POSITIVE AND NEGATIVE IONS IN SILANE PLASMAS

B. Drévillon, J. Huc, A. Lloret, J. Perrin, G. de Rosny and J.P.M. Schmitt
Laboratoires PNHE et PMI. Ecole Polytechnique
91128 PALAISEAU Cédex. France.

ABSTRACT

The mass spectrum of positive and negative ions was analysed in a multipole discharge in silane. Ion oligomerisation was found to favor negative ions, which were hydrogen depleted. In light of the various species density variations as functions of pressure and electron density, some mechanisms are proposed for the ion formation.

1. INTRODUCTION

Positive ion formation and subsequent ion-molecule reactions in silane have received a great deal of attention from basic chemists (1). Owing to a new trend in amorphous thin film synthesis, a growing interest in silane plasma physics has led several teams (2-5) to equip their plasma device with an ion extraction system and a mass spectrometer. The specific features of this experiment are low pressure operation (0.1 - 10 m Torr), allowing analysis of the first few steps in the reaction chain ; and the ability to extract negative ions. This paper reports a quantitative analysis of the primary reaction processes in the low pressure range (below 1 m Torr) and a qualitative analysis of the positive and negative ion spectra at higher pressures.

2. EXPERIMENTAL

The multipole device used for this work is a d.c., low pressure, magnetic confinement plasma source (6) in which the substrate and extracting electrode are symmetrical with respect to the plasma. Ions are extracted from the plasma through a 0.3 mm dia. extracting orifice in the end wall. This orifice is covered by a 200/inch copper grid whose aperture always remains much smaller than the Debye length, thus avoiding spurious lensing effects. This orifice leads to a differentially pumped section in which ions are accelerated by an einzel lens which images the beam on the entrance of a quadrupole mass spectrometer. Typical electrode potentials are shown in fig. 1. Negative ions were detected at the high voltage anode of the electron multiplier through a pulse isolation transformer and pulse counting circuitry. The plasma potential is always positive with respect to the wall, hence positive ions are naturally accelerated on to the walls and readily extracted. Near the substrate a negatively biased collector behind a 200/inch grid attracts positive ions and reflects fast electrons, giving access to the total ion flux to the walls. Negative ions (as well as slow electrons) are trapped in the plasma potential, their extraction thus requiring a strong negative bias (30-70V)

3. POSITIVE IONS

A typical silane plasma positive ion spectrum is shown in fig. 2. Such measurements, along with earlier work, (1-7) confirm the following observations :

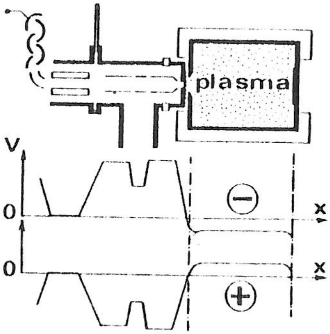

Fig. 1 : Experimental arrangement

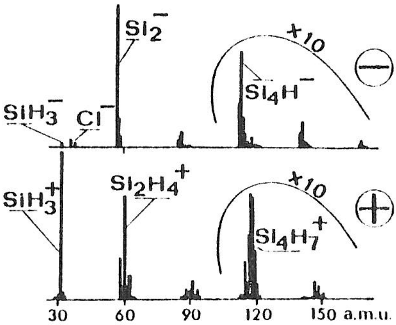

Fig. 2 : Typical positive and negative ion spectra obtained for a 60 V, 20 m A discharge in 5 mTorr of silane.

- the primary ionization fragment pattern (7) is observed only at low pressures (<0.5 m Torr)
- at higher pressures SiH_3^+ is the dominant ion. Depletion of SiH_2^+ is then partially due to the reaction (1-2) :

$$SiH_2^+ + SiH_4 \rightarrow SiH_3^+ + SiH_3$$

- finally, polymerization reactions are observed which sequentially produce oligomeric ions of increasing order for increasing pressure (2-5).

The variation of the oligomeric population for positive and negative ions is shown in fig. 3 as a function of pressure. It was found that the presence of hydrogen in the discharge perturbs certain reaction schemes. Hydrogen is always present in a silane plasma as a product of decomposition ; the faster the deposition rate and the smaller the flow rate, the larger is the hydrogen fraction in the gas. As one example of the role hydrogen plays, the ratio $[SiH_3^+]/[SiH_2^+]$ decreases appreciably as the H_2 partial pressure increases. Detailed analysis of this effect is being pursued, however, the following reaction scheme is offered as a possible primary process involving H_2 :

$$H_2^+ + SiH_4 \rightarrow SiH_2^+ + 2\ H_2$$

Hydrogen is also observed to inhibit ionic polymerization in silane. A possible interpretation relies on reactive dissociation of oligomeric ions which is being further studied.

