

DUSTY PLASMA DEPOSITION OF NANOCOMPOSITE THIN FILMS

NALAGANJE NANOKOMPOZITNIH TANKIH PLASTI S PRAŠNO PLAZMO

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Dusty plasma has traditionally been considered as pollutant species in plasma processes. However, lately it is being regarded as an interesting way of producing nanocomposite thin films. In this paper, the basics of dusty plasma physics are presented. Discussed is the nucleation and growth, which can be either a consequence of homogeneous plasma reactions, heterogeneous reactions on the plasma-surface interface or they can be injected externally into the plasma. The particles are negatively charged, which strongly influences their movement. The most important interaction is the repelling force in the plasma sheath which confines the particles to the plasma volume. Also presented in this paper are the basic properties of nanocomposite thin films and their application in modern technological and industrial applications. Examples of dusty plasma produced nanocomposite thin films are given in the final chapter.

Keywords: dusty plasma, nanocomposite thin films

Navadno so pojav prašne plazme v plazemskih reaktorjih povezovali z nečistočami v plazmi, zadnja leta pa jih dojemajo tudi kot zanimivo orodje za nalaganje nanokompozitnih tankih plasti. V pričujočem prispevku predstavljamo osnove fizike prašnih plazem. Govora je o nukleaciji in rasti, ki je lahko posledica homogenih reakcij v prostornini plazme, posledica heterogenih reakcij na stični plasti med plazmo in trdno površino, ali pa so lahko vstavljeni v plazmo od zunaj. Delci imajo negativen električni naboj, kar močno vpliva na njihovo gibanje. Najpomembnejša interakcija je odbojna sila v plašču plazme, ki zadržuje delce v prostornini plazme. V prispevku so pravtako predstavljene osnovne lastnosti nanokompozitnih tankih plasti in njihove uporabe v sodobnih tehnoloških in industrijskih aplikacijah. V zadnjem poglavju so predstavljeni primeri nanokompozitnih tankih plasti, pripravljene s pomočjo prašne plazme.

Ključne besede: prašna plazma, nanokompozitne tanke plasti

1 INTRODUCTION

The phenomenon of formation of dusty particles in plasmas has been known almost as long as the plasmas themselves¹, however the research of the "dusty plasma" has considerably lagged behind the general knowledge of plasmas. Since then, plasmas have proven to be indispensable tools in research, technological and industrial processes, where their use ranges from relatively benign and non-intrusive surface modification to thermonuclear fusion, encompassing technologies such as selective etching²⁻⁸, cleaning of metallic surfaces⁹⁻¹², biomedical application such as improving bio-compatibility of prosthetics¹³ and sterilization^{14,15}, thin-film deposition, etc^{9,12,16-28}. Regardless of the application, one of the key requirements for the plasma was purity as too high a concentration of impurities would hinder the efficiency of the process, if not outright rendering it useless. In this context, the appearance of dusty particles in the plasma was a most undesired occurrence.

However, in the recent years, there has been a renewed interest in the field of dusty plasmas. The motivation for the research ranges from the intent to increase the efficiency of production of solid particles to avoid the formation of dust altogether. Regardless of the motivation, the importance, and the world-wide interest

in the field is perhaps best illustrated by the fact that one of the physical experiments aboard the International Space Station has been dedicated to the study of dusty plasmas under microgravity conditions²⁹. Moreover, the perception of dusty plasmas in technological processes is also changing as they are not regarded merely as an unwanted side-effect, but also as a very attractive tool for producing nanocomposite thin films.

2 DUSTY PLASMA

2.1 Appearance of dust particles

By definition, dusty plasma is plasma containing solid particles, usually of micrometric or nanometric proportions, however the source of the particles can differ greatly from case to case. The particles can be introduced externally, or they can be a consequence of reactions in the reactor, be it homogeneous reactions in the plasma volume or heterogeneous reactions on the solid surfaces within the reactor.

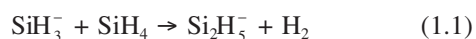
Particles of virtually any material and in sizes ranging from a couple of 10 nm to several μm can be injected into plasmas²⁹⁻³². This kind of particle introduction is especially suited to basic research of dusty plasma properties, since it allows for a high degree of

control over the chemical composition and the size distribution of the solid particles.

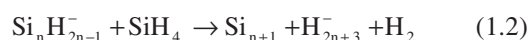
In a way, external introduction of solid particles may also be a consequence of surface reactions in the plasma reactor, in which material from plasma-facing surfaces is ejected into the plasma. Such cases can include sputtering^{33–36}, evaporation, arching, etc.³⁷. Naturally, the control over the size distribution of the particles introduced into the plasma is, in this case, inherently much lower.

