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Process development for synthesizing core-shell nanoparticles with liquid cores utilizing dusty plasma techniques

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Process development for synthesizing core-shell nanoparticles with liquid cores utilizing dusty plasma techniques*

Munaswamy Murugesu

Abstract

Core-shell nanoparticles synthesized by depositing solid shells around liquid cores are useful as a reusable latent heat storage material. However it is challenging to deposit the shell films around liquid cores. This work demonstrates a process flow to deposit amorphous carbon films around liquid tin nanodroplets retained in a capacitively coupled plasma (CCP). High-pressure magnetron sputtering with a tin target, which was placed at the top of a vacuum chamber was used for synthesizing tin nanoparticles. Tin nanoparticles were transported to CCP at the bottom of the chamber, and they were trapped above the sheath which was formed above the rf electrode. Tin nanoparticles were heated above the melting point by ion bombardment in CCP, then, we deposited shell film (an amorphous carbon film) using plasma-enhanced chemical vapor deposition. Core-shell nanoparticles retained in CCP were collected by applying a positive bias voltage to an electrode placed inside the rf electrode. It was observed that the electrode potential was higher than the plasma potential when a bias voltage of +70 V was applied to the electrode, which enabled the efficient transportation of nanoparticles to the electrode surface. The nanoparticles were analyzed using

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electron microscopy (SEM, TEM), energy dispersive spectroscopy and electron diffraction. TEM images of core-shell nanoparticles showed completely spherical cores, indicating the deposition of amorphous carbon films around melted liquid tin nanodroplets. The melting of tin nanoparticles in CCP was confirmed by estimating their temperatures using a heat transfer theory. We observed the melting of cores, which was detected by the change in the electron diffraction pattern from polycrystalline to amorphous, at the melting point of metal tin. The electron diffraction pattern was obtained while heating core-shell nanoparticles inside TEM. We did not observe the breakdown of the shell films at the melting of the cores, suggesting that the amorphous carbon films were robust against the volume expansion of cores. In addition, the amorphous carbon films protected the core from the oxidation.

Keywords:

Process development, Nanoparticles, Dusty plasma, Liquid droplet, Deposition, Core-Shell.

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Nomenclature

n_e	: electron density
n_i	: ion density
n	: plasma density
λ_D	: debye length
T_e	: electron temperature
k_B	: Boltzmann constant
k	: heat capacity ratio (c_p/c_v)
ε_0	: permittivity of Vacuum
e	: charge of electron
J	: Bohm current
V_f	: floating potential w.r.t plasma potential
V_p	: plasma potential
v	: velocity of charged particles
$\vec{v}$	: drift velocity
B	: magnetic field
$\vec{B}$	: magnetic field vector
E	: electric field
$\vec{E}$	: electric field vector
m_i	: mass of ion

ω_c	: cyclotron frequency
r_L	: Larmor radius or gyro-radius
C	: capacitance
m	: mass of charged particles
q	: charge of charged species
PCM	: phase change material
CVD	: chemical vapor deposition
CCP	: capacitively coupled plasma
RF/rf	: radio frequency
V_d	: discharge voltage of sputtering
a	: nanoparticle radius
Q_d	: particle charge
IG	: initial growth phase
GS	: growth saturation phase
RG	: rapid growth phase
F_{es}	: electrostatic force
E	: electric field
F_g	: electrostatic force
m_d	: mass of nanoparticle
ρ_d	: mass density of liquid tin
g	: acceleration due to gravity
F_{th}	: thermophoretic force
k_n	: thermal conductivity of the gas
$v_{th,n}$	: thermal velocity
∇T_n	: gradient of the gas temperature
F_{drag}	: total drag force
F_i	: ion drag force
F_{dir}	: collection force
F_{Col}	: Coulomb force

F_n	: neutral drag force
Δp	: momentum transfer
σ_c	: cross-section of interaction
v_{rel}	: relative velocity
v_s	: mean velocity
u_i	: mean velocity
$b_c, b_{\frac{\pi}{2}}$	: collision parameter
V_B	: dc bias voltage
q_H	: heating energy flux by ion bombardment
ε_i	: ionization potential of argon atom
T_i	: temperature of argon atom
T_g	: gas temperature
T_p	: particle temperature
σ	: Stefan Boltzmann constant
q_R	: heat energy flux of radiation cooling
ϵ	: emissivity of the nanoparticle
a_c	: absorptivity of the nanoparticle
α	: accommodation coefficient
γ	: surface tension
h	: Planks constant
c	: speed of light
B_{12}	: Einsteins B coefficient for absorbing
ν	: laser frequency

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1 Introduction

1.1 Background

Energy management is a common interest in recent years across institutions and scientific communities with increasing awareness over sustainable development goals. In recent decades, throughout the world, economists, scientists, and engineers are actively looking at 1) the strategies to reduce the energy demand, 2) techniques to ensure the security of the supplies, 3) technical advancements in power systems to increase the energy efficiency, and 4) new and renewable sources of energy that can replace the limited and harmful fossil fuels [1].

From the research findings by Farid et al. [2], it can be noted that the heat is stored as the latent heat by the fusion of a commercial paraffin wax. This supports the existing storage heaters which are in use, which utilize the sensible heat storage technique. The convection mechanism of heat transfer is predominant in applications, but there is a mention about the necessity of further developments in the technique. Bruno et al. [3] reported the possibility of significant energy saving from tube-in-tank type thermal energy storage systems (domestic space cooling systems), which were built using phase changing material (PCM). The PCM material used in the findings have the melting point of 10 °C. Buchlin et al. [4] reported the numerical optimization of solar heat storage based on encapsulated PCM which was useful in air heating systems and reducing volume

storage devices. It is certain that applications of PCMs can help to improve efficiency of thermal energy storage devices, which in turn compliments the need for reducing the mismatch between the supply and the demand in thermal energy [2–4].

In general, different forms of energy that can be stored are mechanical, electrical, and thermal. In this research, the mechanical (gravitational, flywheels, compressed air) and electrical (batteries) storage are not considered while thermal energy storage is discussed. Thermal energy storage can be achieved by cooling, heating, melting, solidifying, or vaporizing a material with the energy becoming available as heat when the process is reversed. Thermal energy storage can be classified as latent heat thermal energy storage, sensible heat thermal storage and chemical energy storage [5, 6]. The schematic of thermal energy storage with the common classifications are given in figure 1.1. In this research, sensible heat storage (liquid, solid), chemical energy storage (sorption, chemical reaction) are not considered while latent heat storage (PCMs) is discussed. Latent heat storage is a method of storing heat in a phase change material that utilizes the large latent heat of phase change during melting. Latent heat storage has the advantages of high heat storage density and easy to control the working temperature range and strong security. Out of the three types of PCMs such as inorganic (salt, salt hydrates), organic compounds (fatty acids, polymeric materials) and molten salt and metal based PCMs, the metal based PCMs are discussed in this research. Alloys or pure metal based PCMs exhibit promising properties for high-temperature applications due to their high thermal storage density and excellent thermal conductivity (with high latent heat value). Sensible heat and latent heat storage materials are an important class of modern materials, which have significant contributions in efficient use and storage of heat (waste, solar). King Pielichowska et al. [5] have mentioned that the storage of latent heat provides

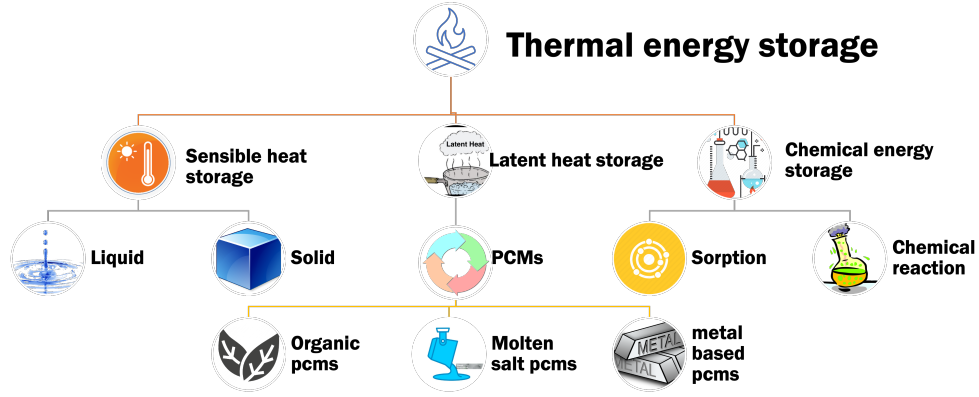


Figure 1.1: Thermal energy storage classification

greater density of energy storage, with small difference in temperature between storing and releasing heat, than the sensible heat storage method. The schematic representation of the PCM and its response on heating and cooling can be seen in figure 1.2, which shows the temperature rise and cool on heating and cooling, respectively.

