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Formation of dense submicronic clouds in low pressure Ar–SiH_4 RF reactor: Diagnostics and growth processes from monomers to large size particulates

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ABSTRACT

The formation of solid particles in the gas phase is a general problem for PECVD technology when looking at high deposition rates of good quality layers. The present paper report an overview on particle growth and associated plasma phenomena in a specific situation: Argon-Silane RF low pressure discharge.The diagnostics developped for this study include laser multi-angle Mie scattering for particle diameter above 35 nm and excimer induced light emission for nm scale particles. The evolution of the free electron concentration is obtained by microwave diagnostics and electron energy is deduced from OES data. In-situ FTIR absorption spectroscopy add insigths on the gas phase chemistry. Four successive steps are evidenced in the story of particle formation: clusterring of negative ions, formation of dense clouds of nm size crystallites, coalescence to few tens nm diameter particulates and a final growth by deposition of a-Si:H on the particles negatively charged and trapped in the discharge. The gas temperature appears as a sensitive parameter for the initial step of crystallites formation and a drastic transition of plasma properties occurs during the coalescence step of dust formation.

INTRODUCTION

The formation of particulates in low pressure discharges has been evidenced during the last years in a very wide range of physical and chemical plasma conditions including for example etching reactors (1,2), or metal sputtering Argon discharges (3). Their electrostatic trapping in the plasma allows negatively charged clusters to grow up to macroscopic sizes, even when slow growth kinetics are involved.

In some situations these clusters are injected by the walls through sputtering (3) or stress-induced flackering phenomena (4). Homogeneous gas phase clustering is the alternative way to lead to a dusty plasma, as in PECVD plasmas (5,6,7,8,9). Recent insights on the mechanism of growth of particles in silane plasma chemistry have been acquired in a join European program with Ecole Polytechnique (J. PERRIN), Ecole Polytechnique Fédérale de Lausanne (Ch. HOLLENSTEIN), Eindhoven University of Technology (G. KROESEN), Orléans University (L. BOUFENDI).

Our experimental study has been achieved in an RF 13.56 MHz parallel plate plasma reactor where we tried to control as far as possible all the growth parameters and previous results obtained on the particle growth kinetics (5), the dusty discharge properties (6) or the coulombian liquid behavior of the dust cloud (7) have been already reported.

A short description of the experimental conditions and of the diagnostics is the introductory part of the paper. The time evolution from the discharge onset for both particle growth and plasma parameters is reported in the second part. The third part concerns an overall discussion of the results in terms of particle growth mechanisms and modelling.

I : EXPERIMENTAL PARAMETERS AND DIAGNOSTICS

I 1 / The plasma reactor and the experimental parameters

Quantitative data for particle growth kinetics are known as closely connected to the precise plasma reactor operating conditions. Our data concern a 13.56 MHz RF discharge confined in a grounded cylindrical stainless steel box, 13 cm diameter. A shower type gas feeding and RF electrode is connected to a standard matching box. Facing the RF electrode, 3.5 cm below, the bottom of the grounded box is a grid with 50% transparency and the gas flow in the reactor is laminar with a vertical velocity near 0.2 m/s. This discharge box can be vertically translated in a stainless steel vacuum vessel (30 cm height, 30 cm diameter). The pumping lateral hole of the vacuum vessel is connected in normal operating conditions to a chemical type primary pump or to a secondary vacuum pump allowing a base pressure below 4 10^{-4} Pa between experimental runs.

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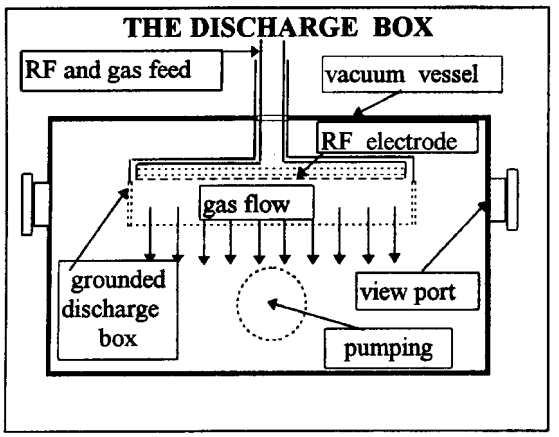


Fig. 1

-Three vertical slits (2mm wide and 90 ° apart) are used for OES and laser scattering studies.

- The whole discharge box is surrounded by an oven, the heating of which is automatically driven in order to obtain a given gas temperature at the exit of the discharge box.

