INFRARED DETECTION OF RADICALS PRODUCED IN A SILANE
DISCHARGE BY MATRIX ISOLATION TECHNIQUE

A. LLORET
Equipe du CNRS Synthèse de Couches Minces pour l'Energétique.
LPNHE, Ecole Polytechnique 91128, PALAISEAU, Cedex. FRANCE

L. ABOUAF-MARQUIN
Laboratoire de Photophysique Moléculaire du CNRS,
associé à l'Université de Paris-Sud.
Université de Paris-Sud 91405 ORSAY. FRANCE

ABSTRACT

Infrared absorption spectra of free radicals trapped in a solid Argon
matrix, after extraction from a low pressure silane hot cathode discharge,
have been clearly observed. First partial results concerning the assignments
of the detected absorption peaks and the energy dependence of neutral
fragmentation pattern of silane by electron impact are presented and
discussed. Matrix isolation technique appears to be a promising tool to
characterise neutral species in discharges devoted to thin film deposition.

1. INTRODUCTION

The study of plasma neutral fragments which is of great importance in
the research on the growth and properties of thin films, is one of the most
arduous in the plasma characterisation field. This is the case of the
hydrogenated amorphous silicon which presents recognized interesting
semiconducting properties. This material is normally deposited in silane
discharges in which free radicals rather than ions are known as being the
dominant species contributing in the film formation (1, 2). Free radicals
of silane plasmas have been studied by emission or absorption spectroscopy
in the UV–visible (3), and IR range (4), by using laser–induced fluorescence
(5), by mass spectrometry (6) and finally by using coherent anti-Stokes
Raman spectroscopy (7). All these techniques present intrinsic difficulties
and limitations. In an attempt to contribute to the study of the plasma free
radicals composition, neutral species reactivity and fragmentation pattern
by electron impact the matrix isolation technique associated with IR
absorption spectrometry is proposed. The analysis of primary processes
electron–molecule needs a very low pressure discharge as the one obtained by
the electrons emitted by a hot cathode and accelerated by a bias voltage
with respect to anodic walls.

The present results are preliminary and systematic measurements
remain to be done, however our data already illustrate the possibilities of
the technique.
2. EXPERIMENTAL

(a) The apparatus

A schematic diagram of the experimental set-up used to generate the plasma and to trap and study the molecular fragments is shown in Fig.1. The apparatus consists of a chamber for the discharge and a cryostat. Both chambers are interconnected by a molecular beam effusion hole and they are independently pumped by two diffusion pumps.

![Schematic Diagram](image)

1 - Filament  
2 - Effusion aperture  
3 - Ar inlet  
4 - CsBr cold window  
5 - Cold finger  
6 - Thermal screen  
7 - KBr window  
8 - IR Spectrometer axis

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**Figure 1 - SCHEMATIC DIAGRAM OF (A) THE PLASMA DEVICE AND (B) THE CRYOSTAT**

The plasma generator is a hot cathode discharge sustained at very low-pressure (0.1-10 mTorr) by thermoionic electrons from a tungsten filament. The energy of primary electrons is adjusted by biasing the filament with respect to the walls. The chamber is a 20mm diameter, 40mm long stainless steel cylinder closed by an end plate where a variable diameter effusion aperture is centered. The plasma chamber protrudes in the cryostat, the effusion orifice being at 30mm from the center of the CsBr cold window. The plasma chamber is insulated and can be biased with respect to the cryostat.

The fresh gases are provided by diffusion through the open end of the
chamber. The silane flow rate ($\sim 5$ sccm) ensures a constant composition despite the plasma consumption. The total pressure is measured by a capacitance manometer.

The cryogenic system is an "Air Liquide" cryostat with a liquid helium flow. The lowest temperature achieved here is 10.5 to 11 K. A carbon resistor, embedded in the CsBr window allows the measurement of the adjustable temperature. The infrared spectra are recorded with a Perkin Elmer 580 spectrophotometer. Typical resolution is $2\text{ cm}^{-1}$.

(b) Experimental conditions

The cold sample is obtained by the spray on technique (8). The gases effusing from the plasma are partially trapped onto the cold window. To ensure a higher dilution of the species, pure Ar is codeposited with an adjustable flow. The deposition is performed at 17K. At this temperature, the growing Ar polycristalline film is not too much optically diffusing and is rigid enough to ensure species isolation. A 1 mm thickness is the maximum allowing a correct spectroscopical signal/noise ratio. The migration of some species inside the matrix is favoured by an annealing at 30K.

In the present studies, a compromise to set reasonable optical density of radicals along with a not too high concentration is found with the following conditions:
- plasma gas: $0.2 \text{ mTorr SiH}_4 + 5 \text{ mTorr Ar}$
- diameter of effusing hole: $4\text{ mm}$
- total mole ratio $R = \text{Ar/SiH}_4 = 300$
- deposition time: 5 hours.