The latent heat storage method relies on the storage material absorbing or releasing heat when it undergoes a solid to liquid (or liquid to solid). In other words PCMs can be defined as the materials that stores thermal energy utilizing the latent heat [7]. On reading through the PCMs in thermal storage systems, the quest arises on the methods to synthesize PCM based core-shell type nanoparticles. Generally, core-shell nanoparticles are prepared in two steps, namely preparation of core and synthesis/deposition of shell layers. According to different principles, the synthesis methods can be discussed under four categories 1) Mechanical mixing, 2) Solid phase reaction, 3) Liquid phase reaction, and 4) Gas phase reaction [8]. In mechanical mixing method, two or more particles with

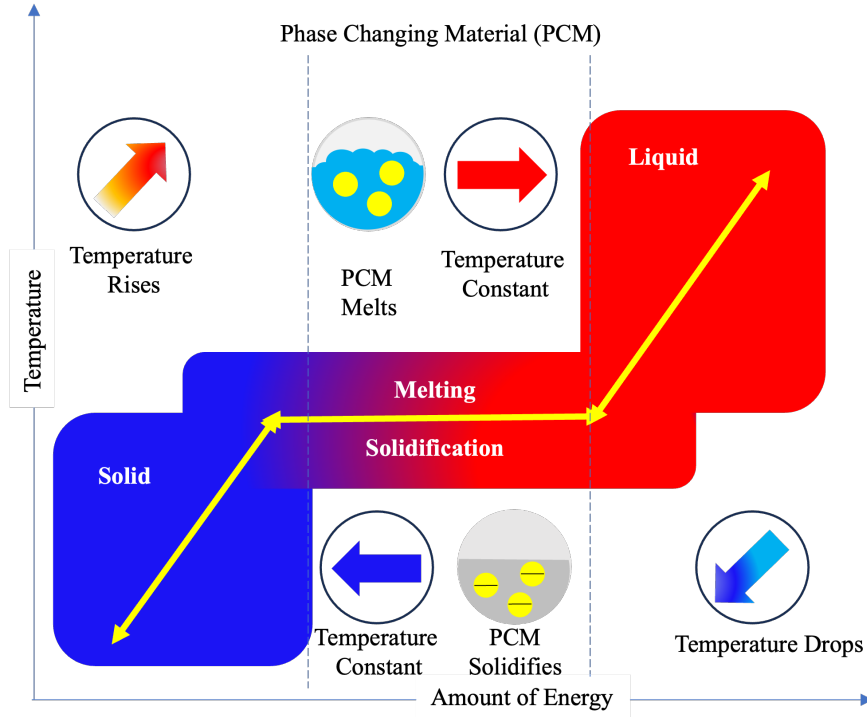


Figure 1.2: Phase changing material (PCM)(Gokhan et al. [20])

good adhesion or adsorption properties at a certain temperature can be evenly adsorbed on the surfaces of the modified particles by convection and diffusion. Afterwards, under the action of external forces (aerodynamic force, gravity, and mechanical force), the particles are closely combined to cover the surfaces of the target particles, thus completing the surface modification or recombination. The process of the solid phase reaction method is that the core materials and shell precursors are sufficiently mixed and calcined according to the required ratio to obtain superfine coated particles. The common ways that are used to obtain this mixing, including solution dispersion, decomposition, mechanical stirring, grinding, and ball-milling. The solid phase reaction method is commonly used for the synthesis of inorganic core-shell nanoparticles. The liquid phase reaction

method refers to the chemical reactions under a wet environment to deposit the film on the surface of pre-formed particles. Compared with other methods, this is widely used in the laboratory and industry to prepare core-shell nanoparticles. The commonly used liquid phase reaction methods include the sol-gel method, hydrolysis method, electrochemical method, hydrothermal method, and emulsion polymerization.

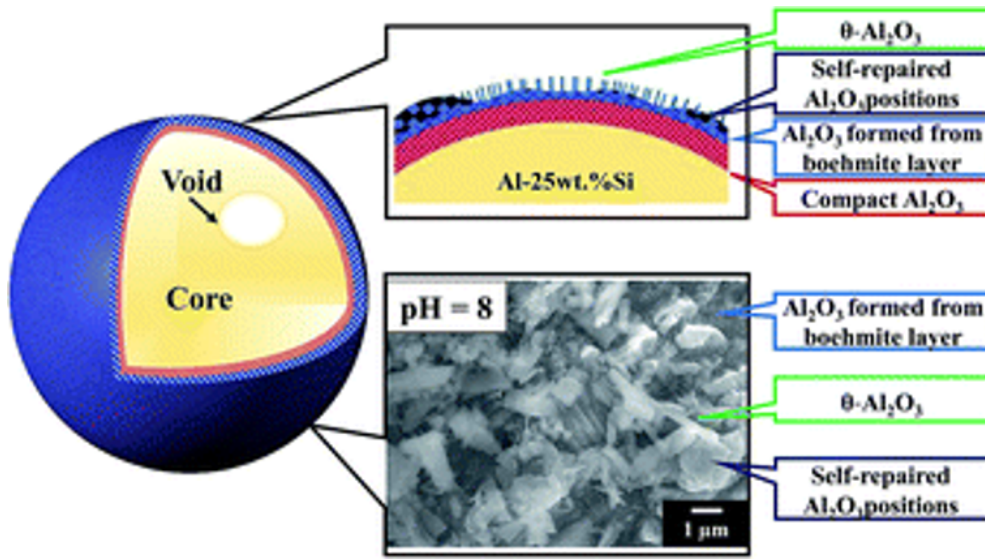


Figure 1.3: PCMs with void to accommodate volume expansion (Sheng et al. [22])

The gas phase reaction method is used to deposit the shell materials in the gas phase supersaturated system on the surfaces of the target particles to form the core-shell nanoparticles, and the method mainly includes physical vapor deposition (PVD) and chemical vapor deposition (CVD). In PVD, the vapor material from solid targets under vacuum conditions are transported by low-pressure gas or plasma to deposit on the surfaces of the core materials. As for CVD, it mainly includes the chemical reactions of gases or steams on the surfaces of core materials to form target core-shell particles. The CVD method can be divided into many forms such as the plasma method (PECVD), atomic-layer CVD (ALCVD),

combustion CVD (CCVD), hot filament CVD (HFCVD) etc. Furthermore, CVD is normally used to deposit materials in ways that are difficult to obtain using traditional techniques. In this gas phase reaction method for nanoparticle synthesis, several attributes uniquely differentiate dusty plasmas from other synthetic routes, such as colloidal solutions or flames. Further, Dusty plasmas refer to plasmas that contain charged solid or liquid particles, commonly known as dust. The interest in the use of non-thermal dusty plasmas for the synthesis of functional nanocrystals were often focused on silicon for use in novel electronic and optical devices. Effective dusty plasma synthesis techniques were developed both at low pressure and atmospheric pressure. In recent years, dusty plasma synthesis of nanoparticles was extended to a wide range of materials, including carbon based materials, metal oxides, sulfides, nitrides, and elemental metals as well as alloys.

The following are the metal based PCM synthesizing methods. Zhuo et al. [19] synthesized micro encapsulated Al-Cu alloy PCMs with a flexible shell by using thermal oxidation and calcination methods. Shell is formed by oxidizing the thin outerlayer from Al-Cu using electric furnace. Wang et al. [21] reported the findings on synthesizing S_nBi_{58} alloy PCM using double -layer coating, sacrificing inner layer methods. In the process, a thermal expansion void was constructed to accommodate volume expansion of PCM. Sheng et al. [22] prepared metal based PCM composed of an Al-Si alloy core (Al-25 wt % Si, with melting point of 577 °C) and a self-healing Al_2O_3 shell. In this method also, the void is prepared to accommodate the volume expansion while checking for leakage or cracks for about 1000 and 3000 thermal cycles. The inclusion of void in the core-shell particles by Sheng et al., was shown in figure 1.3. Comparison of the different methodologies for fabrication of metal based PCMs were summarized in Table 1.1., and the phase change temperature distribution were presented in figure 1.5. In particular, the core materials of PCMs are mostly aluminum and aluminum-

based alloys, in addition to tin, indium, gallium, zinc and their alloys are used. The shell materials of metal based PCMs are mainly inorganic shell materials, mainly including Al_2O_3 , SiO_2 , TiO_2 , CaCO_3 , SnO_2 etc.

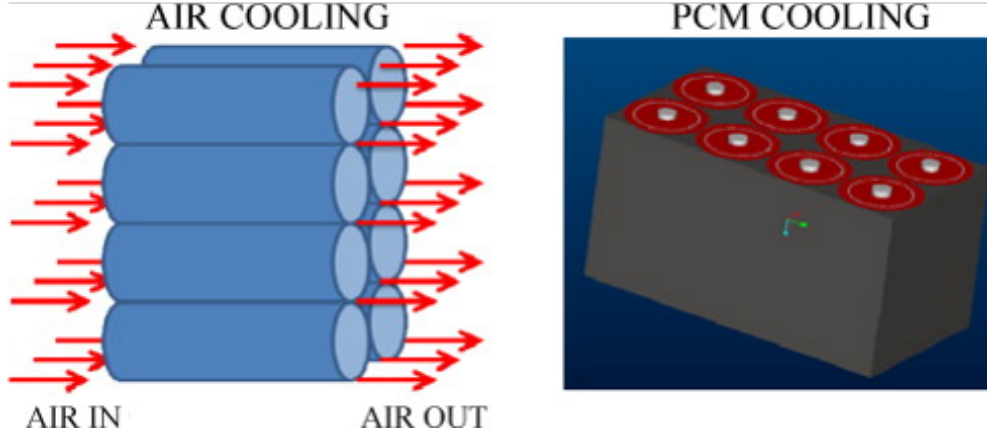


Figure 1.4: Schematic of active (air) cooling vs. passive (PCM) cooling (Riza et al. [16])

PCMs are very well considered attractive for solar applications [23], space heating, cooling in buildings [9], off peak energy storage, and heat exchanger improvements [15]. Teamah et al. [23] reported the effectiveness of using cascaded phase changing materials with multi tank thermal storage system for multi residential solar domestic hot water applications. This also enabled the reduction in storage volume without compromising the solar fraction compared with undersized water based storage systems. Kuta et al. [15] are focussing on storage systems for geothermal energy sources towards heating systems of single family residential buildings. They demonstrated mobilized thermal energy storage (M-TES) type systems based on PCMs. Riza et al. [16] developed an alternative cooling system using PCMs to enhance the safety of Li-ion battery packs. From the findings, it is observed that the compact and properly designed passive thermal management system utilizing PCM provides faster heat dissipation than active cooling during

