*31st EPS Conference on Plasma Phys. London, 28 June - 2 July 2004 ECA Vol.**28G**, O-1.09 (2004)*

Electrical Characterization of Dust Forming Plasma in Different Chemistries

A. Mezeghrane[2], M. Jouanny[1], M. Cavarroc[1], M. Mikikian[1], O. Lamrous[2] and L. Boufendi[1]

[1]*GREMI, Groupe de Recherches sur l'Energétique des Milieux Ionisés*
Université d'Orléans, 45067 Orléans Cedex 2, France
[2]*LPCQ, Université Mouloud Mammeri de Tizi Ouzou, Algérie*

Abstract. The aim of this paper is to present first results on dust forming radio-frequency low pressure plasma in different chemistries. They show that in the CH_4-N_2 plasma the particle growth mechanisms are close to those of silicon particles formed in silane plasmas. The growth phases are evidenced thanks to an electrical diagnostic based on the analysis of the time evolution of the discharge impedance.

1. INTRODUCTION

In the last decade, dusty plasmas, or as adopted now “complex plasmas”, study becomes a very active research field. This is mainly due to on one hand the need of control and removal of the formed particles in the plasma tools used in the microelectronic technologies [1], and on the other hand the connection with the astrophysical and environmental studies. Recently, it has been shown that nanocrystallites embedded in an amorphous matrix give very interesting optoelectronic properties to these thin layers. This opens the way to many potential applications such as polymorphous silicon based solar cells with high and stable efficiency [2]. The nanocrystallites in question here represent the earlier phase of the particle formation [3]. Their size has been measured using both transmission electron microscopy (TEM) and micro-Raman scattering and shown to be in the range of 2-3 nm. They can be used as quantum dots in a wide range of nanotechnology applications like new generation of microelectronic devices such as tera bit storage memories [4], single electronic transistors, cold electron emitters etc…

In this work we compare two plasma chemistries argon-silane and methane-nitrogen plasmas in terms of dust particle formation mechanisms. All these studies have been carried out in a reactor which has already been described in details elsewhere [5]. The 13.56 MHz radio-frequency (rf) discharge is produced in a grounded stainless steel cylindrical box of 130 mm inner diameter, equipped with a shower head type rf electrode. A grid of 20% transparency is used as its bottom to allow a laminar gas flow. The whole system is enclosed in a vacuum vessel of 300 mm inner diameter and equal height. Optical access to the plasma is possible through three vertical slits (2 mm x 40 mm) in the inner cylindrical box and three windows (Φ = 50 mm) on the vacuum vessel. Observation slits and windows are aligned and placed at 90° from each other.

2. IN-SITU PARTICLE DETECTION

The diagnostic used in this work has been developed in the GREMI laboratory. It is based on the modifications induced by the occurrence of the nanoparticles in the electrical characteristics of the discharge. Indeed, their presence affects the electrical conductivity of the plasma and therefore the amplitude of the discharge current is decreased. We used for this purpose the third harmonic (H3) and self-bias voltage V_{DC} to follow the dust particle formation. The different phases are well evidenced through the time evolution of the current signal.

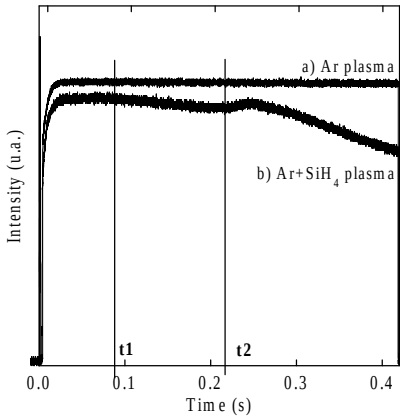

Fig. 1 : *Time evolution of the amplitude of the third harmonic for pure argon and silane-argon gas mixture discharges.*

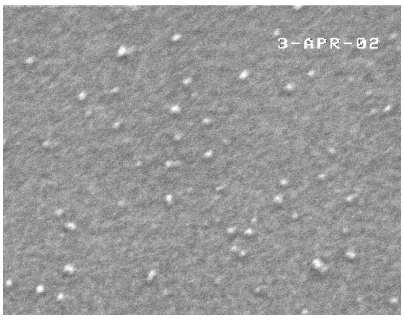

Fig. 2 : *SEM micrographe of a SiO2 substrate on which have been deposited silicon nanocrystallites*

Figure 1 gives an example of this evolution for silicon particles formed in SiH_4-Ar gas mixture plasma. The first phase of this curve (0 to t_2) represents the period during which the silicon nanocrystallites are formed and accumulated until their number density reaches a critical value of about 10^{11} cm^{-3}. At this concentration the nanocrystallites start to coagulate to form bigger dusts. After t_2 the drastic decrease of the current is mainly due to the electron attachment on the particles. In order to confirm this result we collected nanocrystallites on SiO_2 substrate. Figure 2 gives a scanning electron microscope (SEM) picture of these small entities. To collect these nanoparticles the plasma has been stopped before the beginning of the coalescence phase i.e. before t_2.