In contrast to externally injected particles, which are generally composed of different elements and compounds that make up the plasma, particles can also grow from precursors which are at the same time plasma species. Well documented examples of such particle growth are the appearance of solid particles in silane containing plasmas, and in plasmas containing hydrocarbon species such as methane, acetylene, etc.

In silane containing plasmas, the nucleation starts with the reaction³⁸:



in which a negative silane ion SiH_3^- reacts with a silane molecule, creating a heavier negative ion SiH_5^- and a hydrogen molecule. The resulting heavier ion reacts with another silane molecule, forming an even heavier ion, and thus the reaction continues for larger and larger clusters:



Such clusters grow to the size of approximately 2 nm. After that, the attachment of negative ions becomes more likely than the chain formation reaction, and agglomeration of clusters begins. This way, particles can grow up to several 100 nm in size³⁹. An example of such particles is presented in **Figure 1**.

A similar reaction takes place in acetylene plasmas, where a negative ion, C_2H^- reacts with an acetylene molecule⁴⁰:

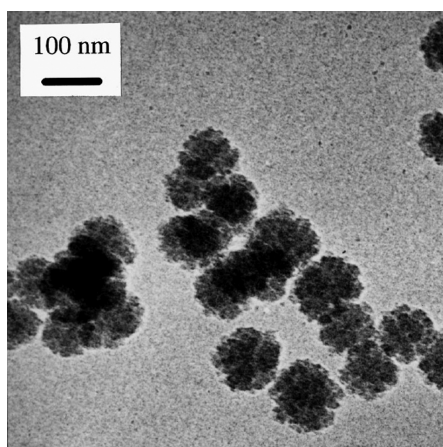


Figure 1: TEM image of Si – based particles, deposited in a dusty RF discharge, created in a mixture of argon and silane, **Figure 6** in³⁹

Slika 1: TEM slika silicijevih delcev, ki so nastali v prašni RF raz-elektrivni mešanici argona in silana, **Slika 6** v³⁹

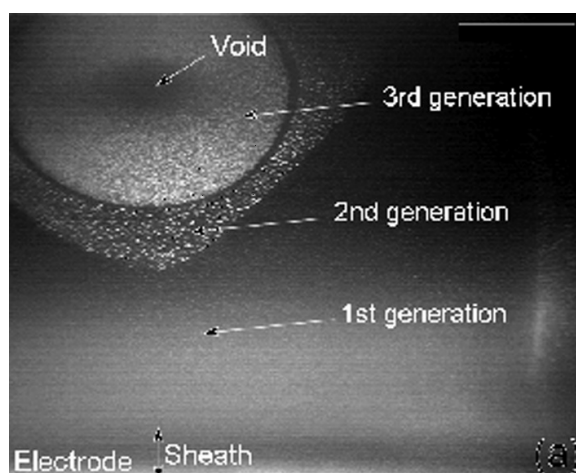
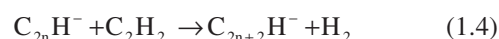


Figure 2: Generations of particles grown in the same discharge, **Figure 4a** in²⁹

Slika 2: Generacije delcev, ki nastanejo v isti razelektrivni, **Slika 4a** v²⁹



The resulting heavier negative ion again engages in growth reactions:



Dust particles composed from plasma species can also be formed in heterogeneous, surface reactions. In this case, plasma species are deposited on solid surfaces within the reactor, forming a thin film. Subsequently, this thin film is degraded in a way that it begins to crack or flake. The flakes peel off the surface and re-enter the plasma. This process generally produces the most random size and shape distribution of the dusty particles.

However, in a realistic case, the growth of particles can rarely be defined as only one of the described processes, rather than a combination of various processes. Erosion of material from solid surfaces does not necessarily result directly in a population of solid particles in the plasma – the material is not only eroded in the form of solid particles, but also in the form of precursors, from which particles grow in the gas phase.

Moreover, the choice of solid surfaces needs not to be limited only on walls of the plasma containing vessel, electrodes, target plates, etc. Indeed, the dust particles themselves can be eroded by the surrounding plasma, thus ejecting precursor species for a new generation of particles to be formed in the plasma^{29,41}. The subsequently formed generations of particles are of course subject to the same erosion mechanism and so further generations are formed, resulting in a periodical growth of particle generations, as seen in **Figure 2**²⁹.

