

Plasma deposition of amorphous silicon alloys from fluorinated gases

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Abstract: Plasma deposition of a-SiGe, a-SiC and a-SiN alloys starting from fluorinated precursors is overviewed. The growth chemistries are examined on the basis of a unique chemisorption model. Some aspects on the role of F atoms in controlling the gas surface interactions and in determining the material properties are also evidenced.

INTRODUCTION

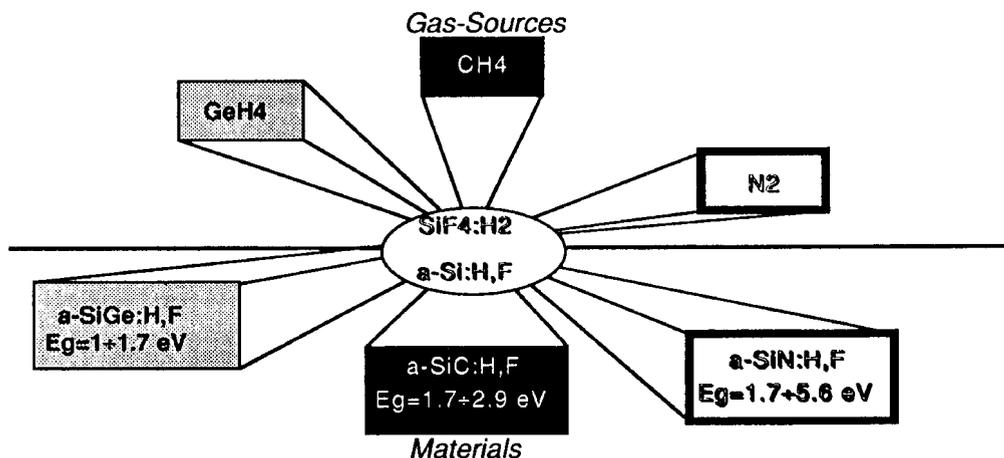
In the last two decades, plasma deposition processes of hydrogenated amorphous silicon and its alloys have been investigated and many applications have been developed (solar cells, photoreceptors and thin film transistors) and others are going to be exploited (memories, bipolar transistors) (1). However, the development of a completely integrated a-Si:H technology is strictly related to the definitive "design" of the silicon-based alloys, such as SiGe, SiC and SiN. These materials have optical and electrical properties continuously adjustable in a wide range, according to the kind and amount of the alloyed atom, since stoichiometry is not required (2).

Nevertheless, the worsening of the photoelectronic properties of SiGe (3) and SiC (4) with increasing the alloyed partner and the uncomplete chemical stability of SiN material are still existing problems (5). Recently, these inconveniences are reserving considerable efforts and significant improvements have been obtained when silicon-based alloys are deposited in new deposition systems (6-8), under H₂-dilution (6, 9) and/or from alternative feed-stock like fluorinated gases (3, 10-19).

In this lecture we report on the plasma deposition of amorphous silicon films and its alloys (SiGe, SiC, SiN) starting from SiF₄ as Si-source alternative to silane and from GeH₄, CH₄ and N₂ as sources of alloying atoms.

Emphasis is given to:

- the plasma and surface chemistry during deposition of a-Si:H,F and its alloys;
- the role of fluorine in the gas and surface reactions and its threshold value as chemical constituent of the material, before observing degradation.



AMORPHOUS SILICON-GERMANIUM AND SILICON-CARBON ALLOYS (a-SiGe:H,F and a-SiC:H,F).

The present state of art of device quality a-Si:H is the result of the enormous number of studies on deposition of silicon from SiH₄ plasmas. These efforts led to a well established procedure for thin film preparation, whose essential elements can be summarized in the following "recipe":

- UHV deposition chamber capacitatively coupled to an r.f. (13.56 MHz) generator with interelectrode distance of 2-3 cm;
- pure SiH₄ or SiH₄ diluted in H₂ or He (SiH₄>10%);
- deposition temperature of about 250 °C;
- power density of about 15 mW/cm².

However, some problems on the material quality, such as metastability, i.e. photodegradation, are still unsolved (20) and are object of the ongoing studies for further developments.

