and high-resolution spectroscopy. Its vibrational frequency in the gas phase is centered at 1970 cm^{-1} [24].

3.1.5. Non-identified lines

A monoradical SiH_n could be responsible for the broad feature at 933 cm^{-1}. The narrower line at 925 cm^{-1}, growing irreversibly upon annealing, could belong to a diradical. As H atoms can be trapped in solid Ar and migrate upon annealing [25], it is impossible to give an assignment for all the species growing irreversibly upon annealing. At 975 cm^{-1}, when the plasma contains NO, a weak line appears, which does not change dramatically upon annealing, it could be a monoradical due to the nitrogen or oxygen atoms from the NO dissociation.

3.2. Nitric oxide effects

As can be observed in spectra C of figs. 1 and 2, the presence of NO in the plasma induces some changes in the relative intensities of the lines in a given spectrum.

The present experimental conditions do not allow a satisfying normalization of the radicals to the non-dissociated silane absorptions. We will discuss here only the relative intensities of the peaks inside a same run. Furthermore, for a given transition, the intensity and the linewidth should remain the same in the Ar matrix, whatever the experiment. So to characterize a given line, it is correct to use

$$\alpha=\ln(I_0/I_{\max}) ,$$

where I_0 is the transmitted intensity at the frequency of the line without absorption (it corresponds to the base line), and $I_{\max}$ is the transmitted intensity at the top of the line (the minimum of transmission). Then, in a same experiment, the relative behaviour of the species is studied by normalizing their α values to the α of a given line.

3.2.1. Toward monosilicon radicals

The NO effect on the monosilicon radicals can be observed in fig. 3A, where the main lines of the spectra are normalized to the 1964 cm^{-1} one. This absorption is a good reference for SiH_2, as it is not affected by any overlap with another species. It appears clearly that the features at 1992, 1973 and 995 cm^{-1} are correlated to the 1964 cm^{-1}, and consequently are due to SiH_2, as mentioned previously.

The apparent correlation observed for 933 and 734 cm^{-1} is not significant. These peaks, as shown in the spectra of annealed matrices (figs. 2B and 2C), are formed by a superposition of different species absorptions, and the α values cannot be well estimated. Therefore, they cannot be attributed to SiH_2.

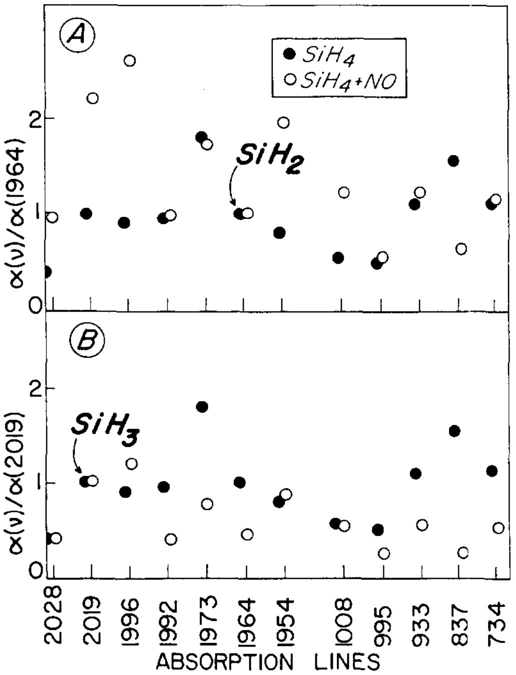

Fig. 3. Relative intensities of various lines without and with NO in the silane plasma. $\alpha=\ln(I_0/I_{max})$. (●) plasma: 0.2 mTorr SiH_4, $V_d=120$ V, $I_d=0.4$ A; (○) plasma: 0.2 mTorr $SiH_4+0.30$ mTorr NO, $V_d=120$ V, $I_d=0.4$ A. (A) Normalization of α to the 1964 cm^{-1} line (SiH_2). (B) Normalization of α to the 2019 cm^{-1} line (SiH_3).

The effect of NO appears as an increase by a factor 2 to 3 of the lines at 2028, 2019, 1996, 1954 and 1008 cm^{-1}.

By normalizing now to the 2019 cm^{-1} line, which is due to SiH_3 (fig. 3B), the absorptions at 2028, 1954 and 1008 cm^{-1} appear correlated. Of course the NO effect is then a decrease of the SiH_2 lines, and the relative intensity of SiH_3 with respect to SiH_2, $[SiH_3]/[SiH_2]$ is multiplied by 2.5.

The 1996 cm^{-1} line (SiH in the present proposed assignment) is not correlated with SiH_3. From both normalizations (figs. 3A and 3B), it is found that the presence of NO increases the proportion $[SiH]/[SiH_3]$ by about 30%.