- Typical gas flows are 30 sccm Ar and few sccm SiH4 with an overall pressure of 15 Pascals
- Typical RF power is 3-10 W

I 2 / Diagnostics

The free electron concentration is determined by using the whole plasma box as a resonant microwave cavity. The plasma -induced shift of its resonance frequency gives in a straightforward way the free electron concentration. The electron energy is deduced from quantitative measurements of Argon spectral lines intensities.
In-situ laser diagnostics of particles have been developped in two ways.
- The first is a DC laser scattering by using Ar^+ laser 514 nm line. During the growth of the particles the Rayleigh-Mie scattering is evidenced by comparisons of 90° and 6° scattered intensities. In order to obtain simultaneous determinations of particle diameter and concentration a multi-angle (81, 90, 99°) scattering technique has been developped. The Mie scattering for monosized spherical particles is used to deduce from the scattered intensities the optical index, the size and the concentration of the particles in the reactor.
- The second is the light induced emission of particles under the illumination of an XeCl excimer laser pulse (10 ns, 400 MW/cm^2) in the center of the discharge. This method is evidenced (8) as a powerful one to reveal the early step of particle formation in their nm size range.
With the collaboration of G. KROESEN (Eidhoven) useful data on plasma chemistry are obtained through in-situ IR absorption diagnostic using an FTIR light beam probing in a single path way the discharge box. Time resolved spectra are recorded as function of the plasma duration. Repetitive experiments (10-100) are used to achieve the required signal to noise ratio on the absorption spectra, as allowed by the high reproducibility of our experiment.

II EXPERIMENTAL RESULTS

II 1 / PARTICLE GROWTH KINETICS

II 1 1 / The early step of formation

The figure 2 represents the time evolution of the light pulse (white broad spectrum) emitted by the center of the discharge under excimer laser illumination (LIPEE signal).

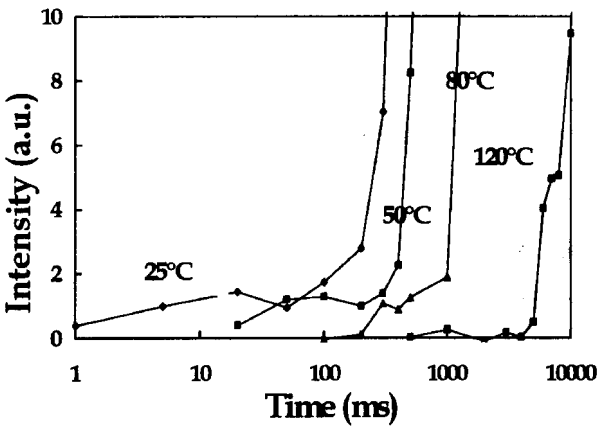


Fig. 2: LIPEE signal
Silane flow: 1.2 sccm, RF 600 Vp-p

- TEM data show that 1s plasma duration is required to grow particles up to 10 nm diameter. These LIPEE data show that the initial values of LIPEE signal are related to the early step of crystallites formation and the very fast increase indicates the start of their coalescence .
- A time delay when the gas temperature increased was observed observed previously by laser scattering, ie large size particles formation. This time delay is here clearly connected to the time required for the formation of the initial nm size crystallites

II 1 2 / Growth from 5 nm to 100 nm diameter

The size kinetics have been obtained in two ways: ex-situ TEM measurements of sizes for given plasma durations (fig 3 a) and in-situ laser scattering (multi-angle and two othogonal light beam polarizations , fig 3 b)
The plasma parameters (a , b) are the same : 30 sccm Ar,.2 sccm Silane, 600 Vp-p RF, 25 °C

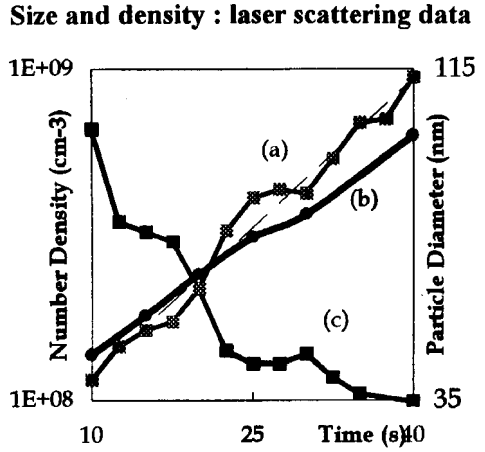


Fig. 3 b : DC laser scattering data
a: size as determined from laser scattering
b: size as measured by TEM
c: concentration determined from laser scattering