Table 1.1: Different methodologies for fabrication of metal-based PCMs

Methodology	Advantages	Disadvantages
Facile self oxidation [10]	Handy operation Uniform shell thickness Dense shell	Consumption of raw materials Limited applicability Single function
Sol-gel polymerization [11]	Various shell materials Inorganic shell with relatively high thermal conductivity Conductive to the development of multifunctional microcapsules	Relatively complex preparation process
In situ polymerization [12]	Various shell materials Uniform shell thickness	Difficult to control the morphology
Atomic layer deposition [13]	Physical process Controllable shell thickness	Costly The process must be continuous
CVD [14]	Chemical process Accurate control	Costly Complex operation

high pulse power discharges while preserving sufficiently uniform cell temperature to ensure the desirable cycle life for the pack. Normal air cooling and PCM based active cooling that was observed in Riza et al., findings can be in figure 1.4. Similar designs are adopted in designs for active building cooling system aswell by sandwiching with concrete or in the doors etc [17]. This arrangement keeps the designed temperature level at different thermal conditions. For electronic devices with pulsed heat flux density, the PCM-based heat sink can effectively absorb the heat during pulse operation and return to the device for devices during

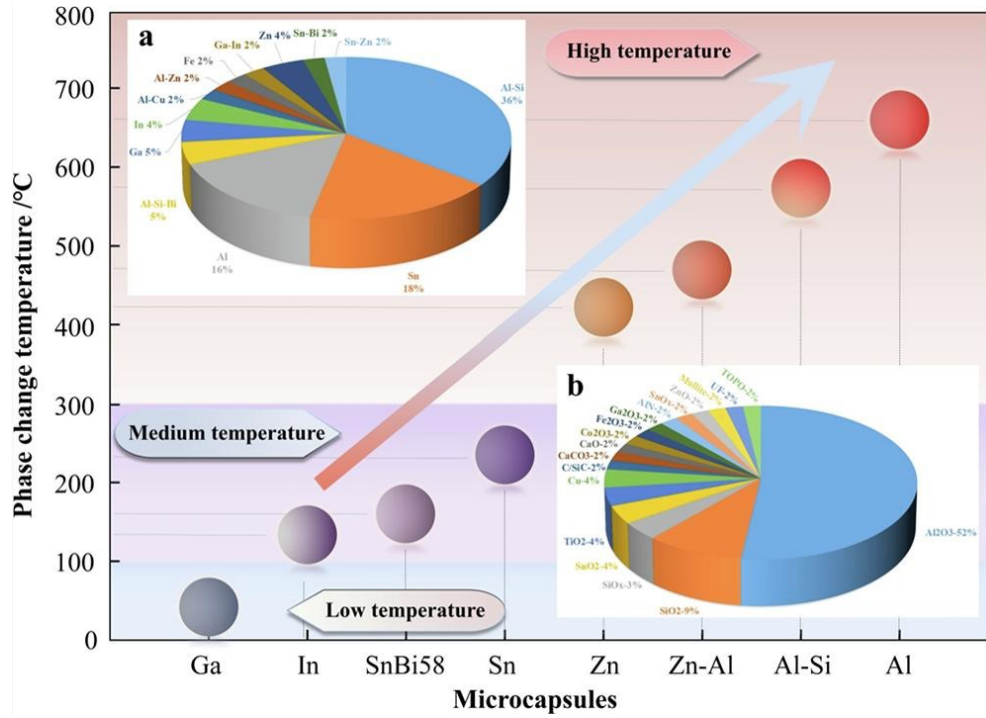


Figure 1.5: PCMs phase change temperature distribution. Core (a) and shell (b) materials used in microencapsulated metal-based PCMs (Shuo Wang et al. [18])

low-temperature operation [24], so electronic devices working temperature can be relatively stable.

From the recent review by Wang et al. [18], it can be observed that among the synthesis methods for metal based PCMs, facile self-oxidation method is the most mature, the PCMs from this method are having good thermal cycle performance and can withstand up to 3000 thermal cycles with no significant attenuation of performance. But it is suitable for less metals, mainly used for the preparation of PCMs of Al and Al-Si alloy for the compactness of alumina layer. In addition, because the PCMs prepared by this method has fixed structure and poor changeability, its function is relatively single and it is difficult to load

other functional particles. On the contrary, the double-layer coating, sacrificial inner layer method based on sol-gel polymerization, so far the most effective and promising method for preparation of metal-based PCMs in recent years. Due to the void design in PCMs from this method, the volume change of core material during phase change can be effectively solved, so as to reduce leakage and enhance the thermal stability of PCMs. Moreover, authors find this is flexible in the operation process. But, if the method can address the substitute for including void is more advantageous such as CVD based method, which gives accurate process control.

1.2 Problem Definition

From the existing literature, it is clear that there is need for effective methods that can enhance energy storage, as well as the effective methods to produce materials that can be used as PCMs for latent heat storage. In this research, the main focus is on producing nanoscale core-shell particles with liquid cores that can be used as PCMs. The nanometre sized PCMs can be used as suspension to cool semiconductor chips in data centers [25] and automobiles, [26] and it can make effective use of the waste heat. For using phase change from solid to liquid in thermal energy storage, it is necessary that the PCM material is coated with another material that has a higher melting temperature [27,28], such as core-shell nanoparticles. A problem of core-shell PCMs is the stress on the shell when the core melts. The melting of a solid state material results in the expansion of its volume, and the multiple stresses due to the repetitive core expansion may cause the breakdown of the shell.

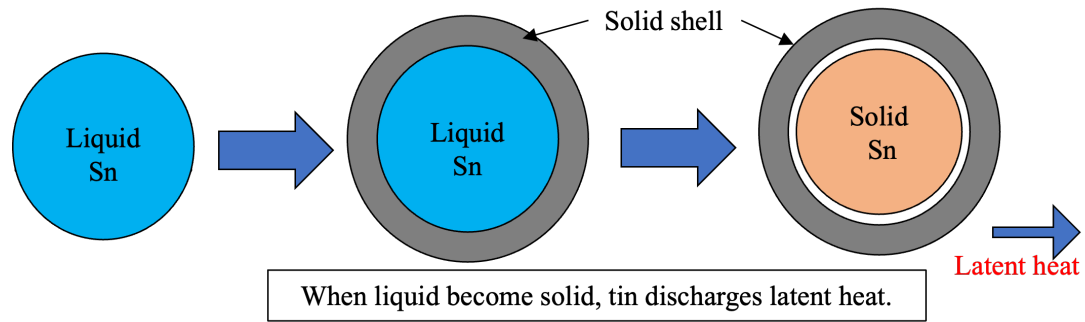


Figure 1.6: Schematic of core-shell tin particle

A solution to this problem is to use Al-25wt%Si for the core, which has a negligible volume expansion at the melting [29,30]. However, since the negligible volume expansion at the melting is realized only in the specific material with a fixed melting point, such materials cannot be used in various temperature ranges.

The issue is solved if we can deposit shell around liquid core. This is because the volume of the liquid core is already expanded before the deposition of the shell. We can expect the shrinkage of the cores if core-shell nanoparticles thus synthesized are cooled down. The shells are not subjected to the stress due to the volume expansion at the remelting of the cores. If the shell material has a higher melting point than the core, it is possible to avoid the breakdown of the shell at the melting of the core. The schematic of proposed solution to realize reusable core-shell PCM is shown in figure 1.6, where tin is used as the core material.

1.3 Objectives

The objective of this work is to establish a synthesis technique for core-shell nanoparticles with melted cores. In general, it is difficult to deposit a thin film uniformly around a liquid droplet. If the droplet is placed on a substrate, it cannot remain the spherical shape and the thin film cannot be deposited on the bottom side of the distorted droplet. We have found the possibility to use a dusty plasma technique in this work [31]. The dusty plasma allows nanoparticles to remain suspended in the space [32]. Further, considered the tin for the core material, tin nanoparticles trapped in the plasma are melted by the heating due to ion bombardment in the plasma. In this work, we deposit amorphous carbon films around tin nanodroplets by plasma-enhanced chemical vapor deposition using methane. The results are analyzed along with the discussion on the robustness of the amorphous carbon shell against the oxidation and the volume expansion at the remelting of the tin core.

1.4 Structure of Thesis

This thesis is divided into 6 chapters from the Introduction to Conclusions.

Ch.1 Introduction: This chapter includes the background literature of this research which includes the need for effective energy management methods, types of thermal energy storage methods and PCMs based thermal energy storage techniques. Also discussed the problem definition with the proposed solution.

Ch.2 Principles underlying the nanoparticles production, transport, retention and collection: This chapter describes underlying physics for generation, heating and transportation of core shell nanoparticles. Also included about particle growth and common forces acting on particles in dusty plasmas along with comparison.

Ch.3 Experimental methods: This chapter discusses the details of experimental setup and methods that are used in the synthesis process to produce core-shell nanoparticles applicable for PCMs. In addition, the configurations used in Langmuir probe measurements, Laser Mie scattering, Gas temperature measurements and Plasma potential using QMS are also described.

Ch.4 Results: This chapter gives the results obtained by experiments to obtain PCMs. Such as synthesis of particles along with their characterization using microscopic techniques. Melting of core against heating and the diffraction pattern on phase change is also described.

Ch.5 Discussion: This chapter gives the discussion from experimental results.

Ch.6 Summary: This chapter includes the conclusions derived by this study followed by future scopes.