Considering the different experiments with NO in similar conditions, we conclude that NO in the silane plasma increases the ratio $[SiH_3]/[SiH_2]$ by a factor 2.5, and decreases the ratio $[SiH_3]/[SiH]$ by a factor 0.8.

3.2.2. Toward disilane formation

The effect of NO on the formation of Si_2H_6 can be observed in the spectra of fig. 2. It has to be noted that the behaviour of the absorption peaks cannot be appreciated directly in the figure without normalization. On the other hand, it is impossible to get an absolute value of the disilane/silane concentration. The lines at 2264 and 2215 cm^{-1} belong to the ν_3 mode of SiH_4 trapped in different sites of the Ar matrix [12]. A normalization can be obtained using a parameter somewhat proportional to the total amount of silane in the sample by adding $\alpha(2264\ cm^{-1})+\alpha(2215\ cm^{-1})$. Then the disilane/silane ratio should be proportional to

$$x=\alpha(837)/[\alpha(2264)+\alpha(2215)]\ .$$

For the typical $SiH_4/Ar=1/1000$ experiment, corresponding to spectra A (no plasma) of figs. 1 and 2, x does not change upon annealing. As expected, nothing can create Si_2H_6 by migration inside the matrix. Spectra B of figs. 1 and 2 show that disilane is produced in the plasma at 0.2 mTorr SiH_4, giving a 6 times larger relative absorption. This absorption increases by about 40% upon annealing, due to the radical–molecule reactions inside the matrix. On the contrary, in a plasma of SiH_4+NO, the disilane intensity normalized to the non-dissociated silane, decreases by about 20%, and the increase upon annealing is only 20% (table 2). Finally, considering the different experiments in similar conditions, the analysis of the spectra indicates about 4–5 times less disilane compared to SiH_3 with NO than without NO, and about 2 times less disilane compared to SiH_2 with NO than without NO (fig. 3).

3.2.3. Toward silane

Spectra C of figs. 1 and 2 show a larger depletion of silane intensity when the silane plasma contains NO. The silane concentration appears 2–3 times smaller in SiH_4–NO plasma than in pure SiH_4. Furthermore, with NO, the intensities of radicals relative to the silane absorptions ($\alpha(2264)+\alpha(2215)$) seem to be about 3 times larger for SiH_3 and 1.3 times larger for SiH_2.

3.2.4. Toward a-Si:H formation

It is also interesting to notice that, in the present silane–nitric oxide plasma experiments, deposition of a transparent, whitish powder is observed on the walls of the multipole discharge chamber, instead of the usual amorphous silicon film. This observation is also reported in ref. [4], and it is essentially attributed to the condensation of siloxanes and SiO_2 produced in the plasma chemical processes.

3.2.5. Toward the solid Ar matrix

To check if the observed NO effects are due to plasma chemical reactions, and not to reactions inside the solid Ar matrix, some experiments with pure silane plasma trapped in NO-doped matrices (Ar/NO = 500) have been performed. They did not show any significant change in the spectra of silane plasmas with respect to those obtained with pure Ar matrix.

Table 2
Effect of NO in the plasma on the formation of Si_2H_6. Analysis of the line at 834 cm^{-1}. x is the proportion of disilane in silane gas cylinder

	SiH_4 (without plasma)	SiH_4 (plasma)	SiH_4+NO (plasma)
before annealing	x	$6x$	$5x$
after annealing	x	$8x$	$6x$

4. Discussion

The nitric oxide effects in silane plasmas, presented in this paper, cannot be directly compared with those observed in the previous studies [4,5], because the present experimental conditions are different: the silane total pressure is about 1000 times lower, and the relative concentration of NO is much higher.

The phenomena observed in the present solid Ar matrix experiments may have different origins: (i) reactions in the gas volume; (ii) reactions of plasma species with the products deposited in the discharge chamber walls; (iii) reactions inside the Ar matrix.

It is very difficult to estimate the reaction probability inside the solid Ar matrix. Nevertheless, as mentioned before, no effect has been observed in the experiments done by adding NO to the Ar gas used to form the solid matrix. So, processes (iii) can be ruled out.

At low silane pressures (< 0.5 mTorr), the plasma chemical processes in gas phase are dominated by the primary electron–molecule reactions [26]. Moreover, more than 80% of Si species impinging the discharge chamber walls are ions [1] and therefore they are not trapped in the solid Ar matrix.

