

Self-Organization and Dynamics of Nanoparticles in Chemically Active Plasmas for Low-Temperature Deposition of Silicon and Carbon-Based Nanostructured Films¹

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Self-organization and dynamic processes of nano/micron-sized solid particles grown in low-temperature chemically active plasmas as well as the associated physico-chemical processes are reviewed. Three specific reactive plasma chemistries, namely, of silane (SiH₄), acetylene (C₂H₂), and octafluorocyclobutane (c-C₄F₈) RF plasma discharges for plasma enhanced chemical vapor deposition of amorphous hydrogenated silicon, hydrogenated and fluorinated carbon films, are considered. It is shown that the particle growth mechanisms and specific self-organization processes in the complex reactive plasma systems are related to the chemical organization and size of the nanoparticles. Correlation between the nanoparticle origin and self-organization in the ionized gas phase and improved thin film properties is reported. Self-organization and dynamic phenomena in relevant reactive plasma environments are studied for equivalent model systems comprising inert buffer gas and mono-dispersed organic particulate powders. Growth kinetics and dynamic properties of the plasma-assembled nanoparticles can be critical for the process quality in microelectronics as well as a number of other industrial applications including production of fine metal or ceramic powders, nanoparticle-unit thin film deposition, nanostructuring of substrates, nucleating agents in polymer and plastics synthesis, drug delivery systems, inorganic additives for sunscreens and UV-absorbers, and several others. Several unique properties of the chemically active plasma-nanoparticle systems are discussed as well.

KEY WORDS: Reactive plasmas; fine particles; self-organization; nanostructured films.

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1. INTRODUCTION

Chemically active plasmas have recently been of remarkably growing interest to the semiconductor and other industries owing to outstanding flexibility and efficiency of numerous surface modification and microstructuring processes involving reactive plasma environments.⁽¹⁾ In particular, such the plasmas offer a great deal of predictability and process control, which is indispensable in a number of ultra-fine Plasma Enhanced Chemical Vapor Deposition (PECVD), Reactive Ion Etching (RIE) and some other techniques for fabrication of Ultra Large Scale Integrated (ULSI) circuits, protective and wear-resistant coatings, solar cell panels, elements of optoelectronic and integrated optics circuits, optical emitters, etc.⁽²⁾

The plasma environments of many of these reactive environments sustain generation and growth of fine particulate matter typically ranging in size from few nanometers to tens of microns.⁽³⁻¹²⁾ Furthermore, the particles in question not only range in size but also remarkably differ by the way they are created and the fundamental physics and chemistry behind their origin, growth, dynamics, as well as their role in the complex particle-reactive plasma systems. Above all, fine particle-plasma systems posed a number of challenges and yet unsolved puzzles to the semiconductor, materials science, and gas discharge communities. Indeed, in early-90s clouds of fine particulates were detected in silane (SiH_4)-based discharges, which are among the major sources of reactive plasmas for semiconductor processing. The particulate powders with sizes in the micrometer range (typical size of line features of ULSI elements at that time) did become a troublesome factor in semiconductor wafer yield.⁽¹³⁾ Furthermore, some of the particles caused unrecoverable defects and line shorts, which totally compromised the entire wafer manufacturing process.

Meanwhile, there have been numerous reports on nano- and micro-sized particles (also often referred to in the literature as “dust,” “dust grains,” “fine particles,” “nano-clusters,” “fine powders,” “powder particles,” “colloidal particles,” “particulates,” etc. depending on their size and microscopic structure) as important parts of various colloid suspensions, charged aerosols, high-pressure ionized gas systems, nucleation catalysts, low-pressure DC and RF plasmas for material synthesis and processing applications, and many others.^(4,6,12) Most recently, embedding of the nano-sized particles have proved instrumental in substantial improvement of the efficiency of amorphous solar cells, creating the entirely new classes of nano-structured materials, exhaust control, catalytic applications, drug delivery systems, etc.⁽¹²⁾ Thus, the accent in the fine particle research is now gradually shifting from the traditional view on them as unwelcome process “killer” contaminants to the desired elements that dramatically improve the basic properties of plasma-made thin films.

Physically, the presence of fine particles in the plasma strongly affects the fundamental properties such as distributions of electron/ion number densities,

temperatures, electromagnetic fields, and plasma potentials. Under some conditions, the entire complex plasma system can self-organize into a strongly coupled Coulomb crystal-like or liquid structure, with strong electrostatic coupling between the colloidal particles.⁽¹⁴⁾ More importantly, the effect of the dusts on the complex plasma system critically depends on the chemical organization/state, size, electric charge, as well as the number density of the particles. Specifically, the smallest (few nanometer range) fine particles appear as a result of either gas phase (chemical) polymerization triggered by certain organic charged/neutral precursor radicals or complexes or gas phase clustering of atoms/molecules released as a result of solid surface (physical) sputtering processes. In this state, the fine particles can either (typically) carry a single-to-few electron negative/positive charge or be charge neutral. The number density of such particles can be relatively high ($\sim 10^8$ – 10^{11} cm^{-3}) and in certain cases (e.g., strongly electronegative plasma discharges) can even be comparable to or even exceed that of the plasma electrons.