The above "recipe" is also valid for silicon alloys deposition (SiGe, SiC), where the amount of the precursors (GeH₄, CH₄,.....) containing the alloying atoms is an additional parameter. Depending on the type of silicon and alloying atom precursors, their relative amounts in the feed can assume very different values, in order to obtain the desired material composition. This feed composition effect is well evidenced by the data in Figs. 1 and 2. Figure 1(a-b) shows the dependence of the Ge content in SiGe alloy on the germane amount in the feed for fluorinated (SiF₄:GeH₄:H₂) (10) and hydrogenated (SiH₄:GeH₄) systems (21). In the same figure the correspondent deposition rate trends are also shown.

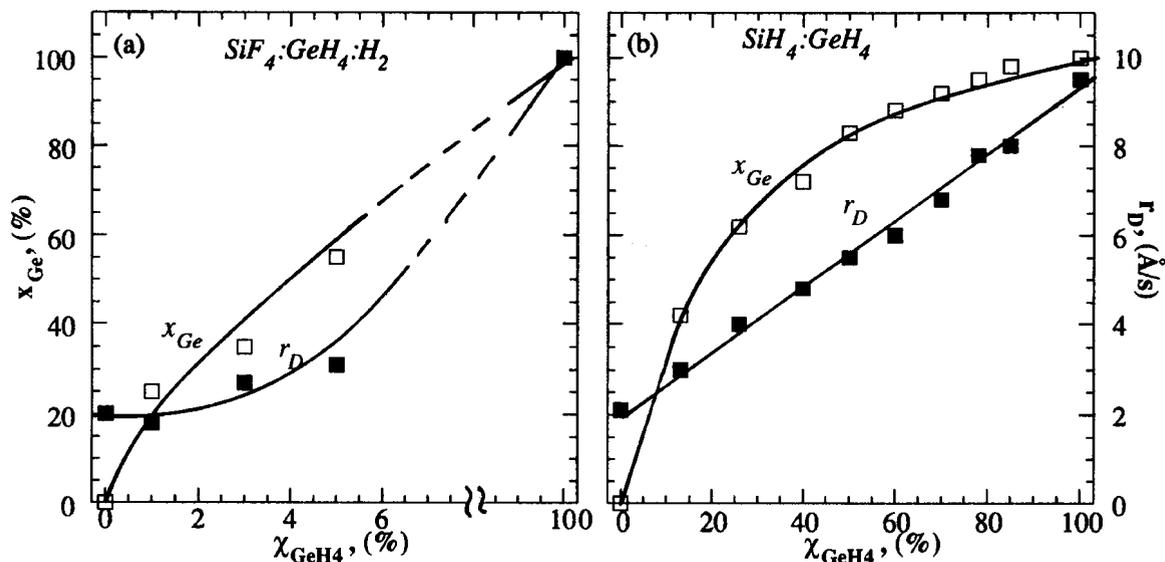


Fig. 1(a-b). Germanium content x_{Ge} (Ge/(Ge+Si)) and deposition rate r_D vs gas compositional ratio, χ_{GeH_4} (GeH₄/(GeH₄+SiX₄)), for (a) SiF₄:GeH₄:H₂ and (b) SiH₄:GeH₄ (from ref. 21) mixtures.

The most striking result is that the deposition of a-SiGe alloys requires GeH₄ addition to SiF₄ about one order of magnitude lower than that to SiH₄. As an example, the deposition of a SiGe layer containing 25% of Ge and having an optical gap of 1.5 eV is performed with 1% of GeH₄ in fluorinated system against 10% in hydrogenated one. This phenomenon can be quantified by using the enrichment factor (E.F.) parameter (22), which is defined as the ratio between the content of Ge in the solid (x_{Ge}) and that in the gas phase (χ_{GeH_4}): $E.F. = x_{Ge}/\chi_{GeH_4}$. Typically, the E.F.(Ge) values are 25 and 2.5 for SiF₄ and SiH₄ systems, respectively. A further increase of E.F.(Ge) in fluorinated system can be achieved when the discharge is operated under modulation (MW) conditions (22), i.e. when the plasma is periodically switched on and off in the audiofrequency range. In particular, the E.F.(Ge) reaches values as high as 450 for 0.1% of GeH₄ added to SiF₄, by using as modulation parameters a period of 50 msec and a duty cycle of 15%.