A comparison between the contribution of processes (i) and (ii) may be done by estimating the probability $1/\tau_r$ that a radical disappears in gas reactions and the probability $1/\tau_d$ that a radical diffuses to the walls (τ_r and τ_d are the corresponding mean lifetimes). If τ is the mean lifetime of radicals in the plasma,

$$1/\tau = 1/\tau_r + 1/\tau_d\,,$$

$$1/\tau_d = D/R^2\,.$$

Taking the diffusion coefficient $D_0 = 400$ $cm^2\ s^{-1}$ for the silane at $p_0 = 1$ Torr [27], at $p = 0.2$ mTorr and for a mean chamber radius $R = 10$ cm,

$$1/\tau_d = D_0 p_0 / R^2 p = 10^4\,.$$

On the other hand,

$$1/\tau_r = k_1 \rho\,.$$

Considering a reaction rate coefficient for the silane at 500 K, $k_1 = 10^{-12}$ cm^3/molecule s [28] and the corresponding density ρ of silane molecules at 0.2 mTorr we arrive at $1/\tau_r = 10$.

Similarly, due to the low pressures, the reactions of radicals in the gas phase, for example SiH_2 with NO, are negligible [29].

The species reaching the walls are involved in different chemical processes and are differently incorporated in the film. Almost all the SiH_n^+ ions are trapped [30]. The sticking probabilities for SiH_2 and SiH_3 are respectively 0.70 (at 335°C) and 0.12 (at 200°C) [31].

In conclusion, it appears that for the present experimental conditions, the radical reactions with the products deposited in the chamber walls are much more important than the reactions in the gas volume, even if NO is added to silane. Therefore, in the following discussions, the effects of radical (or ion)–molecule reactions in the gas phase will be considered as negligible.

Because of surface reactions the SiH_3 radicals are involved in different processes: a proportion S contributes to silane formation, a proportion D contributes to the disilane formation, a proportion F is irreversibly incorporated in the film, a proportion G is sent back to the gas phase. By definition, $S+D+F+G=1$. The silane formed on the surface is attributed to reactions of SiH_3 from the plasma, with bound H of a-Si:H surface, and the disilane is produced in reactions between plasma and surface SiH_3 radicals.

At high NO concentration in silane plasmas, as in the present experiments, the plasma electronic properties and chemical processes in the gas phase and in the chamber walls can change. In fact, the fast electron energy distribution of the plasma is not modified, because the total gas pressure remains very low (0.5 mTorr). However, NO is a very reactive free radical, and can effectively change the chemical processes occurring in the multipole chamber. A mass spectrometric analysis of a 0.5 Torr NO glow discharge shows that the steady-state composition is 86.4% NO and 13.6% O_2, N_2, and N_2O [4].

Because in the gas phase, at the present low pressure, the radical (or ion)–molecule reactions can be considered as negligible, NO is not able to scavenge SiH_3 radicals as reported in ref. [4]. Nevertheless, NO modifies, as we pointed out, the composition of the deposited film and therefore the surface reactions.

In SiH_4–NO plasmas, the previous relation can be written as

$$S'+D'+F'+G'=1\ .$$

The change in the composition of the film, when NO is added to the silane plasma, leads to the inhibition of formation of silane and disilane in surface reactions. As a result, $S'<S$ and $D'<D$.

The difference in the SiH_3/SiH_2 branching ratios measured with and without NO, is also due to the change in the film nature and because SiH_3 radicals are mainly responsible for silane and disilane formation in surface reactions. This implies that $G'>G$.

Probably $F'<F$, but we are not able to check this point quantitatively in the present work.

5. Conclusions

(A) The study of IR absorptions of the low-pressure silane (or silane+NO) plasma radicals trapped in a solid Ar matrix gives the following results concerning the line assignments and NO effects:

(i) The absorption lines attributed to SiH_2 have been confirmed.

(ii) The line assignments proposed for SiH_3 are 2029 and 2019 cm^{-1} for ν_3, 1952 for ν_1 and 1008 for ν_4.

(iii) The line at 1996 cm^{-1} is proposed for SiH.

(iv) Some non-identified features are discussed.

(B) When NO is added to a low-pressure (0.2 mTorr) silane plasma in which the reactions of active species with molecules are negligible, and the chemical processes are essentially due to the surface reactions, the main conclusions are:

(i) The deposited film is not a-Si:H, but a transparent and whitish material composed essentially of siloxanes.

(ii) An inhibition of silane and disilane formation in the surface reactions is observed. It can be explained by a smaller efficiency of the production of these gases by SiH_3 radicals in surface reactions due to the change of deposited film composition.

(iii) An increase of SiH_3/SiH_2 branching ratio suggests that a more important proportion of SiH_3 reaching the surface is sent back to the gas.

Further experiments are planned, with an improved IR spectral analysis (better signal to noise ratio), in different pressure conditions, gas mixtures, and with an extension to rf discharges.

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