2 Principles underlying core-shell nanoparticles generation, growth and collection

2.1 Plasma definition and features

Examples of Plasmas

Plasma can be defined as partially or fully ionized gas consisting of free charged particles (electrons and ions ($n_e \approx n_i$)) and neutrals moving in random directions. The schematic is depicted in figure 2.1. Plasma is the state of matter heated beyond its gaseous state such that the atoms are stripped of at least one electron in their outer shells so that what remains are positive ions and free electrons. It implies, with an increase in temperature, the atoms become more energetic and transform matter in sequence: solid, liquid, gas, and finally plasma which justifies the title, the fourth state of matter. In daily life, in the following two situations, the presence of plasma could be observed: fluorescent lamps and the lightning at earth's surface. However, almost everything outside the earth's ionosphere is in the form of plasma state. Additional examples of plasma are auroras, solar winds, magnetosphere of earth and jupiter, gaseous nebulae, galactic arms, quasars,

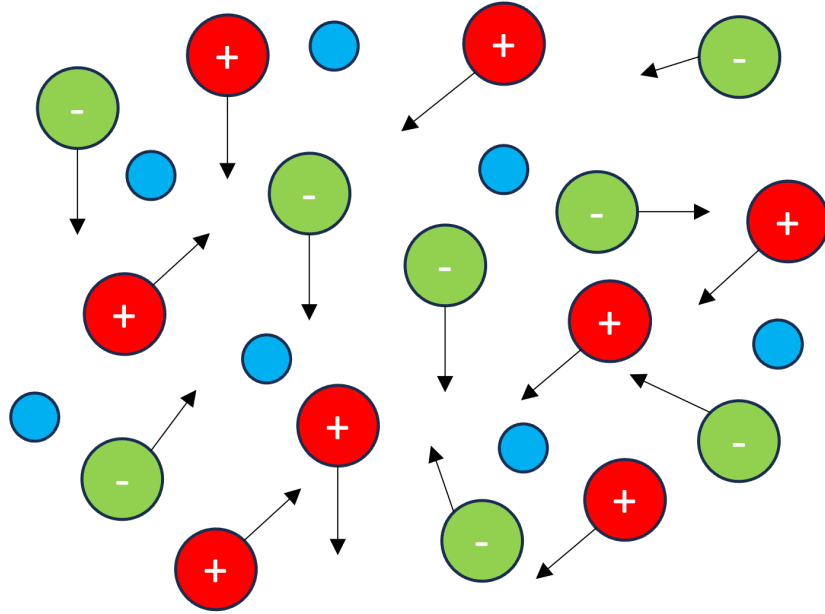


Figure 2.1: Schematic of a plasma showing charged particles movements in the random directions.

pulsars, novas, black holes and fires [33]. Artificially plasma can be generated from neutral gas by heating or subjected to strong electric field up to the state where ionized gaseous particles become electrically conductive, and the behavior of the matter is dominated by the electromagnetic fields in long-range [34]. From recent innovations, the plasma ion engine is developed and adopted in flight of the space probe Hayabusa, Japan [35]. On the other hand, plasma processing is one of the widely used process technologies in microelectronic industry for thin film deposition and etching. Plasma application can also be seen in surface modification, flat panel display fabrication, plasma spray, fabrication of solar cell, plasma micro-discharge and many other growing areas [36]. Recently studies on sterilization and the growth stimulation of the plant have been pushed forward.

Debye Length and Sheath

A fundamental characteristic of the plasma behavior is the ability to shield out electric potentials of individual charged particles that are exposed in it, which is known as Debye shielding. The shielding (electrostatic shielding) of an external electric field from the interior of a plasma can be viewed as a result of high plasma conductivity. This shielding and characteristics of plasma can be further understood by analysing the Debye length. The Debye length indicates the characteristic length in the plasma to which an influence of particular charge can be felt. The electric field caused by the charge is not detected at a distance beyond the Debye length. In other words, the Debye length is the distance over which significant charge separation cannot occur. A space charge can exist within the Debye length. The Debye length λ_D can be expressed by Equation 2.1.

$$\lambda_D = \left(\frac{\varepsilon_0 k_B T_e}{n_i e^2} \right)^{\frac{1}{2}}, \quad (2.1)$$

where T_e , n_i , k_B , and ε_0 are electron temperature, ion density, the Boltzmann constant, and the permittivity of vacuum, respectively. The Debye length increases with the increase in the electron temperature whereas decreases with the plasma density n . For example, Debye length is $140 \mu\text{m}$ for $T_e = 4 \text{ eV}$ and $n_i = 1 \times 10^{10} \text{ cm}^{-3}$.

The Debye shielding is valid when the characteristic size of an object immersed in a plasma is smaller than the Debye length. If the potential of the object is lower than the plasma potential, the ion current toward the object is approximated by the orbital motion limit (OML) theory [37]. In contrast, if the size of an object immersed in a plasma is much larger than the Debye length and the potential of the object is lower than the plasma potential, a layer with the positive space charge, which works for shielding the potential of the object, is formed between the plasma and the object. This layer is called the sheath. According to the

standard Bohm theory, the ion current density towards the object through the sheath is fixed at the Bohm current $J = 0.6ne\sqrt{\frac{k_B T_e}{m_i}}$, where n , e , k_B , m_i and T_e are the plasma density at the start of the pre sheath, charge of electron, Boltzmann constant, mass of ions, and the electron temperature respectively. Note that the Bohm current is independent of the potential difference between the plasma and the object, and in this case, the OML theory cannot be adopted. The thickness of the sheath is usually longer than the Debye length.

Cyclotron Frequency and Larmor Radius

If the plasma is produced in a magnetic field (B field), the motions of the charged particles are affected by the B field and makes the plasma an anisotropic medium. As long as the ion or electron with charge q is moving, it experiences a Lorentz force $q\vec{v} \times \vec{B}$, which is perpendicular to both the directions of the velocity and the magnetic field. This Lorentz force has no effect on the velocity component along the magnetic field, but the velocity components perpendicular to the magnetic field are affected, and the motion of charged particles projected onto the plane perpendicular to the magnetic field becomes circles. The frequency ω_c (the cyclotron frequency) of this circular motion of particle can be represented by the equation

$$\omega_c = qB/m, \quad (2.2)$$

where q and m are charge and mass of the charged particle, respectively. The radius of this circular orbit is called the Larmor radius or the gyro-radius (r_L). The cyclotron frequency is independent of the velocity of the charged particle but the Larmor radius r_L depends on the velocity (v). The expression of the Larmor radius is given by [38]

$$r_L = mv/qB. \quad (2.3)$$

If the Larmor radius is smaller than the size of the vessel and the collision frequency is much lower than the cyclotron frequency, we call that the charged particles is magnetized. Since the electron Larmor radius is much shorter than the ion Larmor radius, electrons are magnetized more easily than ions.

$\mathbf{E} \times \mathbf{B}$ Drift

The orbits of charged particles are different from the cyclotron motions if both the electric and magnetic fields are applied. The analysis of the orbit is rather easy by solving the equation of motion when the magnetic field is perpendicular to the electric field. The orbit in this case is so called cycloid motions, i.e., the orbit becomes the superposition of the successive quad semicircles and the constant velocity in linear motion. This orbit is called the $\vec{E} \times \vec{B}$ drift. The drift velocity or the velocity of the linear motion is given by E/B , and the direction of the linear motion is perpendicular to both the electric and magnetic fields such that,

$$\vec{v} = \frac{\vec{E} \times \vec{B}}{|\vec{B}|^2}. \quad (2.4)$$

2.2 Principles of CVD and PECVD

Principles of CVD

Chemical vapor deposition (CVD) is one of the foremost in the family of processes whereby a solid film is deposited using a vapor produced from a gas by a chemical

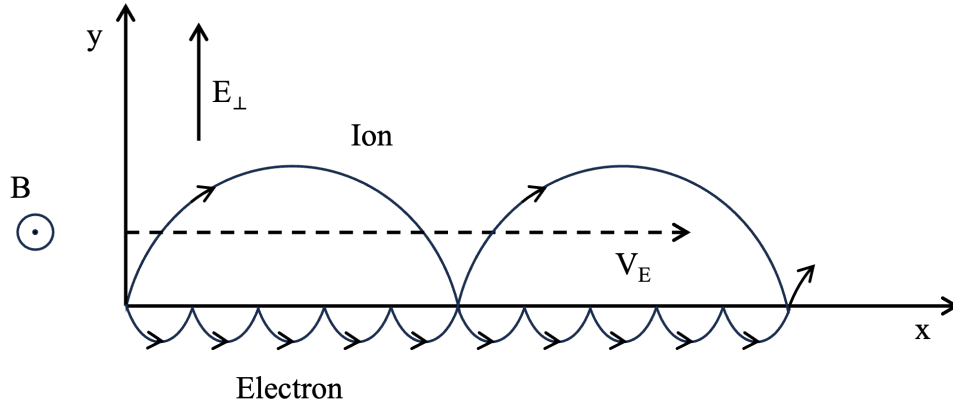


Figure 2.2: Motion of electrons and ions in uniform crossed E and B fields

reaction on or in the vicinity of a heated substrate surface. On the other hand, in the physical vapor deposition (PVD), the vapor is produced from a solid-state material. In CVD, the resulting solid material from vapor is usually in the form of a thin film, but the formations of powders and fibers are also possible by CVD. It is possible to produce most metals and many non-metallic materials including large number of compounds such as nitrides, carbides, oxides and more. It is one of the most used technologies in semiconductor manufacturing industries. CVD is a preferred process in many cases due to its advantages, such as thick coatings can be obtained (some cases up to centimeters thick), and flexible to the changes in deposition of different elements.

Principles of Plasma Enhanced CVD

Even if we do not apply the thermal energy, the condensable radicals are created by the decomposition of precursor gases via electron impact dissociation. In the early reviews, it is used as glow discharge deposition and subsequent reviews it is referred to as plasma deposition, if we employ non equilibrium plasmas.

In the recent reviews, it is referred to as plasma assisted or plasma enhanced chemical vapor deposition (PA or PECVD). PECVD is a well established thin film deposition technique which is useful in producing various types of films. It has very strong position in semiconductor industry due to its applicability to produce coatings on surfaces that would usually not withstand the high temperatures in more conventional CVD processes. The main advantages of PECVD over conventional CVD are good conformity, tighter control of thin film process and high deposition rates along with the low deposition temperatures.

Differences between CVD and PECVD

In thermal CVD a high temperature is necessary to dissociate molecules to form radicals, which are the real precursor for the deposition. In PECVD, high temperature is not necessary since radicals are produced by electron impact dissociation. Note that this is the most important feature of "nonequilibrium plasma", where electrons have much higher energy (temperature) than molecules. PECVD is a vacuum based process usually performed in pressures < 0.1 Torr, allowing a low substrate temperatures. Due to the low temperatures and less stress while depositing using PECVD, the film interface will have stronger bonding. Standard CVD temperatures are usually in the order of 600 °C to 800 °C while PECVD ranges from the room temperature to 350 °C. PECVD can be effective in producing unique compounds and films that are difficult with standard CVD techniques. The deposition at a low temperature directly relates to the synthesis process in this research.