The intermediate size-particles (typically in the range from few tens to few hundreds of nanometers, see e.g., Fig. 1) often appear as a result of gas phase

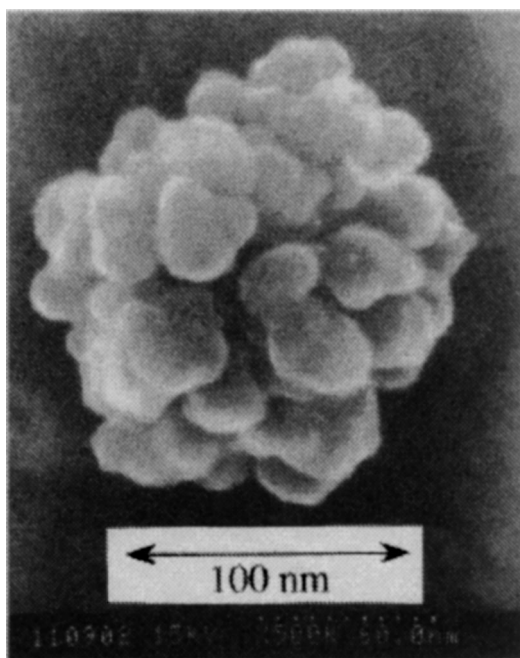


Fig. 1. High-resolution SEM micrograph of a particulate grown in chemically active He + SiH₄ plasmas. Reprinted with permission from Shiratani *et al.*⁽⁹⁾

coagulation of smaller, nanometer-sized particles and clusters and typically exist as agglomerates of different shapes and architectures. Self-organization of the colloidal subsystem in the plasma fluid often results in dramatic modifications of the electric charge distribution in the entire plasma-particle system giving rise to coagulation-induced mode transitions and instabilities. Typically, a number density of the intermediate-sized particles in the stationary state ($\sim 10^6\text{--}10^8\text{ cm}^{-3}$) is a few orders of magnitude lower than that of the nanometer-range protoparticles/clusters. Nevertheless, the particulate matter does cause the apparent charge disbalance between the electron and positive ion species and globally affects the particle and power balance processes in the discharge. The particle-plasma system becomes dynamically coupled so that variations of the macroscopic plasma parameters affect dust generation, which in turn provides positive/negative feedback to the entire complex plasma system.

Although the fine particle size in the chemically active plasma systems typically appear in the nano- and sub-micrometer ranges, micron- and larger sized particles are quite common to many thin film deposition processes and model systems with organic particles. Natural growth of the particulates often proceeds via relatively slow process of ion/radical accretion from the adjacent plasma. Charge states of the particles in this range are conventionally determined via the balance of microscopic electron and ion currents flowing onto the surface.^(15–17) Physically, the complex plasma systems with micron-sized dusts appear to be relatively more stable because of lower probability of fast (similar to agglomeration) self-organization processes. On the other hand, micron-sized dusts typically accumulate a few thousand of electron charges, which is a favorable factor for charge-induced self-organization of the plasma-particle system into strongly coupled ordered structures.⁽¹⁴⁾

Thus, the self-organization, cooperative behavior,⁽¹⁷⁾ and dynamics of nano- and microparticles becomes a matter of the outmost importance for a number of low-pressure chemically active plasmas widely used for plasma-based synthesis and surface modification of advanced materials and is a key focus of this article. In particular, peculiarities of particulate growth in reactive environments of silane (SiH_4), acetylene (C_2H_2), and octafluorocyclobutane ($\text{c-C}_4\text{F}_8$) RF plasmas for Si:H, C:H and C:F low-temperature film deposition are related to chemical structure/composition, size and architecture of the nanoparticles grown in the ionized gas phase. We also emphasize the correlation between the nanoparticle origin and self-organization in the reactive plasmas and modified properties of the thin films. Self-organization and dynamic phenomena, crucial for a number of industrial applications of nanoparticles in relevant reactive plasma environments are usually studied for equivalent model systems that consist of mono-sized organic particulates and inert gas environment used as a buffer gas in a number of applications. The role of fine powders in low-temperature processing plasmas and several challenging applications of nano/micron-sized particles in a number of high-tech industries are discussed as well.

The article is organized as follows. In Section 2, growth and self-organization of nano-sized particles in silane, hydrocarbon, and fluorocarbon reactive plasmas is reviewed and related to the chemical organization and size of nanoparticles. Deposition of nanostructured amorphous silicon films for optoelectronic applications using plasma-grown nanoparticles is reviewed in Section 3. The dust-related dynamic processes in the areas adjacent to materials substrate are reviewed in Section 4 for a number of model ionized gas systems with organic fine powders. Section 5 gives an overview of possible industrial applications of plasma-made nanoparticles and nanoparticle-assembled thin films. The article concludes with the outlook for the potential impact of the reactive plasma-nanoparticle systems in the research areas of nano-/ bio-materials and optoelectronics/photonics.