The different behaviour of fluorinated and hydrogenated systems is also confirmed in silicon carbon alloys deposition. Figure 2(a-b) illustrates the dependence of the C content in SiC alloy on the methane amount in the gas feed for SiF₄:CH₄:H₂ and for SiH₄:CH₄ (23) mixtures. In addition, the trends of the deposition rate are reported. Also in this case, the amount of CH₄ added to SiF₄ is much lower than that required in SiH₄, thus the E.F.(C) in fluorinated system is higher than that in hydrogenated mixture. In

this last case, the values of E.F.(C) are less than unity, in contrast with the E.F. values obtained for all the other systems of Figs. 1, 2. This could be related to CH_x radical density lower than that of SiH_x ; this hypothesis is substantiated by the findings of Catherine et al. (24), who found a dissociation rate of CH_4 one order of magnitude lower than that of SiH_4 . Results obtained at higher power (not reported in Fig. 2b) show an E.F.(C) still behind unity, although the difference in the dissociation degree of CH_4 and SiH_4 is reducing (25). In contrast, the E.F.(C) > 1 found in fluorinated mixtures (Fig. 2a) suggests a CH_4 discharge decomposition more effective than that of SiF_4 . As for the data of Fig. 1, E.F.(Ge) > 1 is ascribable to the easier decomposition of GeH_4 with respect to SiH_4 and, much more, with respect to SiF_4 .

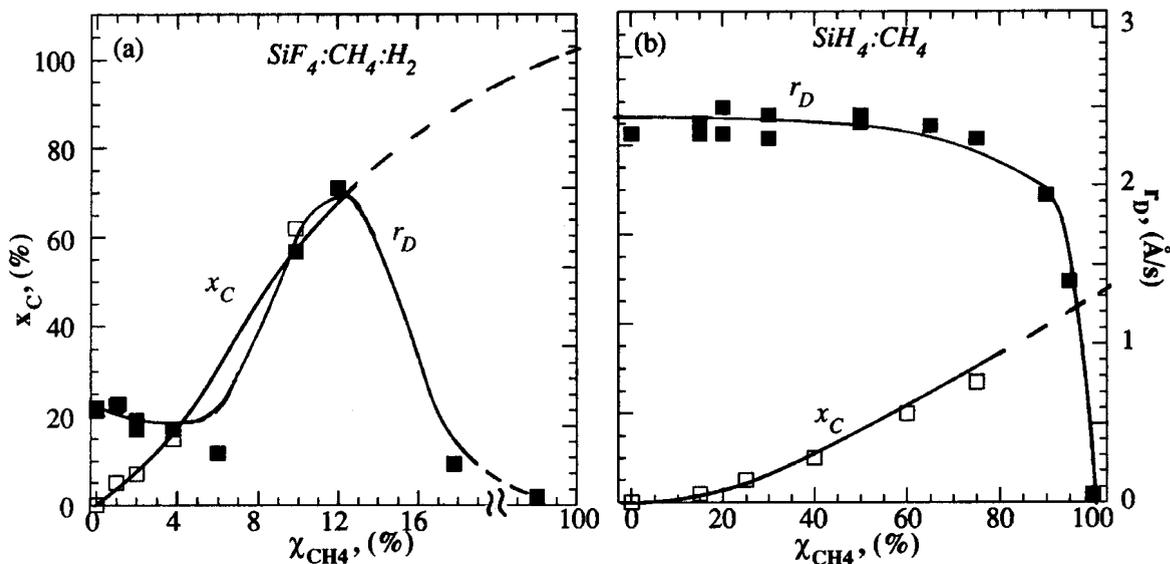


Fig. 2(a-b). Carbon content x_C ($\text{C}/(\text{C}+\text{Si})$) and deposition rate r_D vs gas compositional ratio, χ_{CH_4} ($\text{CH}_4/(\text{CH}_4+\text{SiX}_4)$), for (a) $\text{SiF}_4:\text{CH}_4:\text{H}_2$ and (b) $\text{SiH}_4:\text{CH}_4$ (from ref. 23) mixtures.