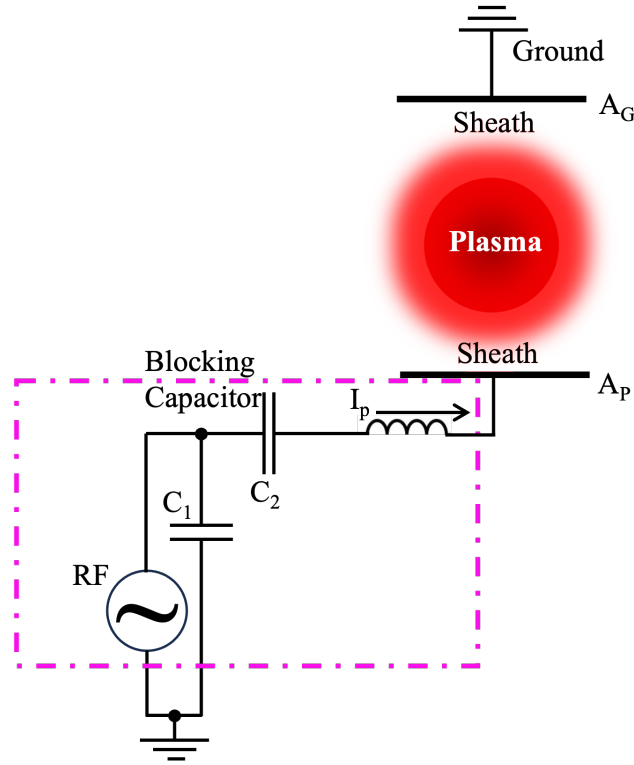


Figure 2.3: Schematic of CCP discharge system

2.3 Features of CCP Discharge

A capacitively coupled plasma (CCP) is one of the most common types of industrial plasma sources. An electrode in CCP system is connected to a radio frequency (RF or rf) power supply, via an impedance matching network. Figure 2.3 shows the CCP system with an impedance matching network schematically, where a capacitor in the impedance matching network plays the role of the blocking capacitor. The production of a stable plasma is impossible if the ion and electron currents from the plasma to the rf power supply, integrated over the period of an rf cycle are not equal. If the blocking capacitor is inserted between an electrode and the rf power supply, a negative dc potential, which is called the

self bias voltage, is formed on the electrode, and the electron and ion currents which are integrated over an rf cycle can be equal. Since 13.56 MHz, which is a typical rf frequency in CCP, is much higher than the ion plasma frequency, the ion motion cannot follow the potential fluctuation at the rf frequency, resulting in the formation of a quasi-dc sheath above the powered electrode.

2.4 Features of DC magnetron sputtering

Magnetron discharges are produced by applying a magnetic field parallel to the cathode surface. Since the electric field is perpendicular to the cathode surface, electrons perform the $\vec{E} \times \vec{B}$ drift motion. If the cathode is planar, the $\vec{E} \times \vec{B}$ drift directs the theta direction, resulting in a closed ring orbit. The discharge systems that utilize $\vec{E} \times \vec{B}$ drift is, in general, called "magnetron discharges". The $\vec{E} \times \vec{B}$ configuration with the closed drift ring is efficient for the confinement of electrons, resulting in high-density plasmas. The high-density plasma is placed in the vicinity of the cathode, and the cathode surface is bombarded by positive ions with a high flux, resulting in a efficient ejection of atomic species from the cathode. A typical configuration of the magnetron sputtering discharge is illustrated in figure 2.4. The radius of the $\vec{E} \times \vec{B}$ ring on the target is determined by the shape of the magnetic field lines, while the thickness of the $\vec{E} \times \vec{B}$ drift is about the Larmor radius (≈ 0.5 cm) Typically, at a pressure of 5 mTorr (argon), a high current density of about 20 mA/cm² and a discharge voltage (V_d) of 600 V are possible to realize.

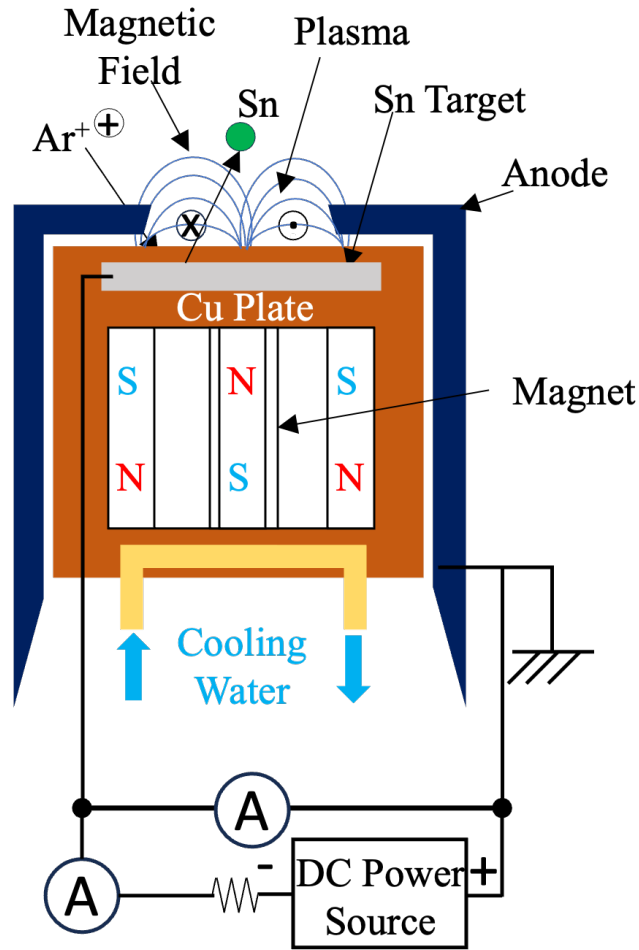


Figure 2.4: DC magnetron sputtering system

2.5 Charging of particles in plasma

Fine particles in plasmas are negatively charged if the surfaces of particles act as a surface of a condensed material. This is because the particles are isolated in the space, and it is not connected to any circuit components. In such case, we have to imagine that the flux of charged species towards the surface must be effectively zero. This situation is realized when the fluxes of electrons and ions

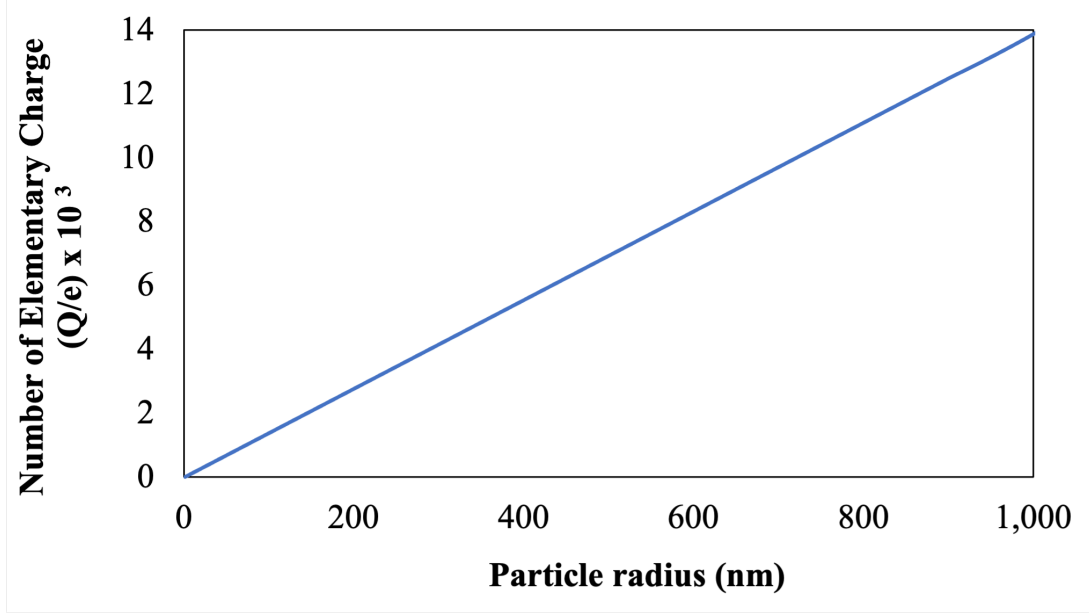


Figure 2.5: Particle charge as a function of particle radius

are balanced. Considering the smaller mass of electron than ion, the potential of the particle surface, which is called the floating potential, is negative with respect to the plasma potential. The negative potential is realized by the accumulation of negative charges. This is the mechanism of negative charging of particles sustained in the plasma. Since the capacitance (C) of a sphere with a radius a is $4\pi\epsilon_0 a$, the amount of the negative charge accumulated on a particle in the plasma is given by

$$Q = CV_f = 4\pi\epsilon_0 a V_f, \quad (2.5)$$

where V_f is the potential difference between the plasma and the particle, which is given by the floating potential with respect to the plasma potential. Under the assumption of $V_f = 20$ V, the number of charge Q/e with e being the elementary charge is plotted in figure 2.5 as a function of the particle radius.

2.6 Growth of nanoparticles in plasma

In plasmas, fine particles are often generated by gas phase reactions of chemically active species and its growth process has been discussed in this section. Particle growth and coagulation between negatively and positively charged particles are discussed under the following three phases as depicted in figure 2.6.

Initial Growth (IG) Phase

In order to elucidate the growth kinetics of clusters in the IG phase, it is important to get information about the kinds of reactive species (precursors) which are responsible for their formation, the region where the precursors are produced, and multistage reaction processes up to nanometers in size. In this phase, in order to differentiate the particles from the next subsequent phases, the fine particles are referred as clusters (size < 10 nm). According to the Boufendi et al. [39], crystallites (clusters) are formed by nucleation of atomic or molecular species (precursors).