2. GROWTH AND SELF-ORGANIZATION OF FINE PARTICLES

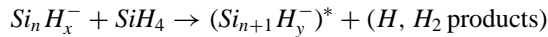
Here, we discuss the major physico-chemical processes involved in the generation and growth of nanoparticles in chemically active environments of silane, hydrocarbon, and fluorocarbon plasmas. Although specific particle generation and growth conditions strongly depend on the plasma chemistry involved, the growth of fine particles in most reactive plasmas starts with heterogeneous and homogeneous nucleation that control the formation of sub-nanometer/nanometer-sized protoparticles. The origin of protoparticles is usually followed by agglomeration and coagulation processes leading to pronounced particulate formation with the size of few tens of nanometers. Eventually, accretion of neutral or ionic monomers results in growth of sub-micron and micron-sized dusts.

2.1. Silane (SiH_4) Plasmas

At present, it is believed that the basic particle formation mechanisms are well understood in silane (SiH_4) plasmas used for advanced silicon technology applications (ULSI silicon devices, solar cells, flat displays, etc.).⁽¹¹⁾ The recent steady-state homogeneous model^(18,19) aims at explaining the initial particle growth in a pure silane discharge. The model assumes that the particles grow primarily from SiH_3^- anions and SiH_m radicals, first into Si_xH_m radicals. While the silicon atom number increases, large clusters, and eventually primary silicon-based particles are formed. Substantial experimental and theoretical efforts have been made in order to identify the fine powder precursors and the dominant gas-phase reactions leading to generation of larger particulates containing 10^4 – 10^6 silicon atoms.

However, there is yet no consensus on the question what the dominant precursors for the nanoparticle generation are. Silane neutral radicals are good candidates for such a purpose as being capable of incorporating into larger-mass saturated molecules. Positive ions can also be potential powder precursors despite high activation barriers preventing the formation of higher-mass cations. On the other hand,

negative hydrosilicon ions can be efficiently trapped and levitated in the plasma sheath/presheath areas and play a key role in the plasma-enhanced polymerization. Under certain conditions, a large number of negative ions can be confined to accumulate and grow towards higher and higher masses in a similar way as the homogeneous model suggests.⁽¹⁹⁾ Subsequent time-resolved mass-spectrometry data have confirmed that the negative ions are the most probable precursors of the nanoparticle generation in RF silane plasmas at low and moderate power densities.⁽¹¹⁾ Above all, it is likely that the polymerization proceeds via the negative ion clustering reaction



where $(Si_{n+1} H_y^-)^*$ is the higher-mass anion in the excited state. At the second stage, the particulate formation proceeds by agglomeration (quick phase) of small clusters into larger (typically $\sim 40\text{--}50$ nm sized) particles, where neutral atoms/molecules can play an important role.⁽²⁰⁾ Finally, after the rapid growth or the coagulation phase, the particle size increases only slowly and with rates comparable with the corresponding thin film growth rates.

It is worth noting that the dominant particle nucleation and growth processes discussed earlier are most relevant to the plasmas of pure silane discharges. However, many real processes require substantial dilution of silane by hydrogen and/or argon thus making the resulting plasma chemistry more complicated. The remarkable difference with the pure silane case is in longer time scales required for the particulate growth. This opens up the possibility to control the particle size by varying the gas feedstock. One should also expect a difference in chemical bonding states, architecture, and surface morphology of the particles grown in pure and buffer gas diluted silane plasmas.

Furthermore, the gas phase residence time of the precursor species appears to be a critical factor in particulate generation and growth. In particular, direct correlation between the residence time and size of protoparticles has been reported.⁽²¹⁾ Physically, the protoparticle's number density should reach the minimum value for coagulation, which can be made possible due to the so-called selective trapping effect of neutral particles proposed by Fridman *et al.*⁽²²⁾ Specifically, nanometer-sized particles can become negatively charged and hence trapped in the near-electrode areas if the rate of electron attachment, which strongly depends on the particle size and electron temperature, exceeds the particle residence time in the discharge. In other words, the residence time of neutral nanoparticles should be long enough to be negatively charged via non-dissociative electron attachment. For the experimental parameters of Fridman *et al.*⁽²²⁾ (Ar flow rate of 30 sccm, silane flow rate of 1.2 sccm, total gas pressure of 117 mTorr, gas temperature in the range of 300–400 K, electron temperature of 2 eV, neutral gas residence time of 150 ms, electron/positive ion number density of $3 \times 10^9 \text{ cm}^{-3}$ and $4 \times 10^9 \text{ cm}^{-3}$,

respectively, further details of the experimental setup can be found.⁽²³⁾ the critical size of the particles that can be trapped and are capable to agglomerate is of the order of 2 nm. Particle size measurements performed by high-resolution transmission electron microscopy (HR TEM) together with laser light scattering (LLS) measurements of the dust number density did confirm that the particle growth process proceeds via formation of a dense ($\sim 10^{10}$ – 10^{11} cm⁻³) powder cloud of fairly monodisperse, 2 nm-sized fine particles.