Most interestingly, combination of various growth mechanisms can result in a heterogeneous structure of the dusty particles. Particles, ejected from the solid plasma facing surfaces can act as nucleation centers for growth of layers deposited by the plasma. This results in particles with a core composed of material ejected from

the surface, and a shell composed of material grown from plasma species.³⁷

2.2 Behavior of dust particles in the plasma

The behavior of the dusty particles inside a plasma is governed most strongly by their electric charge. The most important feature of this interaction is that a negatively charged particle will be repelled away from the plasma sheath, thus being confined to the plasma volume. This significantly increases the residence time of the particles, allowing them to grow by several orders of magnitude before the electrostatic force is finally overcome by other forces acting on the particles. Most commonly, the chief force which counteracts the electrostatic repulsion is gravity, though experiments have also been performed in microgravity conditions.²⁹ Another important force is the drag force of the gas in flow-through experimental set-ups.

In magnetized plasmas, the magnetic field has also a prominent effect on the behavior of particles, provided they are moving around the plasma volume, rather than being stationary. The effect of the magnetic field is manifested in the curved trajectories of the particles^{37,42}. It also contributes to the confinement of the particles to the plasma volume.

As any non-biased solid surface accumulates electrons from the plasma, we can expect the dusty particles to be negatively charged as well. However, this may not always be the case.

When we consider the particles grown in homogeneous gas-phase reactions in the plasma volume, we should keep in mind that particles acquire electric charge differently in different stages of their growth. The particle growth begins with the formation of negative clusters, that although increasing in size, they never appear to have more than one excess electron. Moreover, the negatively charged clusters are likely to transfer the electron to a positive ion (such as Ar⁺), becoming neutral particles in the process. The electric charge of the clusters then depends on the electron affinity of the samples and the probability of the charge-transfer reaction. By losing an electron, and thus becoming electrically neutral, the growth of the cluster is terminated, as only negative ions engage in growth reactions. Moreover, the neutral particle is not confined by the potential drop and faces the danger of being carried away from the discharge region by the gas drift velocity. By electron attachment, the cluster becomes negative again, and both growth reactions and entrapment by electric field are resumed. Once the clusters reach a certain critical size, the attachment of negative ions becomes more likely than the growth of the original chain of the cluster. Thus, the electric charge can accumulate to greater quantities.

Conversely, when considering bigger particles, the situation is much different. We can consider the surface of the particle as any other plasma facing surface. This means that it will accumulate as much charge as

necessary until the surface achieves the floating potential. This quantity of charge can be calculated if we consider the particle as a spherical capacitor with the capacity C :

$$C = \frac{4\pi\epsilon_0}{\frac{1}{r} - \frac{1}{r+d_s}} \quad (1.5)$$

where r is the particle diameter, d_s is the sheath thickness and ϵ_0 is the vacuum permittivity constant. Of course, this equation is only valid when the particles are spherically shaped, which may not always be the case. The amount of charge, q , accumulated on the particle surface is:

$$q = CU_{fl} \quad (1.6)$$

where U_{fl} is the floating potential of the plasma. Again, this evaluation is valid only when the density of the particles in the plasma is low enough for the particles to be considered as independent.

However, when the density of the dusty particles increases so much that the average distance between particles becomes of the order of the Debye length, it is no longer possible to neglect the effect of the high density of the particles. An immediate effect of the high particle density is that the plasma is unable to provide the particles with enough electrons as required by to sustain the floating potential. Then, the average amount of charge carried by a single particle is:

$$q \approx \frac{n_i}{n_e} q_0 \quad (1.7)$$

where n_i is the density of ions, n_e is the density of electrons in the plasma and q_0 is the elementary charge. In such cases, the majority of the negative charge in the plasma is represented by the solid particles, rather than electrons. Obviously, the plasma can not remain unaffected by the dust particles.

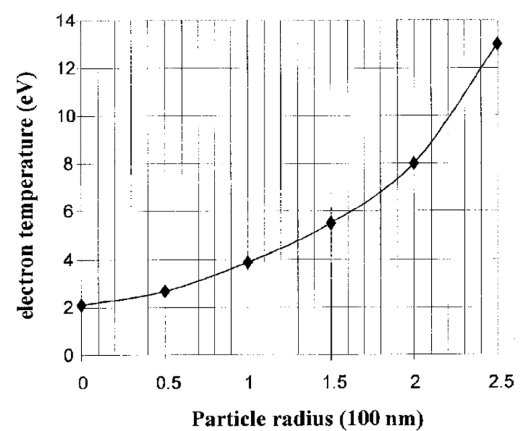


Figure 3: Theoretical prediction of the electron temperature as a function of the dust-particle size, **Figure 8** in⁴³

Slika 3: Teoretična napoved temperature elektronov v odvisnosti od velikosti prašnih delcev, **Slika 8** v⁴³

The most noticeable consequence of the increase of dust population is a significant decrease of the electron population. It has been shown that once the dust particles grow over a certain critical value, the electron density drops for a factor of about 5⁴³.