Rapid Growth (RG) Phase

At the start of this phase, a large proportion of particles tend to be electrically neutral, and a small fraction tends to be negatively and positively charged, because of a statistic fluctuation of charges. RG phase starts while particles colliding into one another and sticking (a process often called as the coagulation), grown particles gets charged negatively by collecting electrons from the plasma. Further the growth is accelerated by attracting more strongly positively charged particles. This growth continues until most of the particles have negative charges.

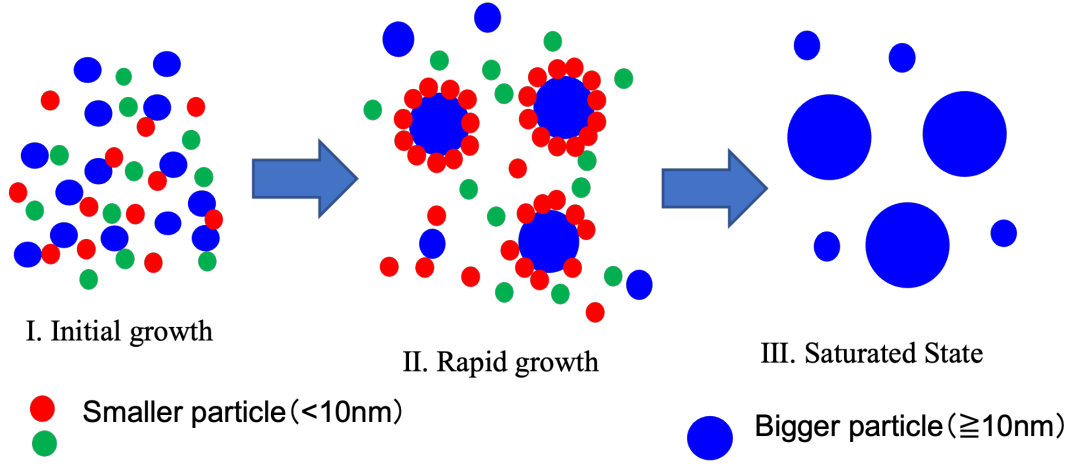


Figure 2.6: Particle growth in plasma

Growth Saturation (GS) Phase

In this phase, the particle growth is saturated by the disappearance of positively charged clusters. The further growth of the particle size is owing to the transport of mono radicals, positive ions and higher order species. In this phase, the electron density n_e tends to be lower than the ion density n_i because large proportion of the negative charge to keep the space charge neutrality is sustained by negatively charged particles. The particle size in this phase is larger than that in the initial and rapid growth phases. According to a review paper by Watanabe et al. [40], the transition from the rapid growth to saturation phases happens at 2 seconds after the initiation of a silane discharge, where the nanoparticle density is $5 \times 10^7 \text{ cm}^{-3}$. In the case of nanoparticle synthesis using sputtering, Nafarizal et al. [41] observed the presence of nanoparticle cloud from 2 seconds after the initiation of the discharge at the nanoparticle density in the order of 10^7 to 10^9 cm^{-3} . These findings from literature, resembles the transition from the RG to GS phases occurs at approximately 2 seconds after the initiation of the discharge, when the particle density is in the order of 10^7 to 10^9 cm^{-3} .

2.7 Forces acting on particles in plasma

Nanoparticles stored in plasmas are subjected to various forces which confine them in the plasma or drag them to the walls or chamber ports. Typical forces acting on dust particles are as follows: electrostatic force, gravity force, thermophoretic force and drag (ion and neutral) forces.

Electrostatic force

Electrostatic force is a governing force, if the size of the nanoparticle is smaller than $1\text{ }\mu\text{m}$. It is a confining force because nanoparticles have negative charges and the plasma potential is higher than the potential of the chamber. CCP discharges is very efficient for trapping nanoparticles because the time averaged potential of the powered electrode is at least several tens of volts lower than the plasma potential. The expression for electrostatic force is given by equation 2.8.

$$F_{\text{es}} = Q_{\text{d}}E = 4\pi\epsilon_0aV_{\text{f}}E, \quad (2.6)$$

where Q_{d} is the particle charge and E is the electric field. F_{es} depends on the particle radius linearly. If we suppose the electric fields in the sheath and the presheath region above the powered electrode of CCP, it is a sensitive function of the distance from the electrode. In other words, the electrostatic force acting on nanoparticle is significantly dependent on the location.

Gravity

The gravitational force can be expressed in simple terms as follows

$$F_g = m_{\text{d}}g = \frac{4}{3}\pi a^3\rho_{\text{d}}g, \quad (2.7)$$

where, g denotes the gravitational acceleration, m_d is the mass of nanoparticle, and ρ_d is the weight density of nanoparticle. Gravitational force is proportional to the mass of the particles i.e., the mass density and the volume. Since the gravitational force is proportional to a^3 , it becomes the dominant force for large particles, and it becomes negligible for clusters.

Thermophoretic force

The thermophoretic force is induced by the gradient of the gas temperature. This force drives the particles from hot to cold regions. According to the gas kinetic theory [42], the thermophoretic force is given by equation 2.8,

$$F_{th} = -\frac{32}{15} \frac{a^2 k_n}{v_{th,n}} \nabla T_n, \quad (2.8)$$

with ∇T_n (example = 200 K/m) being the gradient of the gas temperature, and k_n , $v_{th,n}$ are being the thermal conductivity of the gas and thermal velocity, respectively. The thermophoretic force is considered to be important for sub-micron particles due to heating of the gas by the plasma discharge. It has been intentionally applied for the levitation of micron sized particles using strong temperature gradients.

Drag forces

The next two forces (ion drag force, neutral drag force) arise from the relative motion of plasma species to nanoparticle. The number of particles interacting with the dust per unit time dt is given by $\frac{dN}{dt} = n\sigma_c v_{rel} dt$, where n is plasma density, σ_c is the cross-section of interaction and v_{rel} is the relative velocity. The

drag force can be given from the momentum transfer Δp per time interval dt as

$$F_{\text{drag}} = \frac{dN}{dt} \Delta p = n \sigma_c v_{\text{rel}} \Delta p, \quad (2.9)$$

The ion drag consists of two parts, the collection force (F_{dir}) due to ions hitting directly the nanoparticles and the Coulomb force (F_{Coul}) due to Coulomb scattering of the ions in the electric field of the nanoparticle. According to Barns et al. [43], the collection part of the ion drag force is given by,

$$F_{\text{dir}} = \pi a^2 m_i n_i v_s u_i \left(1 - \frac{2eV_f}{m_i v_s^2} \right). \quad (2.10)$$

Here, $m_i v_s$ is the momentum transfer of the ion at the mean velocity $v_s = \sqrt{(u_i^2 + v_{\text{th},i}^2)}$ with $v_{\text{th},i}$ and u_i being the ion thermal velocity and the ion drift velocity respectively. The Coulomb force is given by

$$F_{\text{Coul}} = 2\pi \frac{a^2 e^2 V_p^2}{m_i v_s^3} n_i u_i \ln \left(\frac{\lambda_D^2 + b_{\pi/2}^2}{b_c^2 + b_{\pi/2}^2} \right). \quad (2.11)$$

Here, the collision parameters $b_{\pi/2} = \frac{aeV_p}{m_i v_s^2}$, and $b_c = a \left[1 - \frac{2e(V_p - V_f)}{m_i v_s^2} \right]$. Now, the total ion drag force is just the sum of the direct and Coulomb collision force ($F_{\text{ion}} = F_{\text{dir}} + F_{\text{Coul}}$),

$$F_{\text{ion}} = \pi a^2 m_i n_i v_s u_i \left(1 - \frac{2eV_f}{m_i v_s^2} \right) + 2\pi \frac{a^2 e^2 V_p^2}{m_i v_s^3} n_i u_i \ln \left(\frac{\lambda_D^2 + b_{\pi/2}^2}{b_c^2 + b_{\pi/2}^2} \right). \quad (2.12)$$

The mechanism of the gas drag force is similar to that of ion drag force. Neutral gas atoms or molecules that hit a nanoparticle results in the gas drag force. If the fluid velocity of the gas is v_d , the gas drag force is given by

$$F_n = -\delta \frac{4}{3} \pi a^2 m_n v_{\text{th},n} n_n v_d. \quad (2.13)$$

Here, $\delta = 1.44$, m_n , n_n and $v_{\text{th},n}$ [44] are the mass, the density and the thermal velocity of the neutral gas atoms, respectively. The cross-section for interaction

is just the geometrical particle cross-section πa^2 . The momentum transfer of the neutral gas onto the dust is of the order of $m_n v_{th,n}$ and slightly depends on how the gas atoms are reflected from the particle surface, e.g. diffuse, by specular reflection, isotropic etc.

Comparison among forces, levitation and trapping

Different kinds of forces acting on a dust particle inside the plasma have different power law dependencies on the particle radius. In particular, electrostatic force is proportional to the particle radius a , the ion drag, neutral drag and thermophoretic forces are proportional to the square of the particle radius, and gravitational force is proportional to the cube of the radius. From the relationship between the forces and the particle radius, it can be inferred that the electrostatic force is dominant for clusters while the gravitational force become dominant in particles larger than $1\ \mu\text{m}$.