Apparently, the physics and chemistry behind the particle growth in reactive plasmas critically depends on the prevailing experimental conditions. Hence, in the short residence time situations one could expect that short-lifetime, highly reactive neutral radicals can efficiently sustain homogeneous nucleation processes. In particular, neutral radicals SiH_m ($m = 0$ – 2) can be responsible for the nanopowder formation in dense helium or argon-diluted silane discharges.^(24,25)

The picture of particulate growth in silane-based reactive plasmas would not be complete without a brief discussion of the critical phenomena following the selective trapping stage. After the particulate cloud has reached the critical density ($\sim 10^{10}$ – 10^{11} cm⁻³ for the experimental conditions of Fridman *et al.*⁽²²⁾) for the coagulation to start, the new protoparticle formation terminates and larger aggregates, with the size in the range of 40–50 nm, are generated as a result of a relatively fast coagulation process. One of the possible explanations of this critical value for the dust number density is a competition between the rates of particle polymerization and attachment of small negative ions (e.g., SiH₃⁻) to the nanoparticles.⁽²²⁾ It is notable that before and after the aggregation stage, the dust charging processes are physically different. Indeed, as was explained previously, small (nanometer range) dusts presumably acquire negative charge due to attachment of negative ions. However, larger (40–50 nm) particles are charged by electron and ion flows onto the surface caused by the difference between the plasma and dust surface electrostatic potentials. In that case, the dust charge can be calculated using the Orbit Motion Limited approximation for the microscopic currents of the plasma species.^(15,16,26,27) Furthermore, large negative electric charge on larger particles appears to be a factor limiting further agglomeration/coagulation of particulates.^(11,18,19)

Another critical phenomenon is a fast variation of the discharge parameters during the coagulation stage caused by a rapid increase of the powder size and diminishing of the particle number density. This results in a dramatic modification of the power and particle balance in the discharge mostly due to the newly emerged electron/ion sink channel via the combined surface area of the dust agglomerates. In certain cases, the rate of the electron/ion sink onto the dusts can exceed that onto the discharge walls and the system can eventually become unstable giving rise to so-called $\alpha - \gamma'$ transitions.^(5,21,22) Physically, the additional loss of the plasma particles is to be compensated by the enhanced creation of the electron-ion pairs. Thus, the plasma-particle system generates a self-consistent feedback by elevating

the electron temperature, which further results in enhanced ionization/dissociation rates. Elevated ($\sim 8\text{--}10$ eV) electron temperatures have frequently been reported at this stage for a number of silane-based discharges.^(5,11,21,22,28)

2.2. Hydrocarbon (C_xH_y) Plasmas

Several attempts to investigate the plasma chemistry and growth of nano-sized particles in hydrocarbon (e.g., methane, CH_4 or acetylene, C_2H_2) discharges have recently been reported. In particular, a model describing the chemical clustering kinetics in the low-pressure acetylene capacitively coupled plasmas has been proposed and tested experimentally.⁽²⁹⁾ The simulation includes numerous gas-phase processes including electron impact dissociation, electron attachment leading to negative ion generation, ion-ion recombination, ion-neutral clustering, chemical reactions involving hydrocarbon (chain and aromatic) neutrals, as well as diffusion losses of the plasma species to the discharge walls. Presumably, the initial stage of the clustering process is triggered by the electron-impact abstraction of hydrogen from acetylene $C_2H_2 + e \rightarrow C_2H + H + e$ followed by generation of higher C_xH_y radicals via a number of successive reactions.⁽²⁹⁾

The model predicts the time evolution of the species concentrations and the prevailing clustering pathways. Specifically, the clustering proceeds via addition of the anion species $C_iH_j^-$ to the neutrals C_mH_n with the corresponding elimination of hydrogen and generation of higher-mass negative ions $C_iH_j^- + C_mH_n \rightarrow C_{i+m}H_{j+n-1}^- + H$. After the rates of the new species production have become comparable to that of the particle loss to the walls, the rapid chemical nucleation stage evolves into the steady state, the latter being strongly affected by the gas temperature, RF power density, and working gas pressure. Likewise, the enhanced and inhibited coagulation regimes were identified and related to the discharge operating conditions. Even though the clustering occurs mainly through formation of linear molecules, the amount of aromatic hydrocarbons is not negligible and becomes significant at higher gas temperatures. Relevant Fourier Transform Infrared (FTIR) spectroscopy data collected from the powder samples confirm predominant production of the acetylenic compounds in the ionized gas phase, although presence of aromatic compounds appears to be non-negligible.