However, it is opinion of the present authors that the different precursors reactivity is not sufficient to explain the large incorporation of Ge in the material deposited from the fluorinated system with respect to that found starting from hydrogenated mixture. In fact, it is well known that the deposition process involves, besides reactions occurring in the plasma phase, also plasma-surface interactions in which chemisorption plays a relevant role. A chemisorption of GeH_4 more efficient than that of SiF_4 has been invoked by us to explain the strong Ge enrichment in fluorinated systems. To a lower extent, a similar competition accounts for the results in completely hydrogenated systems (Fig. 1b).

The chemisorption based deposition model (26-28) has been demonstrated by studying the dopant effect on the deposition rate in halogenated (SiF_4 , SiCl_4) and hydrogenated (SiH_4) systems. An opposite behaviour of the deposition rate has been found, depending on the presence of n- or p-type dopant, being chemisorption a process strongly affected by the electronic character of the semiconductor surface. In particular, when halogenated silicon compounds are used as reactants (27, 29) it has been found that the film deposition rate, r_D , increases with PH_3 and decreases with B_2H_6 addition. On the contrary, the addition of dopants to SiH_4 exhibits an opposite behaviour: r_D increases with B_2H_6 and slightly decreases with PH_3 addition (30). This apparent discrepancy can be accounted for by referring to the chemisorption model on a semiconductor surface according to the boundary-layer theory (31). In conformity with this theory, the chemisorption of halogenated compounds (SiF_4) is promoted by the presence of n-doped surfaces, which transfer an electron from their donor levels to the adsorbed molecule, so becoming an anion, referred to as "anionic chemisorption". In contrast, in the presence of hydrogenated reactants (SiH_4 , GeH_4), the chemisorption process is favoured by the presence of p-doped surfaces, receiving in their acceptor levels an electron from the adsorbed molecule, which transforms to a correspondent cation and is known as "cationic chemisorption" (32). The different behaviour of halogenated and hydrogenated precursors with respect to chemisorption on doped substrates has been confirmed in a study on the doping effect in the deposition of SiGe alloys from $\text{SiF}_4:\text{GeH}_4$ mixtures (33) as illustrated in Fig. 3. The partial Si and Ge deposition rates (r_{Si} , r_{Ge}) have opposite trends and are those expected according to the above mentioned model, coming Si from halogenated (SiF_4) and Ge from hydrogenated (GeH_4) compounds. Once again, there is clear evidence that hydrogenated species (GeH_4 like SiH_4) preferentially chemisorb on p-type materials, while halogenated species (SiF_4) on n-type materials.