The forces acting on the nanoparticles in the plasma is shown in figure 2.7. The assumptions for the calculations are taken from the literature [45] as follows: $V_f = 4\ \text{V}$, $T_e = 2\ \text{eV}$, $E = 2250\ \text{V/m}$, $\rho_d = 2436\ \text{kg/m}^3$, $v_{th,n} = u_i = 400\ \text{m/s}$, $k_n = 0.016\ \text{kgm/s}^3$, $n_i = 10^{15}\ \text{m}^{-3}$, $\nabla T_n = 200\ \text{K/m}$. If we suppose a plasma with a uniform gas temperature distribution, negligible gas stream, and the negligible ion current, the balance of the forces acting on nanoparticle is determined by the magnitudes of electrostatic and gravitational forces. Figure 2.8 shows the comparison between the gravitational force (the downward direction) and the electrostatic force (the upward direction) at various electric fields. As shown in the figure, the balance between the gravitational and electrostatic forces is realized at a high electric field of $10\ \text{kV/m}$ if the radius of nanoparticle is greater than $10\ \mu\text{m}$, whereas a weak electric field of $1\ \text{V/m}$ is sufficient for the balance if

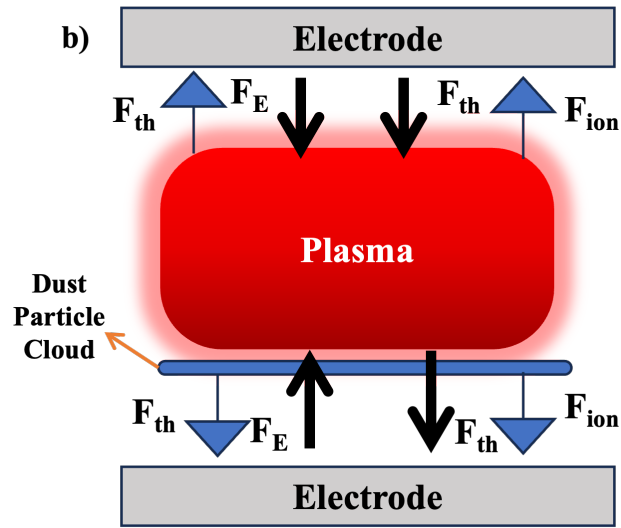
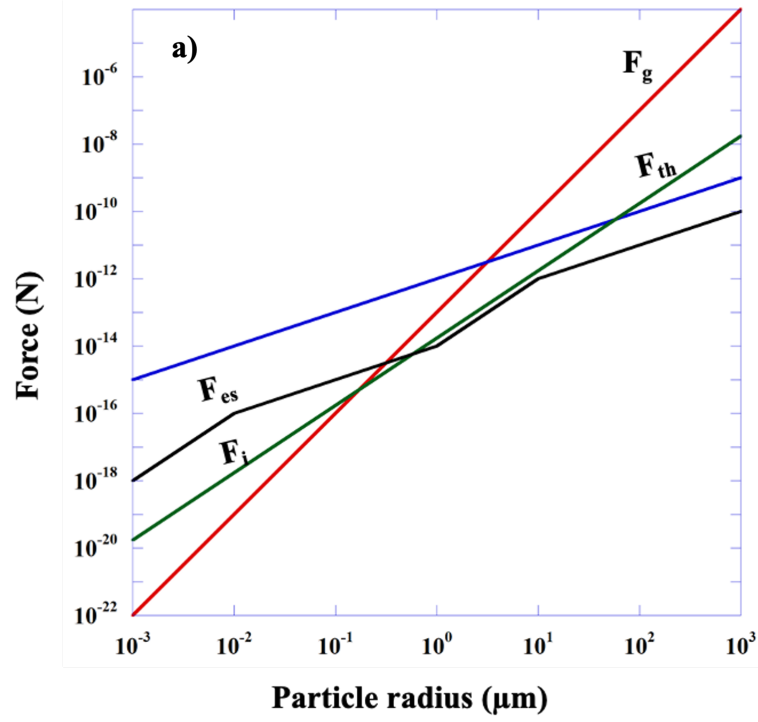


Figure 2.7: Strength of various forces as a function of dust particle radius.

the radius of nanoparticle is 100 nm. Since the electric field inside and around the sheath is sensitive to the distance from the electrode, the location of nanoparticles

trapped in a plasma is sensitively dependent on the radius of nanoparticle.

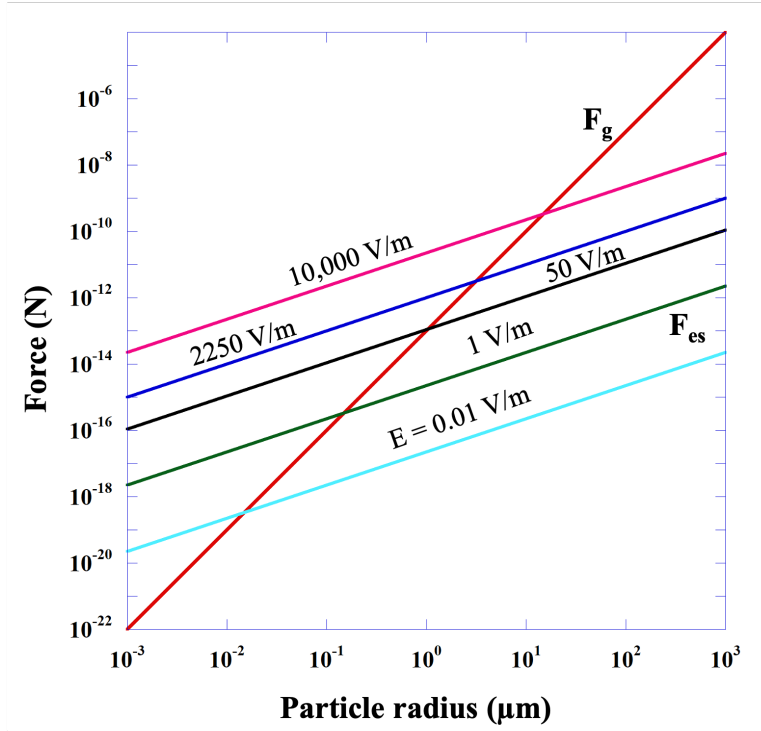


Figure 2.8: Electrostatic force at different electric field strengths as a function of dust particle radius.

3 Experimental Methods

3.1 Experimental Apparatus

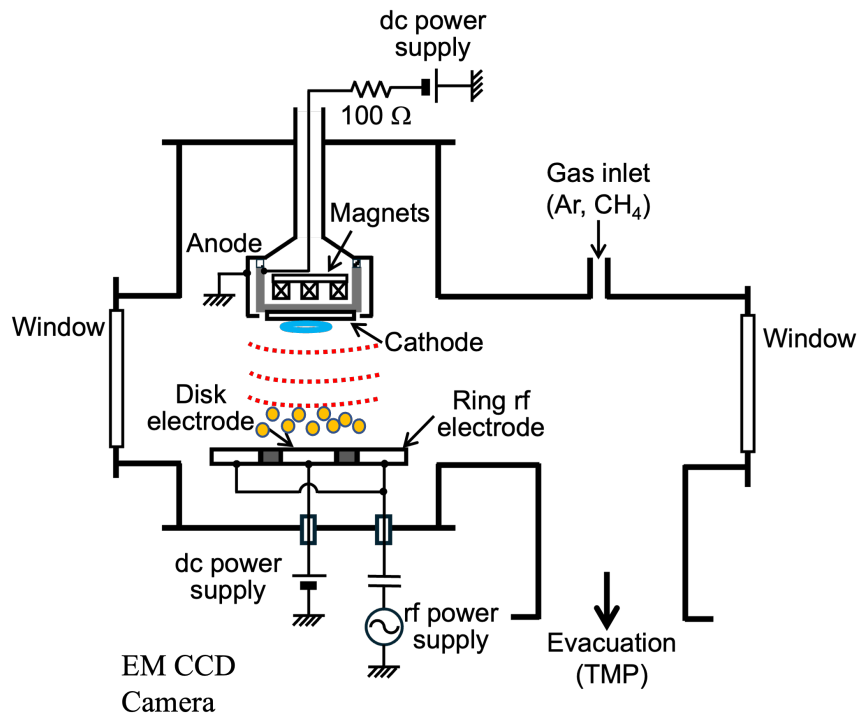


Figure 3.1: Schematic illustration of experimental apparatus

A process flow has been developed which enabled the nanoparticle formation, the retention, the heating, the shell film deposition, and the collection of core-shell

nanoparticles. The experimental apparatus to realize the developed process flow is illustrated in figure 3.1. The first step was the synthesis of tin nanoparticles using magnetron sputtering.

3.2 Magnetron Sputtering

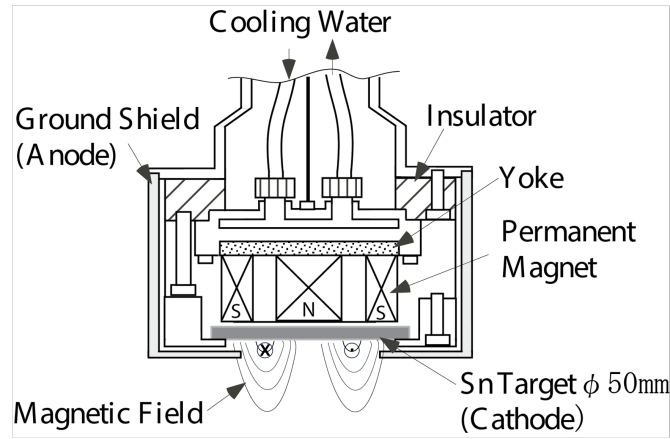


Figure 3.2: Details of magnetron sputtering source

A conventional balanced magnetic sputtering source with a pair of permanent magnets was inserted into a cylindrical vacuum chamber from the top. The diameter and the length of the vacuum chamber were 16 and 50 cm, respectively. The details of the magnetron sputtering source is shown in the figure 3.2. The sputtering target was a tin disk with a diameter of 50 mm. The tin target was bonded on a copper backing plate for efficient water cooling. The cooling water was connected to be recirculated above the magnets. The tin target was connected to the negative side of a dc power supply via a resistor of $100\ \Omega$, and it worked as the cathode. The cathode was surrounded by a ring grounded electrode that was used as the anode of the discharge. Argon was used for the discharge, which was introduced into the vacuum chamber using a mass flow controller after

evacuating it below 5×10^{-4} Pa using a turbo molecular pump. Magnetron sputtering discharges for thin film deposition usually employ an argon pressure below 1 Pa, but in this work, the argon pressure was adjusted at a pressure of 40 - 120 Pa to promote the gas phase aggregation of tin atoms ejected from the target. The flow rate of argon was constant at 14 sccm, and the argon pressure was adjusted by reducing the evacuation speed using a gate valve. The low flow rate and the long distance between the discharge zone and the gas inlet were employed to avoid the gas drag force, which was problematic for retaining nanoparticles in the plasma. The duration of the magnetron sputtering discharge was 60 - 120 s. Tin nanoparticles synthesized in the gas phase were transported to the bottom side of the vacuum chamber. The transport was owing to the gravitational force, since the electric field in the region below the magnetron sputtering source was negligible.