The relatively low pressure in the discharge ensures a monokinetic energy distribution for the active electrons. The energy defined by the discharge voltage was varied from 30 to 100 eV. Due to the low pressure secondary reactions involving radicals can be excluded, hence the present experiments are significant for the fragmentation pattern of silane by electron impact. In order to avoid radical formation within the matrix, due to positive ions bombardment, the plasma chamber was biased at $-20\text{V}$ with respect to the cryostat. A magnetic barrier in front of the cold window stopped electrons.

3. RESULTS

The main results of the present study are the observation of free radicals produced in the silane discharge and their intensity dependence on primary electron energy. The attention will not be focused on the assignment of absorption lines, for which more refined experiments are needed. In a previous study, D.E. Milligan and M.E. Jacox (9), by using vacuum UV photolysis of $\text{SiH}_4$ and $\text{Si}_2\text{H}_6$ in $\text{Ar}$ matrices, have tentatively assigned the observed spectra to $\text{SiH}_3$, $\text{SiH}_2^0$, and $\text{SiH}_3$ (Table I).

Fig. 2 shows typical spectra in the bending and sketching region. The spectra (a) correspond to a $\text{SiH}_4$ without plasma. The intense absorptions in the (920–900) cm$^{-1}$ and (2230–2190) cm$^{-1}$ range are due to silane. The lines centered at 836 cm$^{-1}$ and 940 cm$^{-1}$ are unambiguously assigned to $\text{Si}_2\text{H}_6$ contained in small proportion ($\sim 10^{-3}$) in the silane tank (Alphagaz).
Figure 2 - INFRARED ABSORPTION SPECTRA IN SOLID ARGON.
Mole ratio: \( R = \text{Ar/} \text{SiH}_4 = 300 \)

A: bending range.
B: stretching range.
a) 3 hours deposition at 17K without plasma.
b) 5 hours deposition at 17K with plasma (0.2 mTorr \text{SiH}_4 + 5 \text{ mTorr Ar}, 650 \text{ mA}, 80V)
c) same sample as b), after 30 min of annealing at 30K, then cooling to 11K.
Many new features, appearing when the discharge is on (spectra (b) in Fig. 2), are listed in Table I. The absorption at 2138 cm\(^{-1}\), attributed to CO, allows the wavenumber calibration (10).

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Table I – OBSERVED ABSORPTIONS LINES (cm\(^{-1}\))

In the bending range (spectrum (c) in Fig. 2), after annealing a peak is growing at 940 cm\(^{-1}\) from the large shoulder observed before, and a new line appears at 773 cm\(^{-1}\). These new features are probably due to the recombination of reactive species. It appears that the intensity of Si\(_2\)H\(_6\) (837 cm\(^{-1}\)) is not significantly increased by the annealing. This suggests that the growing line at 940 cm\(^{-1}\) can not be attributed to Si\(_2\)H\(_6\) only but also another hydrogenated Si dimer and/or trisilane, generated by the recombination of radicals. In the stretching range, the signal/noise ratio is low, however the absorption seems to decrease slightly after annealing. The free radicals intensities are dependent upon the plasma primary electron energy. This dependence is shown in Fig. 3 for four typical absorptions observed in identical conditions. It seems, within the measurement accuracy, that close to 60–80 eV, there is a maximum in the efficiency of producing these radicals. These results present a behaviour similar to the electron energy dependence of the silane dissociation cross section (11) as it would be expected from the ionic core model (5).

4. CONCLUSION

The preliminary results show the efficiency of the matrix isolation technique as a method of characterisation of radicals created in a low pressure discharge. More refined experiments are in progress to identify accurately the radicals and quantitative measurements of their intensity dependence with the parameters of the plasma.

ACKNOWLEDGMENT

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Figure 3 - ln $I_0/I$ VERSUS PRIMARY ELECTRON ENERGY. $I_0$ is the incident light intensity and I is the transmitted intensity at the maximum absorption.

- 1008 cm$^{-1}$ (SiH$_2$)
- 1972 cm$^{-1}$ (SiH)
- 2016 cm$^{-1}$ (SiH$_2$)
- 2029 cm$^{-1}$ (SiH$_2$)

REFERENCES

1 - G. TURBAN, Y. CATHERINE, B. GROLLEAU
2 - B. DREVillon, J. HUC, A. LLORET, G. de ROSNY and J.P.M. SCHMITT
3 - J. PERRIN and E. DELAFOSSE
   K. TASHIBANA, H. TADUKARO, H. HARIMA, Y. URANO
4 - J.C. KNIGHTS, J.P.M. SCHMITT, J. PERRIN, G. GUELACHVILI
5 - J.P.M. SCHMITT, P. GRESSIER, M. KRISHNAN, G. de ROSNY, J. PERRIN
6 - R. ROBERTSON, D. HILS, H. CHATHAM, A. GALLAGHER
7 - N. HATA, A. MATSUDA, K. TANAKA
8 - A.M. BASS and H.P. BROIDA
9 - D.E. MILLIGAN and M.E. JACOX
10 - H. DUBOST, L. ABOUAF-MARQUIN
11 - J. PERRIN, J.P.M. SCHMITT, G. de ROSNY, B. DREVillon, J. HUC, A. LLORET
    Chem. phys. 73, 383 (1982).