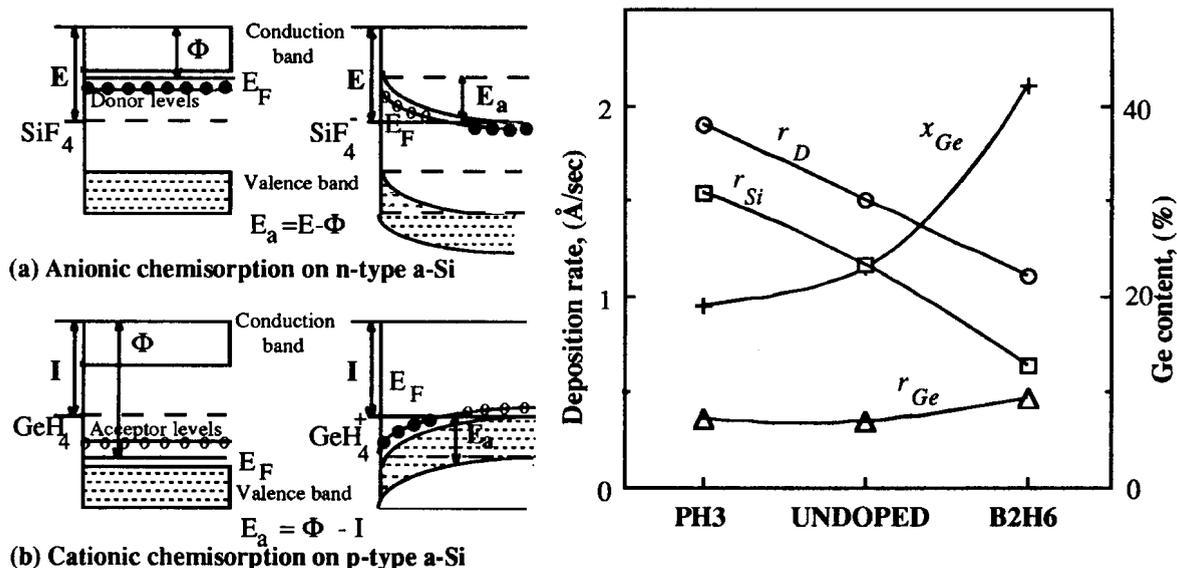


Fig. 3. Energy band structure and band bending at the surfaces of a n- and p-doped a-SiGe:H,F film in the case of SiF_4 anionic chemisorption (a) and GeH_4 cationic chemisorption (b), respectively. Total deposition rate (r_D), Si and Ge partial deposition rate (r_{Si} , r_{Ge}), and Ge content (x_{Ge}) for undoped and doped a-SiGe:H,F films from SiF_4 - GeH_4 - H_2 plasmas.

The presence of catalytic effect of the dopant on the growth kinetics and on the material composition in the deposition of silicon and silicon carbon alloys has also been evidenced by other authors (34-36). Specifically, they observed an increase of deposition rate and of SiH_2 content in the material by adding diborane to SiH_4 , and an increase of C content when B_2H_6 was added to SiH_4 : CH_4 mixture. The common explanation was based on the existence of a sort of boron surface complex, which easily desorbs with two H atoms and leaves two dangling bonds on the surface; this causes an increment in the sticking coefficient of SiH_3 radical, considered by the authors the dominant growth precursors. It is evident that the above phenomena, and in particular the higher E.F.(C) in presence of diborane, can be simply explained by a more efficient chemisorption on p-doped surface of hydrogenated precursors, with preference for CH_4 . Thus, the chemisorption of reactants on the growing surface can be invoked to explain the strong difference in E.F.(C) going from SiF_4 : CH_4 : H_2 to SiH_4 : CH_4 system: CH_4 is adsorbed much more than SiF_4 and less than SiH_4 .

In addition, the fact that the chemisorption on a semiconductor surface is reported to be increasingly hindered by increasing its gap value (37) accounts for the sharp decreases of the deposition rate (see Fig. 2(a-b)), for C content values as high as 60%, corresponding to a gap value of about 2.6 eV. In contrast, the decreasing gap value in SiGe alloys with Ge incorporation could justify a more effective chemisorption and, hence, the increasing trends of deposition rate of Fig. 1(a-b). All these findings suggest that, in addition to the activation of the reactants occurring in the plasma phase, the competitive chemisorption of the reactants on the growing surface strongly influences the surface coverage and then the material composition.

AMORPHOUS SILICON-NITROGEN ALLOYS (a-SiN:H,F).

For an insulator alloy like silicon nitride it is difficult to refer to a chemisorption-based deposition mechanism, due to its high energy gap value. It can be presumed that, for this type of material, the activation of the growth precursors in the plasma phase and the direct interaction of all the active species with the surface will play the most relevant role in the deposition kinetics. Silicon nitride films produced by PECVD are not stoichiometric and are described usually by the general formula $\text{a-Si}_x\text{N}_y\text{H}_z$. According to y/x values, the silicon nitride can be a quasi-stoichiometric ($y/x = 1.3$), silicon-rich ($y/x < 1.3$) and nitrogen-rich ($y/x > 1.3$) alloy. The best material quality is obtained from quasi-stoichiometric composition and low H content. However, some authors (38, 39) have reported that an enrichment in nitrogen content and a shift of H bond from Si-H to N-H are favourable.

The actual efforts in the production of SiN thin films have been directed towards the development of materials exhibiting high dielectric constant, low hydrogen concentration, low leakage current, high

breakdown strength and low interface trap density. When silicon nitride films are used as encapsulation layers for III-V compounds (GaAs, InP) or in Metal-Oxide-Semiconductor devices, they require low plasma bombardment, low deposition temperature ($< 300\text{ }^{\circ}\text{C}$) and low H-content, in order to achieve a good electrical semiconductor/ Si_3N_4 interface. These requirements can be reached by substituting the conventional PECVD process with some modified systems or by replacing the classical feed gas mixture of SiH_4 and NH_3 . The modified techniques investigated are: Remote Plasma Enhanced Chemical Vapor Deposition (RPECVD), Electron Cyclotron Resonance Plasma CVD (ECR-PCVD), Multipolar Plasma CVD (MPCVD), Photo-CVD and Plasma Enhanced Evaporation (PEE).