The carbon nitride chemistry is studied for two main interests. The first one is the simulation of the atmosphere of Titan, the satellite of Saturn that will be studied during the CASSINI mission. The second one is the synthesis of nanostructured thin layers of a-CN:H which are very interesting in terms of hardness and optoelectronic properties. Figure 3 shows the time evolution of both the third harmonics of the discharge current and the self-bias voltage V_{DC}. The growth kinetics is much slower when compared to the one in silane based plasmas. The peak appearing at the discharge ignition is related to the formation of the negative ions that

are the precursors of the dust formation as evidenced by the electron density n_e in figure 4. The insert in this last figure emphasizes its evolution during the first few hundreds ms of the plasma. The decrease of n_e corresponds to the formation of the first nucleus of the particle growth process. The comparison with the silane plasma shows that this phase corresponds to the formation of the nanocrystallites. During this phase the current evolves slowly (Fig.3) and then starts to decrease when the coalescence phase begins. We can see on Fig. 4 that during the formation of the nanocrystallites n_e has also a slow evolution and decreases at the same time as H3. The self-bias V_{DC} exhibits the same trends as H3.

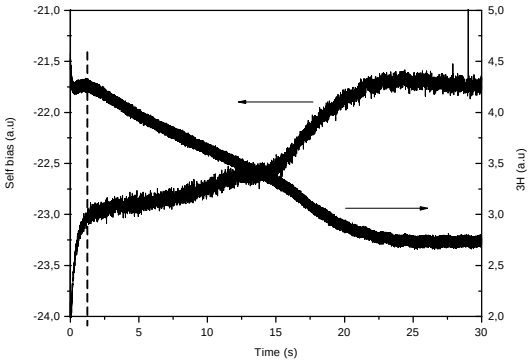

Fig. 3: *Time evolution of the H3 and* V_{DC} *during the dust particle formation.*

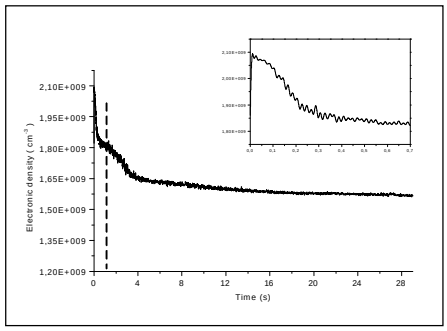

Fig.4: *Time evolution of the electron density during the dust particle formation.*

In order to confirm the formation of the nanocrystallites as in the case of silane plasmas, we grew up thin layers on silicon substrates and analyzed them thanks to FTIR spectroscopy. Figure 5 gives typical infra red absorption spectra of the obtained films for different experimental conditions where we mainly varied the ion bombardment. The presence of the embedded nanocrystallites in the layers is evidenced by the peaks at: 1012 and 1460 cm^{-1} for the α-C_3N_4 nanocrystallites and 852 and 1420 cm^{-1} for the β phase as predicted by theoretical calculations [6]. These observations clearly show that for the CH4-N2 plasmas the dust particle formation follows the same mechanisms as demonstrated for the silane based ones. It means that the negative ions are in this case also the first nucleus. The second phase corresponds to the chemical reactions of these ions with the other species to form the nanocrystallites that accumulate in the plasma glow. When their number density becomes important they start to coagulate to form big particles.

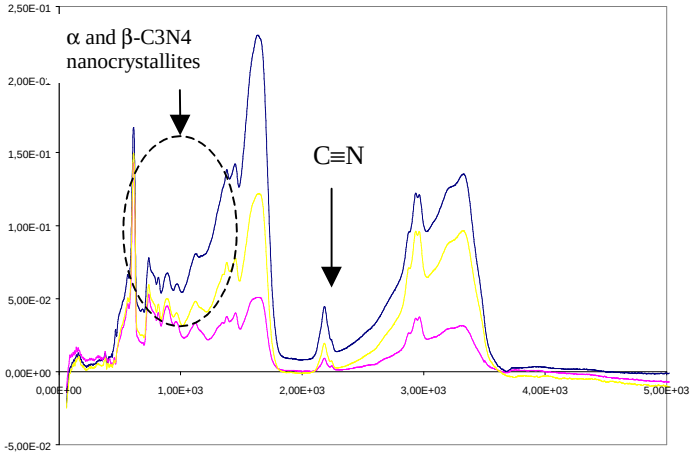

Fig. 5 : *FTIR absorption spectra of carbon nitride layers deposited on Si substrate.*

3. CONCLUSION

The objective of this paper is to demonstrate that the dust particle growth mechanisms in CH4-N2 plasma chemistry are the same as in a silane based one. This means that the first phase of this process is the formation of nanocrystallites that coagulate to form big particles. The nanocrystallites have been evidenced in the deposited thin layers through their infra red absorption spectroscopy analysis. The nanostructured material grown in this work looks like the polymorphous silicon used for higher and more stable efficiency solar cells.

AKNOWLEDGMENTS

The authors would like to express their thanks to Dr. Domingos DE SOUSA MENESES for his help with the FTIR measurements.

REFERENCES:

[1] G.S. Selwyn, J. Singh and R.S. Bennett, J. Vac. Sci. Technol. A7, 2758 (1989).

[2] P. R. i Cabarrocas, A. Fontcuberta, and Y. Poissant, Thin Solid Films, **403-404**, 39 (2002).

[3] L. Boufendi, J. Hermann, A. Bouchoule, B. Dubreuil, E. Stoffels, W.W. Stoffels, M.L. de Giorgi, J. Appl. Phys. **76** (1994) 148-153.

[4] T. Baron et al, Applied Surface Science **164**, 29-34 (2000)

[5] L. Boufendi, A. Plain, J. Ph. Blondeau, A. Bouchoule, C. Laure, M. Toogood, *Appl. Phys. Lett.*, **60,** 169 (1992)

[6] N. Wada, S.A. Solin, J. Wong and S. Prochazka, J. Non-Crystal. Solids 43, 7 (1981)