4. NEGATIVE IONS

A typical negative ion spectrum is shown in fig. 2. The Cl^- ions were found to originate from chlorine impurity in the silane feed gas. SiH_3^- is the dominant monomeric ion. Si_2^- is the dominant dimeric ion. Oligomeric negative ions appear depleted in hydrogen. The total negative ion population is difficult to estimate, but careful Langmuir probe analyses indicate that their density is smaller than the electron density. At low electron densities, ion extraction is not perturbed by Debye screening, and the various ionic populations studied as functions of current I and silane pressure P are shown in fig. 4. The following functional dependences are observed :

$$[1] \qquad [SiH_3^-] \sim PI^2$$

$$[2] \qquad [Si_n^-] \sim P^{n+1}\ I, \ n = 2,3,4$$

Eq. [1] suggests for SiH_3^- formation a process via dissociative attachment of a slow secondary electron on a vibrationally excited SiH_4 molecule, as earlier demonstrated for H^- formation in H_2 (8-9) :

$$SiH_4 + e\ (fast) \rightarrow (SiH_4)^v + e$$

$$(SiH_4)^v + e(slow) \rightarrow SiH_3^- + H$$

The SiH_3^- subsequently reacts with silane leading to dimeric ions.
The detailed mechanism for Si_2^- formation is still to be elucidated, but eq.[2] reveals that several collisions with silane are required before hydrogen is totally detached from dimeric ions. Moreover, Si_2^- appears to be mainly destroyed either by electron impact or dissociative recombination with a positive ion. At a slower rate Si_2^- ions polymerize into longer chains.

As a consequence of their long lifetime in the plasma, oligomeric negative ions appear at lower pressures than the positive oligomeric ions (see fig.3). Indeed, the long negative ion lifetime may lead, at higher pressures, to an almost total thermal relaxation of negative ion clusters to their bare ionic states. As shown in fig. 5, under similar conditions, positive ions, whose

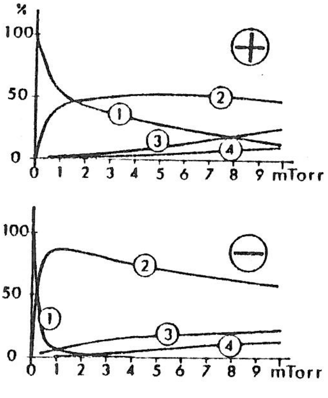

Fig. 3 : Relative variations of the various oligomeric ions classified according to their number of silicon atoms as a function of silane pressure in a 60 V-20 m A discharge.

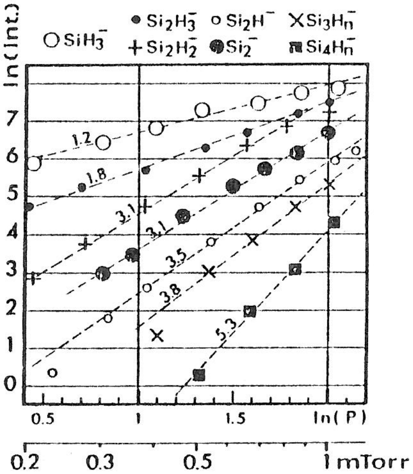

Fig. 4 Ionic current intensity as a function of pressure. The slope is shown on each straight lines on the log-log plot.

plasma lifetime is considerably shorter, retain more than half the possible hydrogen atoms.

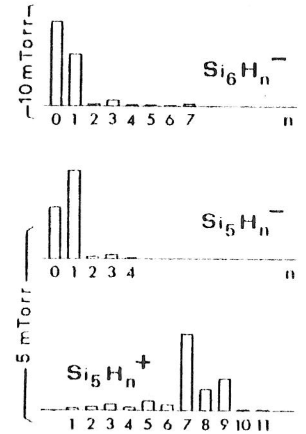

Fig. 5 : Large ion mass spectra after isotopic correction

5. CONCLUSIONS

Silane positive ion chemistry is now well studied. This work revealed that hydrogen may play an important role in silane discharges. Further study is needed to elaborate this role. A rich family of negative ions was observed in silane. Negative ion analysis is a useful tool for detection of impurity ions in silane discharges (such as the halogens). The primary hydro-silicon negative ion formation scheme seems elucidated but secondary processes remain to be clarified. In spite of the fundamental interest that these negative ions represent it should be stressed that they are present as a very small fraction in these discharges. Moreover, even at higher densities they remain trapped in the plasma, thus their influence on amorphous thin film deposition is at best indirect. Study of larger negative silicon clusters could aid microscopic analysis of nucleation ; in particular such clusters may well be percursors to powder formation which jeopardizes high deposition rates in silane devices.

REFERENCES

(1) F.W. LAMPE, "Ion-Molecule Reactions" Ed. by J.L. Frankin.London Butterworths p. 610 (1972)
J.M.S. HENIS, G.W. STEWARD and P.P. GASPAR , J. Chem. Phys. 58, 3639 (1973)

(2) G. TURBAN, Y. CATHERINE and B. GROLLEAU, Thin solids Films 60, 147 (1979) ; 67, 309 (1980) ; 77, 287 (1981).

(3) I. HALLER, App. Phys. Lett. 37, 282 (1980)

(4) H.A. WEAKLIEM, 13th A.I.A.A. Fluid and Plasma Dyn. Conf., July 1980

(5) G. TURBAN, A complete survey of the subject can be found in "Thèse d'Etat" Université de Nantes (France) 1981.

(6) B. DREVILLON, J. HUC, A. LLORET, J. PERRIN, G. DE ROSNY and J.P.M. SCHMITT Appl. Phys. Lett. 37, 646 (1980)

(7) P. POTZINGER and F. W. LAMPE, J. Phys. Chem. 73, 3912 (1969)

(8) M. BACAL and G.W. HAMILTON, Phys. Rev. Lett. 42, 1538 (1979)

(9) M. ALLAN and S.F. WONG, Phys. Rev. Lett. 41, 1791 (1978)