These results are also consistent with recent experiments on dust particle generation, size-controlled growth, diagnostics and deposition in 13.56 MHz capacitively coupled plasmas of argon/methane and argon/acetylene mixtures in a GEC Reference Cell plasma reactor.⁽³⁰⁾ The most efficient dust particle generation has been reported for the $C_2H_2 + Ar$ and $CH_4 + C_2H_2 + Ar$ mixtures at elevated RF powers, which indicates the importance of the adequate amounts of the particle growth precursor molecules C_2H_x .⁽³⁰⁾

2.3. Fluorocarbon (C_xF_y) Plasmas

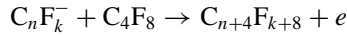
Fluorocarbon (C_xF_y) plasmas have recently been widely used for ultrafine and highly selective etching of polysilicon and a number of CVD processes. Recently, highly polymerized molecules were detected and related to gas-phase polymerization processes in RF discharges of octafluorocyclobutane ($c-C_4F_8$)—based gas mixtures.⁽³¹⁾ It is worthwhile to mention that the mechanisms involved can indeed be similar to those in silane- or hydrocarbon-based plasmas. Furthermore, the gas-phase polymerized higher-fluorocarbons can cause formation of nano-sized particles in a manner similar to what was described in Section 2.1, and also directly participate in the thin film formation processes.

Generation of solid particles and agglomerates in fluorocarbon plasmas for reactive ion etching of SiO_2 and CVD of low-dielectric constant polymeric films was demonstrated.⁽³²⁾ The generation of particles was directly examined by the Scanning Electron Microscopy (SEM) observations of the solid particles deposited on the wafer surface. Takahashi and Tachibana⁽³¹⁾ also elucidates the correlation between the polymerization in the ionized gas phase and the relevant surface processes, as well as proposes a mechanism for the fine particle generation in chemically active environments of fluorocarbon plasmas. Specifically, the particles were grown in a parallel plate 13.56 MHz capacitively coupled plasma discharge in the $c-C_4F_8$ gas feedstock sustained with RF power densities of 0.15 W/cm^2 in the pressure range from 23–250 mTorr. The fluorinated amorphous carbon ($a-C:F$) thin films were deposited on the substrate, with the fine particles and agglomerates clearly dispersed over the wafer surface after deposition from the plasma discharge. The SEM results suggest that mostly spherical, 0.5 to 2.3 microns in diameter, particles were formed in the ionized gas phase and deposited on the surface. The agglomerates, typically sized in the few tens of micrometer range and composed of the primary spherical particles, were also detected in the pressure range above 50 mTorr. Moreover, the number of primary particles involved in the aggregation process became larger at higher pressures. In particular, the agglomerate size was found approximately 30 microns at 250 mTorr.

In the experiments, the dependence of the film deposition rate on the gas feedstock pressure was a clear indicator of the particle polymerization in the gas phase. Indeed, in the pressure range above 50 mTorr, the $a-C:F$ deposition rate declined, which was directly related to predominant consumption of the gas-phase polymer precursors by the particle generation processes. It is remarkable that neither CF_4 nor C_2F_6 plasmas featured pronounced particle formation in the ionized gas phase. Furthermore, according to the feed gas pressure dependence of the deposition rate, it was suggested that stable CF_4 and C_2F_6 molecules cannot act as precursors for the particle growth.

Although the reactive plasma species that can trigger gas-phase polymerization of the solid particles are yet to be identified, it becomes clear that the particle

production can be induced by the formation of clusters acting as nuclei. As a possible particle polymerization scheme, the following reaction was proposed:



which is a chain associative electron detachment polymerization process. It is supported by the monotonous increase of the particle production rate with the working gas pressure, which also implies a direct correlation of the polymerization rate to the density of the gas source molecules or the products of the first-order reactions in the gas phase. It is imperative to note that similar to silane and hydrocarbon plasmas, the anions (negative ions) also play a pivotal role in the polymerization process in fluorocarbon plasmas. Elucidation of the particle production mechanism, including proper experimental identification of the reactive plasma catalyst species, is an apparent forthcoming challenge in this area of research.

At the end of this section, we note that modern particle detection techniques (e.g., laser light scattering) allow one to successfully monitor the growth and dynamics of submicron-sized particles. However, detection and diagnostics of nano-sized particles as well as investigation of the complex physical/chemical mechanisms leading to nucleation of particle precursors, appears to be a challenging problem for the coming years. Finally, it is also worth noting that nano/micron-sized particles of numerous materials (graphite, titanium, copper, silicon, aluminum, etc.) can be successfully generated in plasma-enhanced sputtering facilities.^(6,8)

3. ROLE OF PLASMA-GROWN NANOPARTICLES IN PECVD OF NANOSTRUCTURED SILICON FILMS FOR OPTOELECTRONIC APPLICATIONS

Plasma enhanced chemical vapor deposition (PECVD) of amorphous silicon (a-Si) films is one of the key established techniques in fabrication of solar cells, flat panel displays, thin film transistors, and other opto-electronic devices.⁽³³⁾ However, the basic properties of such films, and hence the deposition process, need to be continuously improved to meet the demands of the emerging optoelectronic industry. In particular, it has been observed that transport and stability properties of the films prepared in the gamma (powder generating) regime (see Section 2.1) can be remarkably better than those of the films deposited in another regimes.^(34–36) Clearly, such an improvement was related to generation of silicon-based nano-sized powders in reactive environments of silane-based discharges, see Section 2.1. Relevant thin film analytic techniques confirmed that the nanoparticle-made silicon films appear to be nanostructured, some of them containing ordered silicon nanocrystals.⁽³⁶⁾ Thus, appropriate powder management is becoming a critical issue in controllable and predictable deposition of nanostructured thin films. Martins *et al.*⁽³⁷⁾ reports on successful PECVD of nanostructured silicon films in highly

hydrogen-diluted silane discharges at elevated deposition pressure and low ion bombardment conditions, to enable sufficient surface activation/passivation. As a result of gas-phase nanopowder formation and embedding in the amorphous silicon matrix, high-quality films with low density of states and high mobility-lifetime product were deposited.