The choice of the alternative gas mixtures must be aimed at a material with low etching rate, high density and with H content sufficiently low to reduce its diffusion in the network, in order to achieve high stability and low degradation of the final devices. It has been found that the substitution of NH_3 with N_2 , although results in a strong decrease in the H content of the material, it also decreases the deposition rate and deteriorates the nitride electrical properties (40). The dilution of $\text{SiH}_4:\text{N}_2$ in He (41) produces silicon nitride which exhibits physical and electrical properties similar to high quality films prepared at $700\text{ }^{\circ}\text{C}$ by LPCVD, and a H content lower than in absence of He. The He-dilution causes the reduction of the SiH_x species, and hence inhibits the formation of polymeric silicon species in the gas phase. He-dilution also causes an increase in the incorporation of N, reaching a quasi-stoichiometric nitride, because the He metastable species can increase, through collisional energy transfer, the density of excited molecular nitrogen and also the amount of N-H bonds in the structure.

The H content in the silicon nitride alloys can also be reduced by utilizing fluorinated gaseous mixtures from $\text{SiH}_4:\text{NH}_3:\text{NF}_3$ (42), $\text{SiH}_4:\text{N}_2:\text{NF}_3$ (19), $\text{SiH}_2\text{F}_2:\text{NH}_3$ (43) and $\text{SiF}_4(\text{SiF}_2):\text{N}_2:\text{H}_2$ (17, 18) giving materials in which H is replaced by F atoms. The fluorinated films have been found to exhibit higher resistivity ($10^{14}\text{-}10^{16}\text{ }\Omega\cdot\text{cm}$), higher breakdown strength (10 MV/cm), and lower trap density (18) than samples without fluorine, in a wide range of y/x ratio (0.6-1.3). Cicala et al. (17) have prepared stable and quasi-stoichiometric fluorinated silicon nitride with a threshold value of incorporated F $\leq 20\text{ at.}\%$ from $\text{SiF}_4:\text{N}_2:\text{H}_2$ mixtures under H_2 -rich conditions. In fact, among the various gas mixtures utilized and shown in the ternary diagram of Fig. 4, H_2 -rich feeds have produced samples with good quality

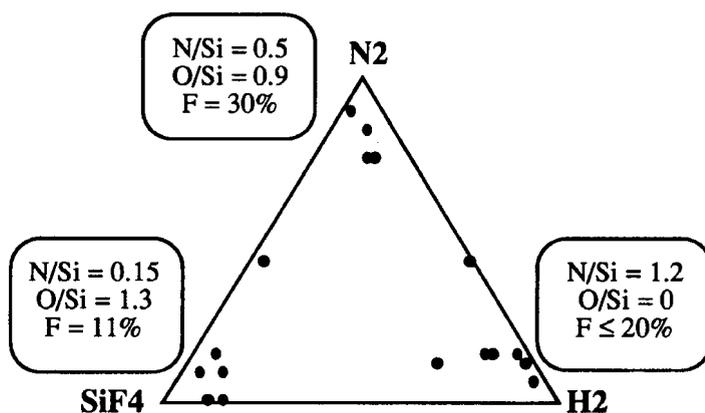


Fig. 4. $\text{SiF}_4:\text{N}_2:\text{H}_2$ ternary diagram showing the various gas feed mixtures used for the deposition experiments. Chemical composition data refer to typical films deposited from SiF_4 , N_2 and H_2 rich mixtures ($p = 1\text{ Torr}$, $W = 50\text{ watt}$, $T_D = 300\text{ }^{\circ}\text{C}$).