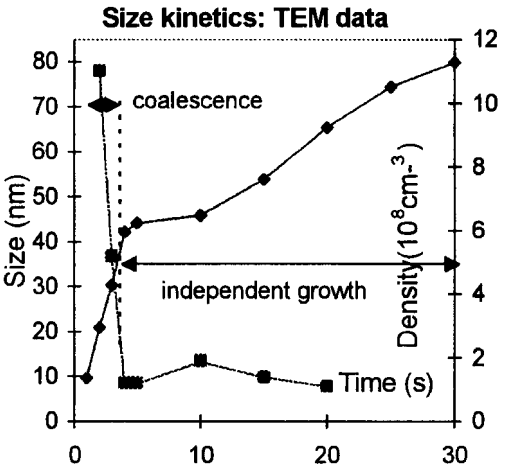


Fig 3 a : TEM data
a : very fast initial increase of particle size
b : Concentrations are deduced from scattered intensity, using the diameters determined by TEM

The size determinations (fig 3b) obtained in-situ by the multi-angle laser scattering method are restricted to large particle diameters. Results are in good agreement with previous data obtained by TEM. The laser scattering data are obtained on the discharge axis and the observation of a decrease of particle concentration between 10 and 40 s is related to the observed slowly varying radial distribution of the particle cloud.

II 2 / Free electron concentration evolution

The free electron concentration evolution, as determined by the microwave method, has been studied in the same conditions as the previous LIPEE study of the initial step of particles formation. The figure 4 gives an example of the results obtained for a gas temperature of 25 °C.

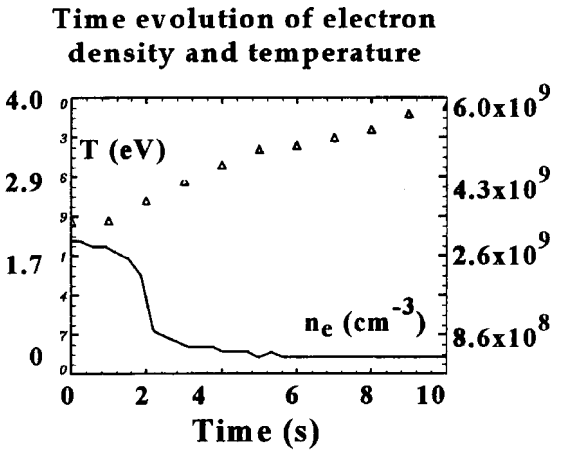


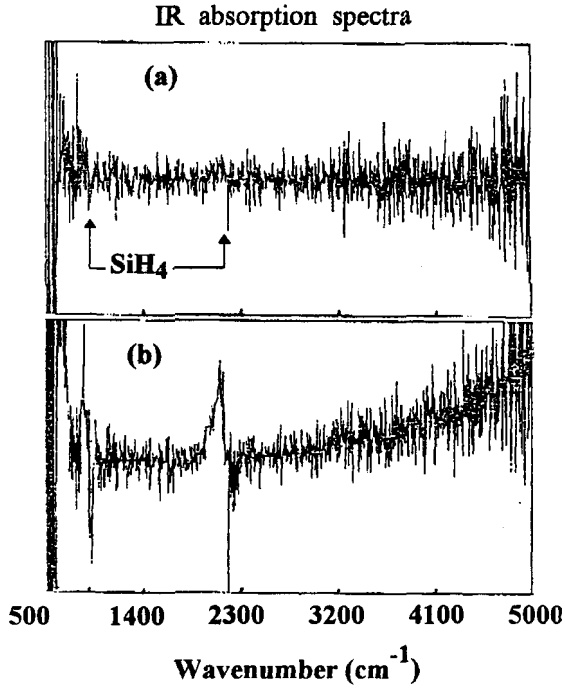
Fig. 4 : Microwave and OES data

A drastic modification occurs here at time close to 2 s. Same behaviors are observed at later times for higher gas temperatures, as for LIPEE signal. These jumps in electron concentration are related to the so-called α-γ' transition as described by JP BOEUF(14) and J. PERRIN (15). As the ion current collected on negatively biased probe shows only a small increase in this transition the jump of the electron density is connected to an increase of the negative charge density attached on the particles.
Absolute measurements of the emissivity of Ar lines intensities are used for electron temperature temperature determination. The increase of plasma emission show that free electrons become much more energetic.