It is notable that since the powder particles are charged negatively in the plasma (see Section 2.1), the selective ion/particle deposition process can be controlled by a DC substrate bias. Indeed, the positive bias promotes incorporation of the plasma-grown particles into the films, whereas the negative one hinders this process. Furthermore, the films deposited at positive substrate bias, appear to be more compact and dense, with remarkably smaller surface roughness, as compared to the films grown at a negative DC bias. The latter films feature more porous structure and random distribution of the morphology elements over the surface. It has also been reported that the film deposition rate was clearly higher for the negative bias conditions.

However, to infer the specific role of the gas-phase grown nano-sized particles in the actual film modification process, one should exercise a certain degree of caution because of the large number of concurrent physico-chemical processes involved. In particular, selective etching of the amorphous silicon matrix by hydrogen atoms favors enrichment of the crystalline (*c-Si*) phase of silicon and can be a critical factor in nano-crystalline silicon (*nc-Si*) film fabrication.

It is also remarkable that embedding of the nano-sized silicon clusters can result in the widening optical bandgap and the decreasing density of states of the film material. Thus, the film growth process can indeed benefit from the nanoparticles grown in the ionized gas phase that can incorporate into the film. Further studies on nanoparticle-surface interaction and nanoparticle-embedded film growth kinetics are therefore warranted.

4. DYNAMIC PHENOMENA IN MODEL SYSTEMS WITH ORGANIC FINE PARTICLES

In this Section, we consider, with a few examples, dynamic processes in complex plasma systems. Since most of the laboratory plasmas have natural boundaries such as chamber walls, internal electrodes, substrate holders, etc., a large number of experiments with plasma-particle systems involved investigation of dynamic processes in the vicinity of the boundaries. The transition area between the plasma and the boundary includes sheath and pre-sheath regions^(38–40) where dust grains can levitate due to a dynamic balance of several forces acting on a particle.^(41,42) Such forces include but are not limited to the force of gravity, electrostatic force, ion and neutral drag forces, etc.^(26,41,42) Since the plasma parameters vary dramatically in the sheath/pre-sheath areas, so does the equilibrium electric charge on a particle, which dynamically affects the force balance while the particle moves towards the

wall.^(41,42) Another key feature of the plasma-wall transition areas is the presence of established supersonic ion flows directed to the walls^(43,44) that can affect levitation and dynamics of dust particles. We thus focus here on the dynamic processes of dust levitation in the near-wall areas of argon^(41,42) and fluorocarbon^(45,46) plasmas, effects of ion flows on levitation of rod-like particles.⁽⁴⁷⁾ It is notable that adequate description of many of the dynamic phenomena in complex plasma systems critically depends on the prevailing particle source and sink mechanisms^(48–51) that self-consistently determine the equilibrium state of the dusty plasma discharge.^(52–55) Self-excited vertical oscillations of dust grains in capacitively coupled RF discharge in argon^(56–58) will be discussed as well.

Equilibrium, stability, and levitation of dust particles in collisional argon plasmas with an ionization source are investigated by Vladimirov and Cramer.⁽⁴²⁾ Vertical motions of the dusts in the near-wall area are considered by self-consistently including the dependence of the dust charge, ion flow velocity, electron/ion number density, etc., on the local position in the sheath/pre-sheath region. It is demonstrated that an increase of the ionization rates strongly affects the equilibrium positions of the dust particles, shifting them towards the electrode as well as elevating the maximum equilibrium grain size that can be levitated in the near-electrode area. The change of the ionization power in the discharge can strongly affect dust charge distributions. Specifically, decline in the ionization power can result in diminishing of the equilibrium size of particles capable of levitating, with the heaviest grains falling down to the electrode. In this way, the charge/mass distribution of dust grains can be substantially modified. Note also that another experimental possibility to force dust particles to fall down to the electrode is to apply a low frequency modulated voltage to the lower electrode thus forcing particles to oscillate. When the amplitude of oscillations becomes large enough to overcome the potential barrier, the dusts fall down and therefore are removed from the sheath region. Other options to control the nano/micron-sized particles in the near-wall areas can be found.⁽⁴²⁾

Charging and confinement of nano/micron-sized particles in the plasma bulk and near-electrode regions of octafluorocyclobutane—argon ($c\text{-C}_4\text{F}_8 + \text{Ar}$) etching plasmas is considered.^(45,46) The model near-electrode area comprises the electronegative and electropositive pre-sheath regions as well as the sheath itself. The composition of the plasma is representative to quadruple mass spectrometry experiments in low-pressure RF inductively coupled and microwave surface-wave sustained plasmas of 10% $c\text{-C}_4\text{F}_8 + 90\%$ Ar gas mixtures for deep-micron ultra-fine selective etching of silicon.⁽⁵⁹⁾ It is shown that the equilibrium particle charge in the electronegative region is lower than it would be in electropositive plasmas, and increases towards the electrode. In the vicinity of the wall, the ion density decreases, as does the charge on nano/micron-sized particles. The negative ions affect the particle charging and levitation through notable modification of the sheath/pre-sheath structure. Meanwhile, the particle dynamics in nearly the whole near-wall

area is controlled by competition of the electrostatic and ion drag forces, whereas other forces play the role only in the electronegative plasma bulk.