At the same time, in order to sustain the same rate of ionization, the electron temperature drastically increases, up to 6 – 8 eV⁴³, illustrated in **Figure 3**. This in turn enhances the dissociation of source gas molecules by almost an order of magnitude. This phenomenon can be utilized in plasma processes, where a high degree of dissociation is required, such as PECVD. Particles are introduced into the discharge and effectively extracted (by electric or thermophoretic forces) in order to increase the efficiency of the plasma process. Dust can also cause instabilities in the plasma, which are reflected on the self-bias voltage, emitted light and plasma current^{44,45}.

The dusty particles do not influence only the discharge, but also each other. Once their density increases enough that they can not be considered independent, the interparticle interaction become increasingly important. Independent particles experience a confinement force only in the sheath region, whereas in the plasma volume, they are subject to other forces which govern their movement – gravity, drag forces of the gas flow, thermophoretic forces, etc. Thus independent particles would concentrate around the sheath region – the only place where the electrostatic interaction would counteract other forces, acting on the particles. In dusty dense plasmas, however, the particles fill out a fraction of the plasma volume which is considerably larger than the narrow sheath region, forming a cloud of particles⁴⁶. The cloud is pressed against the sheath, however interparticle interactions are preventing it from collapsing. Particle clouds have been also observed to show collective movement⁴⁷ or even form crystalline structures^{30–32}.

2.3 Deposition of nanocomposite thin films by dusty plasma

Although certain forms of nanocomposite materials have been in use for a long time, the current level of interest appeared – and the term "nanocomposite" was coined – with the advent of diagnostic techniques which allow for analyses of materials on the nanometric scale. Composite materials with nanometric components are particularly interesting because the nano-size of filler particles brings novel properties in practically any aspect, be it mechanical, electric, thermal, optical, electrochemical, catalytic, etc.

Nanocomposite thin films are no exception as they, too, feature very interesting properties and can be used as hard, nonflammable^{48,49} or biocompatible coatings³³, field emitting materials^{50–52}, etc. Such nanocomposite thin films have thus many potential application in the field of aerospace, biotechnology or microelectronics, where they could be used to produce non-volatile memory devices⁵³, light emitting diodes⁵⁴, chemical

sensors⁵⁵, absorbent layers for solar cells⁵⁶, quantum dots⁵⁷, etc.

An example of a biomedical application of such nanocomposite thin films are organosilicon thin films with embedded silver nanoclusters³³. Silver ions and compounds have been long known to exhibit antimicrobial properties⁵⁸, however the price of silver is rather prohibitive for construction of massively used food containers, and due to its mechanical properties, it is also perhaps not the ideal material for medical devices such as orthopedic prosthesis, dental implants, etc. However, by embedding nanometric grains of silver into a matrix of polymer or organosilicon materials, it is possible to have the antimicrobial activities of silver for the price of plastics.

Silver nanograined organosilicon films were prepared in a capacitively coupled radiofrequency plasma reactor by a dual action of a simultaneous PE-CVD in an argon-hexamethyldisiloxane plasma and sputtering of a silver target on the powered electrode, which were applied alternately.³³ During the PE-CVD stage, SiC_xO_yH_z complexes were deposited on the substrate surface and were polymerized. During the sputtering phase, a beam of energetic argon ions was used to sputter atoms of silver from the target. The silver atoms formed silver clusters which were embedded in the matrix. Thusly produced thin films exhibited an improved antifungal activity, which could be put to good use in various bio-medical and other applications.

Another interesting field of plasma deposited nanocomposite thin films are thin films with an amorphous hydrogenated carbon (a-C:H) matrix in which are embedded graphite-like nanograins. The a-C:H was extensively studied as it exhibits low-k and insulating properties, which makes it suitable a material as dielectric in ULSI chips, passivation or optical layer^{59–61}. As a result, the methods of plasma deposition of a-C:H are now at the stage of high control of film quality, high efficiency and reproducibility⁶². Unfortunately, the thermal stability of a-C:H thin films leaves much to be desired – at the temperature of 200 °C, the structure is already degraded, which in turn leads to a degradation of the dielectric properties. Addition of graphite-like nanograins into an a-C:H matrix results in a semi-insulating material with a considerably higher thermal stability. Moreover, such nanocomposite thin films also exhibit photoconductive properties. The carbon-grained, a-C:H nanocomposites can be also used in biomedical applications⁶³. Carbon-based materials are attractive as coatings of prostheses due to their biocompatibility, chemical inertness^{64,65} and non-corrosiveness.