characteristics. However, the deposition rate values ($24\text{-}72\text{ \AA}/\text{min}$) are very low in comparison to those ($500\text{-}1500\text{ \AA}/\text{min}$) obtained from $\text{SiH}_4:\text{NF}_3:\text{N}_2$ mixture (19). This suggests that NF_3 produces nitriding species more efficiently than other nitrogen sources such as NH_3 or N_2 for the obvious great difference in dissociation energy ($\text{NF}_2\text{-F}=57$; $\text{NH}_2\text{-H}=104$, $\text{N}_2= 226\text{ Kcal/mole}$). In $\text{SiF}_4:\text{N}_2:\text{H}_2$ system, crossed species derived by intercombination reaction between N_2 and SiF_4 are absent, similarly to the $\text{SiH}_4:\text{N}_2$ system where the deposition process is due to a direct surface reaction of SiH_x species and N atoms (44). The crossed products become important in $\text{SiH}_4:\text{NH}_3$, where the triaminosilane radical $\text{SiH}(\text{NH}_2)_3$ is considered a key growth precursor in PECVD, as revealed unambiguously by a triple quadrupole mass spectrometer by D.L. Smith (45) and in Photo-CVD by D.B. Beach et al. (46). Once adsorbed on the surface, $\text{SiH}(\text{NH}_2)_3$ decomposes thermally by condensing to Si_3N_4 with evolution of NH_3 and H_2 .

ROLE OF FLUORINE IN AMORPHOUS SILICON DEPOSITION

The interest of fluorinated gases dates back to the pioneering investigation of A. Madan *et al.* (47) on the properties of a-SiH_xF film and to W. Paul's speculation (48) that F might be a better bond terminator in the alloys than unalloyed Si. Concerning silicon based materials from fluorinated gases, there is a controversy as to whether F plays a key role either in the "deposition process" or as a "chemical constituent" of the film (49) and as for whether F incorporation causes improvement or degradation in the material quality. There are many different hypotheses:

- 1) Oda *et al.* (50) believe that the possible role of F in the film is as a dangling bond terminator and/or a strain reliever.
- 2) Slobodin *et al.* (12) assert that F may play an indirect role in producing material with better microstructure, since in plasma phase the fluorinated gases have fewer polymerization reactions than hydrogenated ones.
- 3) Mackenzie *et al.* (3) say that the reduced heterostructure in a-SiGe:H_xF from SiF₄:GeF₄:H₂ is due to the role of F in the plasma. In fact, the substitution of H with F cannot be responsible for the improved photoresponse, since only 1% of F is incorporated in the film. Thus, the cause of the improved photoresponse must be found in the different microstructure between hydrogenated and fluorinated materials.
- 4) Chang *et al.* (19) and A.A. Langford *et al.* (51) believe that the F content in the silicon based alloys is critical: high concentrations induce hydrolysis and oxidation, and degrade the optoelectronic properties.
- 5) Bruno *et al.* (28) regard F as etchant; the net deposition rate of a-Si:H_xF films grown from SiF₄ and H₂ mixture is determined by a balance between deposition and etching processes. The distinguishing feature of fluorinated gases with respect to hydrogenated one is therefore the concomitant existence of etching and deposition processes. The efficient etchant activity of F removes the weakly bonded Si atoms and controls the structure of the resultant film, with a F content in the network not exceeding 1% at.. A similar etchant role can be played by H atoms in highly diluted hydrogenated systems or in hydrogen radical assisted CVD (HR-CVD) technique, where the role of H atoms is combined with F atoms.

The drastic improvement of photoelectric and physical properties of silicon based alloys (e.g. SiC, SiGe, SiN) using H₂-dilution technique or fluoro-containing gases is principally due to the similar role played by fluorine and hydrogen atoms during the growth at the plasma-surface interface: they cause material densification. And also, the F is able to control the H content (7% at.) in the film during the growth.

When the F content is less than 1% at., the material modifications are attributed to the effect of F on the growth process. Firstly, the low F content in the material could be principally due to the elimination of fluorine through a release of HF, in processes like:



occurring in the gas phase and/or on the surface. Secondly, the balance of these reactions and the deposition/etching competition determine the amorphous/microcrystalline structure of the material, which has been reported (52) as fluorine-enhanced crystallization effect.

With increasing fluorine content, c_F , the material properties get worse and worse. In particular, fluorinated a-Si:H_xF, a-SiC:H_xF and a-SiGe:H_xF films with $c_F > 1\%$ at. exhibit:

- easy oxidation upon air exposure (17, 19);
- increased amount of SiH₂ groups, in the material (53) and
- decreased photoconductivity values (51).

In contrast, a-SiN:H_xF films become unstable when the fluorine content exceed 20% at. (see Fig. 4) (19).

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