The interaction of rod-like charged particles with ion flows in the near-wall region of low-temperature plasma is studied by Vladimirov and Nambu.⁽⁴⁷⁾ It is well known that ion flows strongly influence formation of dust-plasma crystals as well as aligned particle structures in the direction of ion flows.⁽¹⁴⁾ Physically, according to Bohm's criterion, ion flows in the plasma sheaths are supersonic, which naturally leads to excitation of wake fields that affect levitation of dust grains and self-consistently generate the attracting wake potentials between the grains of the like electric charge.^(43,44) Article⁽⁴⁷⁾ reports a new step in the study of interactions of dust particles with the established ion flows by involving elongated (rod-like) particles into consideration. In many experiments, such particles typically have longitudinal size of few tens of microns to few millimeters while their transverse size ranges from few tens of nanometers to few microns (Fig. 2, see also Annaratone *et al.*⁽⁶⁰⁾).

Likewise, self-excited vertical oscillations in a sheath region of the RF discharge (0.5–20 Pa, 15 MHz capacitively coupled argon plasmas) dusty plasma have been observed,⁽⁵⁸⁾ where micron-sized carbon particles had been dispensed into the plasma. Thereafter, the dusts acquire sufficient negative charge for the electric force in a sheath region to compensate gravity and ion drag forces so that they can stay in equilibrium vertical positions. It was found that when the pressure decreased below a critical value, the dust particles began to oscillate spontaneously in the vertical direction, with the amplitude and frequency of few millimeters and about 10 Hz, respectively. Two possible excitation mechanisms, which treat a dust plasma layer as a static or dynamic dissipative structure,⁽³⁸⁾ and account for spatial variation of the dust charge and instability of the layer of charged particles as a virtual wall (resonator), have been proposed. Research in this direction should be continued to explain frequently observed self-organized ordered structures (some examples are shown in Fig. 3) in low-temperature laboratory plasmas and account for specifics of the reactive plasma environments and polymerization/dust growth in real PECVD systems.

5. INDUSTRIAL APPLICATIONS OF PLASMA-GROWN NANOPARTICLES AND NANOPARTICLE-ASSEMBLED THIN FILMS

Traditionally, plasma enhanced chemical vapor deposition (PECVD) systems for deposition and microstructuring of silicon films for microelectronic devices suffered from gas-phase polymerization of micron-sized and nano-sized particles. Indeed, the fallout of submicron-sized particles can be a killer effect for the microstructured wafers with the achieved feature sizes of microns to fractions of microns. Furthermore, particle contamination can result in pinholes, delamination

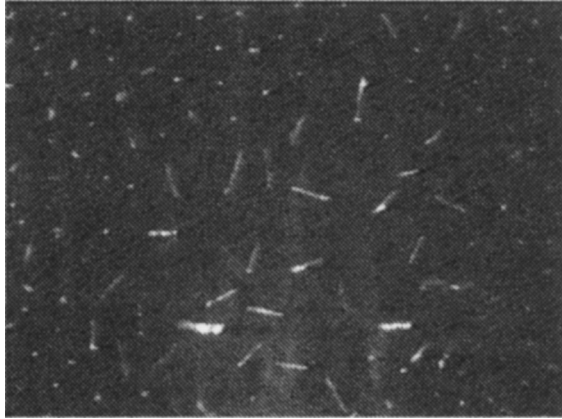


Fig. 2. Rod-like micron-sized particles levitated in krypton plasmas. The dots are vertically aligned micro-rods. Reprinted with permission from Annaratone *et al.*⁽⁶⁰⁾

and interconnection shorts or opens in ULSI structures. Data storage disks are also affected by read-write errors, damaged sectors, and total failure caused by excessive dust contamination. In the last few years, there has been a notable progress