The conventional way of producing such nanocomposites is based on chemical synthesis⁶⁶. It requires several steps involving different procedures, from synthesis of nanoparticles, mixing them with the matrix to the thin film deposition. This leads to a low level of control of the nanocomposite structure and the process

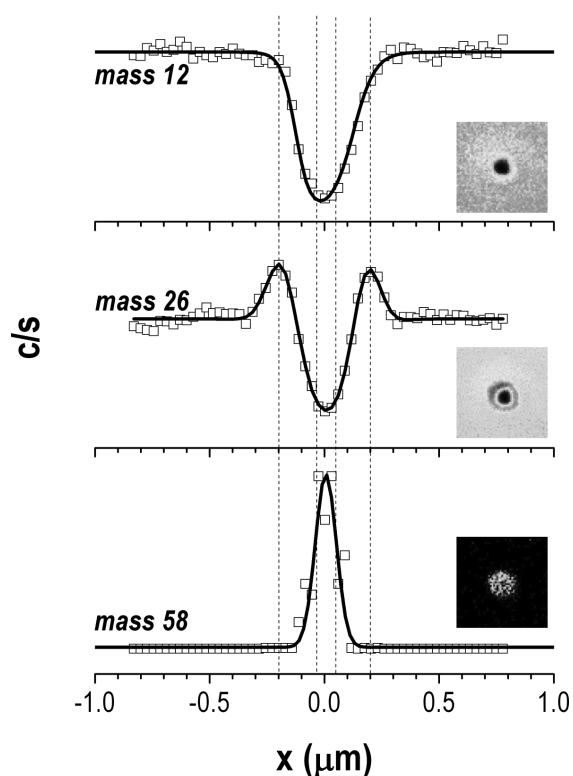


Figure 4: SIMS analysis of particles with a carbon-based shell around a metallic core, **Figure 8c** in³⁷

Slika 4: SIMS analiza delcev z lupino iz ogljika okrog kovinskega jedra, **Slika 8c** v³⁷

reproducibility. In contrast, using a dusty plasma as a deposition tool, the whole process is completed in a single step.

Graphite-like – a-C:H nanocomposites were deposited in a multipolar electron cyclotron resonance (ECR) microwave plasma, created in hydrocarbon containing gases such as methane and acetylene^{37,42}. The key to the growth of powder particles in these cases was the magnetic field of the ECR reactor, which was used to confine the negatively charged particles to the plasma volume. The films were produced at relatively low pressures (0.1 Pa), where heterogeneous, surface-based reactions are much more probable than homogeneous reactions in the plasma volume, however, the magnetic confinement of negative ions facilitated the nucleation and growth of particles in the plasma volume. This procedure resulted in films with an a-C:H matrix and several 100 nm thick graphite-like grains³⁷. However, in certain cases, the grains embedded in the film were found to have a heterogeneous structure. They were composed of an approximately 100 nm thick graphite-like shell around an approximately 20 nm thick metallic core, as seen in **Figure 4**. The metallic core originates in the erosion of the wall materials. Metallic particles enter the plasma where they act as nucleation center for growth of the graphite-like carbon layers.

3 CONCLUSION

Dusty plasma is, by definition, plasma which contains solid particles, usually of micrometric or nanometric dimensions. The particles can enter the plasma either by external injection, erosion of plasma-facing surfaces, heterogeneous surface reactions of plasma species or homogeneous reactions in the plasma volume, or a combination of various methods.

The particles acquire a negative electric charge, which strongly influences their behavior in the plasma volume. The most striking feature is that the electrostatic forces in the sheath region repel them from the walls of the plasma-containing vessel and confine them to the plasma volume. The particles have been observed also to interact with one-another, showing collective movement or forming crystalline structures. Moreover, the population of dust changes the properties of the discharge, where a significant drop in the electron density and a significant increase of the electron temperature are most notable.

The dusty plasmas are presented as an attractive tool for depositing nanocomposite thin films. Contrary to conventional methods where the deposition process involves several steps, in plasma deposition all phases of the process are completed in a single step. Such deposition techniques could be gainfully applied in many industrial and technological applications, ranging from microelectronic industry to aerospace industry and biomedical applications.

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