II 3 / FTIR absorption data

A preliminary experiment on time resolved IR absorption spectroscopy showed clearly a sensitive evolution of the silane dissociation as function of time during the particle growth . In-situ absorption spectra of the particles material have also been evidenced in the final step of growth with the same FTIR system.

Fig. 5 FTIR absorption data
These spectra represent ratios of absorptions measured with plasma ON to the reference, plasma-OFF, spectrum
conditions 1.2 sccmSiH4, 25°C, 6OOV pp.
a : plasma duration 1 sec b: 20 sec
The silane bands at around 900 and 2200 cm^{-1} are evidenced by intense negative peaks for 20 sec plasma duration. In agreement with previous measurements (mass spectrometry) the silane dissociation is at least 80% for these plasma durations. For short times (fig. a) the silane dissociation is much less effective and at most 30%. . The plasma transition due to dust formation is shown to be very effective in terms of enhancement of the silane dissociation, leading to high growth rate values of the particle diameter by radicals sticking on their surfaces. An apparent absorption continuum, increasing with the wave number, is also clearly evidenced on the spectrum b. That is the result of a Rayleigh scattering of the IR light beam (cloud of 65 nm diameter particles)



III DISCUSSION

The above data concern only particles already grown to nm size. A dark field analysis of the particles collected on TEM microscope grids particles (40 nm diameter) reveals that rather well defined 2nm size Si crystallites represent the elementary stucture of these particles. These particles are formed in the fast coalescence step of growth and that means that these crystallites must be the initial entities leading to this coalescence step. The LIPEE signal (fig 2) reaveals the presence of these entities and is rapidly enhanced when their coalescence starts.

The ways to grow such nm scale entities in Silane plasmas are suggested as open by neutral (11) or ionic paths (12) involving collisions of clusters with Silane and Silane radicals. In our plasma situation the negative ion path is clearly implied: recent results (9) of mass spectrometry of neutral, positive and negative Si_nH_p systems in a similar low pressure RF reactor demonstrate negative ion clustering (up to 1000 amu). A low content of hydrogen has been evidenced for these ion clusters trapped in the plasma. That seems to be also a peculiarity of the crystallites as deduced from electron diffraction patterns measured on 40 nm diameter particles.

The LIPEE data at several temperatures suggest that the concentration of these crystallites has to reach a critical value for which a coalescence process is induced. If we assume that in the fast coalescence process the total condensed mass is conserved the concentration of crystallites at the beginning of the coalescence can be deduced from the measured sizes and concentrations at the end of the process. Taking into account these values this critical concentration is of the order of 10^{11} cm^{-3} . The above hypothesis remains valid as soon as we can neglect the formation of new crystallites when the coalescence starts. That is probably not a too crude approximation: the already formed particles when the coagulation starts are very efficient traps blocking the formation of new chains leading to new crystallites. In any case, the critical concentration of crystallites cannot be much less than the above value.

The overall plasma neutrality must be realized at any time. The data on free electron concentration ($3\ 10^9$ cm^{-3}) and positive ions ($6\ 10^9$ cm^{-3}) when the coalescence starts show that the mean charge of these crystallites is of the order of 0.03 electron. The characteristic time for neutralization of a negatively charged crystallite by collision of a positive ion Ar^+ is estimated with a ion-ion reaction rate of the order of 10^{-7} cm^3 s^{-1} and is of the order of 1.5 ms. That means that the characteristic time required for a neutral crystallite to be negatively charged by electron impact is larger than 50 ms, value deduced from the particle mean charge.

The trapping of crystallites in the discharge requires that the elapsed time between successive attachment events has to be less than the dwell time of the neutral crystallites in the discharge volume(13). The dwell time is of the order of 150 ms in our reactor and the condition for crystallites trapping is that the characteristic time constant for electron attachment has to be less than this dwell time value. That is consistent with the above evaluation.

The coagulation step cannot be described by neutral-neutral collisions. The thermal energy of the crystallites is assumed to be the thermal energy of the gas and the collisionnal cross-section is given by the geometrical value. The calculated collision time is 0.09 s for crystallites concentrations of the order of 10^{11} cm^{-3}. These values cannot explain the initial rate of coagulation (10 nm diameter at 1s). That means that the charging effects, even when they exist on a limited fraction of time, could play a major role in this coagulation step.