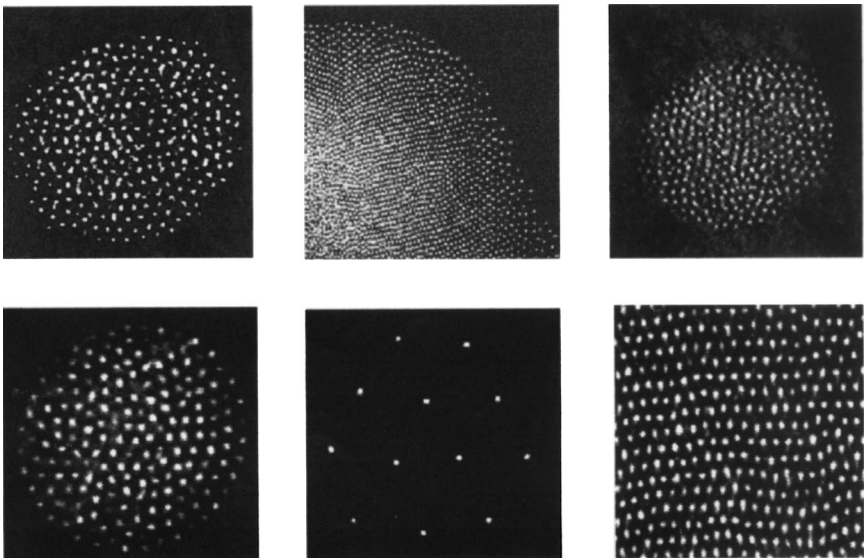


Fig. 3. Optical images of typical self-organized dust structures in low-pressure capacitively coupled plasmas [courtesy of Alex Samarian, Complex Plasma Laboratory, University of Sydney (unpublished)].

in developing efficient techniques to remove micron-sized particulates from the reactor volume or suppress nanoparticle growth processes at the initial stages.⁽⁶¹⁾ Therefore, the nano-sized gas-phase nucleated silicon-based particles generated in large amounts in the prevailing sub-micron silicon plasma technologies are too small to be of any concern.⁽⁶²⁾ However, it is expected that within the next ten years, the feature size of microelectronic circuit elements will shrink to 50 nm,⁽⁶³⁾ and removal/suppression of growth of nanoparticles from the reactor volume will definitely become a critical issue.

Apart from the traditional deleterious aspect, fine particles have recently emerged as useful elements of a number of challenging applications in material engineering, optical coatings, polymer industry, mineral/ore processing and several others. In particular, nano-sized particles can be efficiently combined with polymeric/ceramic materials to form a variety of novel nano-structured materials for optoelectronic, protective coating, fire-resistant and other applications. Furthermore, fine powders of ~10 nm-sized particles are extensively used as improved nucleating reagents for plastics, inorganic, ultra-fine UV-absorbing additives for outdoor applications. For example, currently zinc-oxide nano-powders capture more than a half of the Australian sunscreen market. Other applications include cosmetics, inks, pigments, textiles, wear-resistant ceramics, improved nano-crystalline materials, air and water pollution control, waste management, colloidal suspensions for mining, metallurgical, chemical, pharmaceutical industries, and food processing. However, the plasma route for production of bulk quantities of nano-/micro-particles poses a number of technological/economical challenges. We thus expect that in the near future the plasma-grown powder technologies will be mostly limited by small-scale ultra-fine tailoring of particle functionalities to meet the requirements of the specific industrial processes targeted.

Most recently, nano-sized particles have emerged as the key elements of several technologies allowing one to manipulate the properties of the matter at nanoscales and synthesize previously unknown powder-assembled materials with unique nano-scale architectures, morphologies, as well as optical, thermal, catalytic, mechanical, structural and other properties.⁽⁶⁴⁾ The quickly emerging applications of nano-sized particles include nanostructured and nanocomposite films, nanocrystalline powders and consolidated structures, nanoparticle superlattices and other 3D assemblies that represent new forms of supramolecular crystalline matter, nano-scale inorganic synthesis, dispersions and suspensions with controlled fluid dynamic properties, nano-sized single/few-electron data storage units and many others.

Plasma-based CVD methods have recently proven to be very efficient in the fabrication of various nanostructures wherein the gas-phase grown nanoparticles play a pivotal role. Thus, the question about the controlled dynamics of fine particles in the areas adjacent to the structure being fabricated becomes critical.

6. OUTLOOK FOR FUTURE RESEARCH

The fine particles are ubiquitous to a number of chemically active plasma environments. The role of such particles in plasma processing and materials synthesis applications is rapidly increasing. In particular, the major attention they have attracted is due to tremendous recent advance in nanoscience and technology. In particular, the remarkable interest in the plasma production of nanocrystalline silicon particles is regarded as a new challenging route for fabrication of nanostructured silicon thin films.⁽⁶⁵⁾ This opens up a new horizon of problems associated with the precise control of the size and number density of gas-phase grown silicon-based nanocrystals. Furthermore, the detailed physics and chemistry leading to particle generation and subsequent growth in complex reactive gas mixtures still remains a challenge for theoretical, computation, and experimental efforts for the next few years. The understanding of nano/micron-sized particle origin and growth should be extended to more complex reactive plasma chemistries relevant to advanced fabrication processes at the nano-scale. Hence, greater modeling and computation efforts should be directed towards investigation of complex dynamic phenomena, including charging, motion, levitation of nano/micron-sized particles in near-electrode areas of chemically active plasmas. Experimentally, diagnostics of complex plasma systems with nano-sized colloid particles should include real-time, *in situ* monitoring of dynamic variations of nanoparticle size and chemical composition simultaneously with the plasma species number densities and composition.

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