This coalescence step is stopped when the particle sizes is of the order of 40-50 nm after which the particle concentration remains almost constant. The mean electrostatic charge on the particles becomes high enough leading to a permanently repulsive particle-particle interaction.
Further growth of the particles is achieved by a surface deposition process leading to a-Si:H layers of growing thickness. The deposition rate is evaluated from the size measurement data to 1.25 nm s^{-1} This value is high but consistent with the almost complete dissociation of SiH_4 measured by FTIR in this dusty situation.
To summarize, the formation of particles is achieved in four successive steps: .(1)growth of negative ions electrostatically trapped in the discharge, (2)accumulation of nm scale crystallites trapped by transient charging effects (3)coagulation step when the concentration of these small entities reach a critical value (4) stop of the coalescence by electrostatic charging effect and further growth by surface deposition on independently growing particles.
A model of the particle formation, initiated by R. K. PORTEUS , has been tested in our plasma conditions.
- The particles are considered as distributed in 128 boxes. The first 16 boxes represent 1 to 16 Silicon-bounded radicals and initial clusters. The other boxes represent successive ranges of Si_n systems: eg 1 box for n= 17-18,..., n= 100-115,....., $n=10^9$ -510^9.
- Each box contains two types of particles: neutrals or negatively charged
- The electron concentration and mean energy is determined under the assumption that the positive ion concentration (mainly argon) is maintained constant, at the experimental value.
- For each time step the gain and losses of the number density in each box are determined by the electron-particle, positive Ar^+ -particle and particle-particle interaction . The losses of neutrals by finite dwell time or diffusive effects are included.
- each step of calculation is automatically adjusted in order to obtain less than 10% for the number of particles in all the boxes.
The known reaction rates are used for the low mass particles. For heavier systems the electron-particle attachment rate is defined as mass dependent (accommodation factor).
This box-type model will be described in a forthcoming paper. An example of the present results for experimental plasma conditions (Ar^+ density, Argon and Silane partial pressure, total gas flow, reactor geometry) is given below.

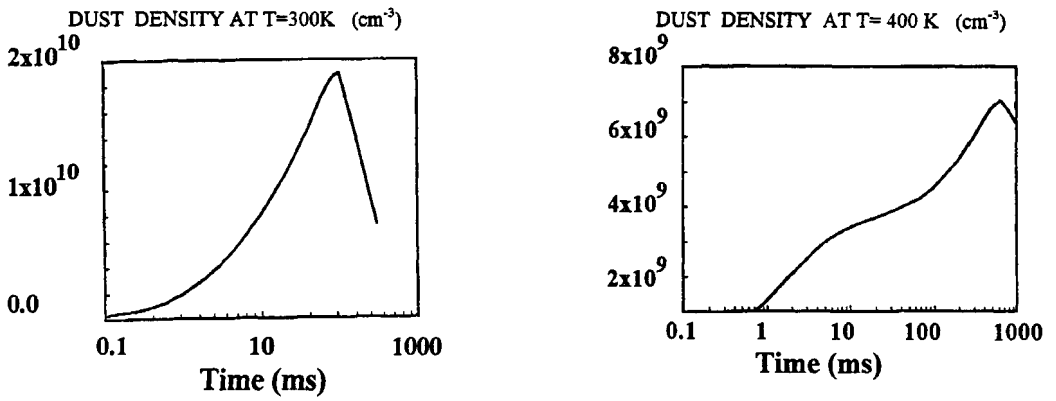


Fig. 6: results of modelling (particle overall density) at two reactor temperatures

The coagulation is evidenced by the decrease of the particle concentration at time delays and concentrations which are in rather good agreement with the experimental values. The same model gives a mean diameter value at coalescence time close to 2 nm in the two situation, also very consistent with the observed sizes of the elementary crystallites. That means that the physical assumptions (eg electron-small systems interaction) are also consistent .

CONCLUSION

Study of the formation of solid particles in a low pressure Argon-Silane RF discharge lead to a multi-step description of the growth process. Initial step, leading to nm scale cristallytes is achieved through negative ion clusterring, as shown by Ch HOLLENSTEIN group (10). A fast coagulation process starts when a critical density of nanometer size crystallites is achieved. This coagulation step is stopped by electric repulsive forces. The final step of growth is a a-Si:H deposition process on particles surface enhanced the high dissociation level of Silane obtained in the dusty situation. A modeling of the whole growth story is proposed through a box-tool model.
The preliminary results are encouraging, quantitatively consistent with experimental data.

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