3.3 Capacitively Coupled Plasma

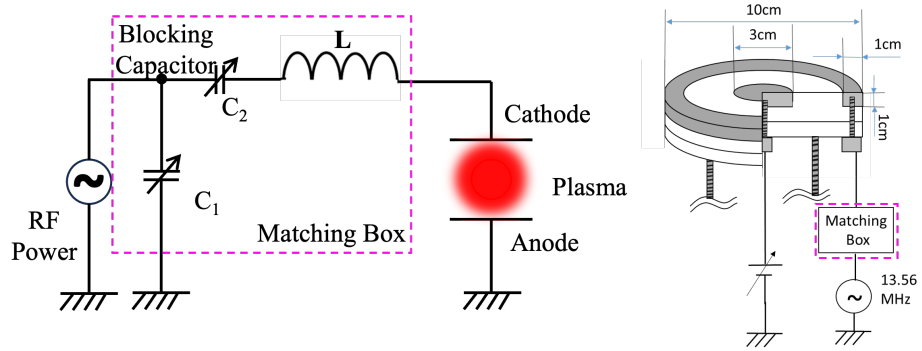


Figure 3.3: Configuration of CCP electrode and the matching circuit

The disk and ring electrodes, which were arranged coaxially, were inserted into the vacuum chamber from the bottom. The inner and outer diameters of

the ring electrode were 5 and 10 cm, respectively, and the diameter of the disk electrode was 3 cm. The ring and disk electrodes were insulated using a ceramic ring. The distance between the magnetron sputtering source and the electrodes inserted from the bottom was 7 cm. The ring electrode was connected to an rf power supply at 13.56 MHz via an impedance matching circuit. The circuit of the matching network used in this work is shown in figure 3.3. By applying the rf power, CCP discharge was generated above the bottom electrode. The rf power was 40 - 100 W. The surface of the vacuum chamber and the disk electrode, which were electrically grounded, worked as the anode of the CCP discharge. The thickness of the region with the bright optical emission from the discharge was approximately 2 cm. The CCP discharge was initiated before igniting the magnetron sputtering, and it was maintained even after the magnetron discharge was terminated. Since one of the capacitors in the impedance matching circuit worked as a blocking capacitor, the ring electrode had a negative DC bias voltage with respect to the electrical ground. Since nanoparticles transported from the magnetron sputtering discharge had negative charges in the plasma as described in Sec 2.4, they were trapped above the sheath electric field that was formed above the ring rf electrode [31]. The trapping position was determined by the balance between the gravitational and electrostatic forces acting on nanoparticles as described in Sec 2.7. We retained tin nanoparticles for 120 - 600 s in CCP.

3.4 Deposition of amorphous carbon film

After the retention of nanoparticles for 120 - 600 s, we admixed methane into argon CCP using a mass flow controller to deposit hydrogenated amorphous carbon film around nanoparticles by PECVD. The partial pressure of methane was 4 - 10 Pa, which was realized at a flow rate of 1.6 sccm. The duration of the de-

position, which was fixed at 180 s, was determined by the period of the methane injection. The CCP discharge was maintained even after stopping the methane injection. The blow off of nanoparticles, which was caused by the gas drag force, was inevitable without considering the gas flow control when injecting methane. We controlled it by performing the slow and steady increase of the valve opening connected to the mass flow controller in the experiment.

3.5 Nanoparticle Collection

After finishing the deposition of amorphous carbon film using methane, a dc voltage from +10 to +70 V was applied with respect to the ground potential to the disk electrode placed inside the ring rf electrode. The intention of the positive bias voltage was to transport synthesized core-shell nanoparticles (which had negative charges in the plasma) towards the electrode. Since a substantial amount of electrons was transported towards the electrode together with nanoparticles, the current through the electrode easily exceeded the limit of the dc power supply. To avoid the higher current than the limit value, we reduced the rf power of the CCP discharge close to 2.5 W before applying the dc bias voltage to decrease the plasma density.

3.6 Measurement of Electron Temperature, Ion Density, Floating Potential and Plasma Potential

A Langmuir single probe made in house was adopted for measuring the floating potential (V_f), and a Langmuir double probe [46] was used for obtaining the

electron temperature (T_e) and the plasma density (n). The probe arrangement while measurements is schematically represented in figure 3.4. A typical relationship between the current and the voltage between the two probe tips of the double is shown in figure 3.5. The electron temperature was deduced from the slope of the curve shown in figure 3.5, and the plasma density was deduced from the amplitude of the saturated current. The probes were positioned close to

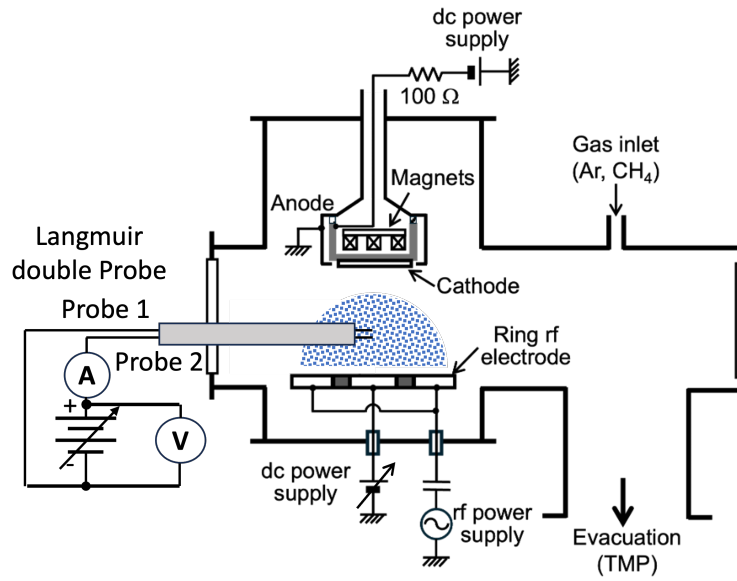


Figure 3.4: Schematic of Langmuir double probe measurements

the CCP electrode to get the effective measurements at the given plasma conditions. Floating potential was obtained by connecting the single Langmuir probe to a voltage meter with high input impedance. The fluctuation of the floating potential was measured by connecting the probe to an oscilloscope with a high input impedance. We tried the estimation of the electron temperature based on the relation between the voltage and the current of a single probe, but it is well known that the relation between the current and the voltage of a single probe is distorted due to the fluctuation of the plasma potential in CCPs. Therefore, we

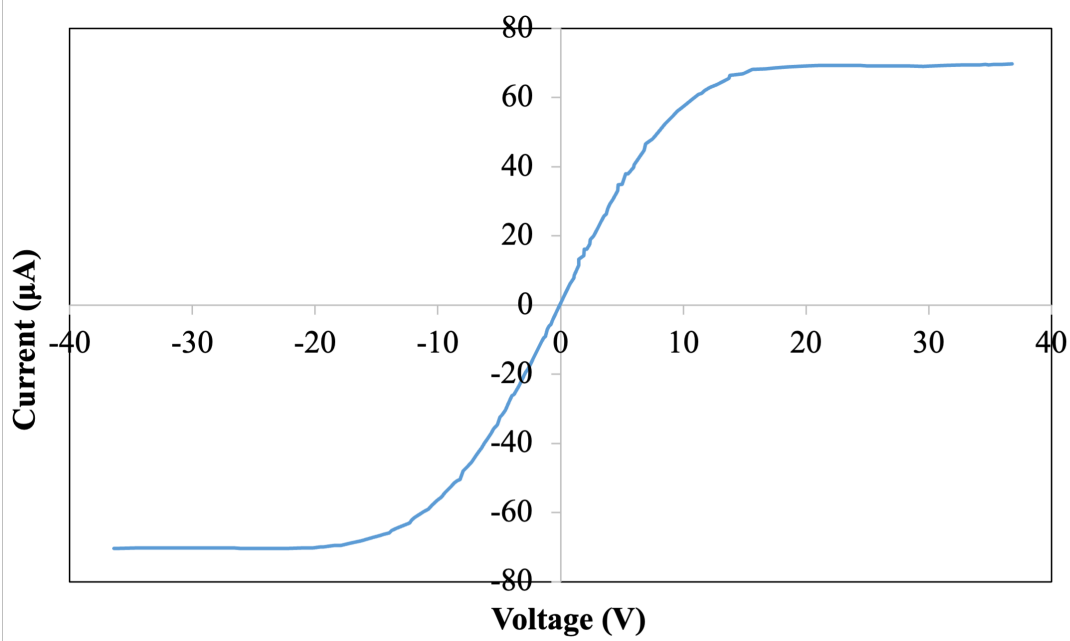


Figure 3.5: Example $V - I$ plot using double probe measurement

employed the Langmuir double probe, which was affected by the rf fluctuation less significantly, to estimate the electron temperature.

The plasma potential was estimated by measuring the ion energy distribution using a quadrupole mass spectrometer (QMS, Hiden PSM003) with a Bessel-box energy analyzer [47, 48]. The schematic of QMS arrangement for the measurements is shown in figure 3.6. The orifice is positioned inside the plasma. The vacuum for QMS, is prepared using differential pumping system. However, the estimation of the plasma potential was limited at CCP pressures between 0.5 and 10 Pa, since the peak in the ion energy distribution disappeared at a higher pressure due to charge-exchange collision in the sheath [49]. QMS was installed in another vacuum chamber with a differential pumping system, and the QMS chamber and the main chamber were connected via an orifice with a diameter of 0.5 mm. Ions in the plasma were sampled into the QMS chamber via the ori-

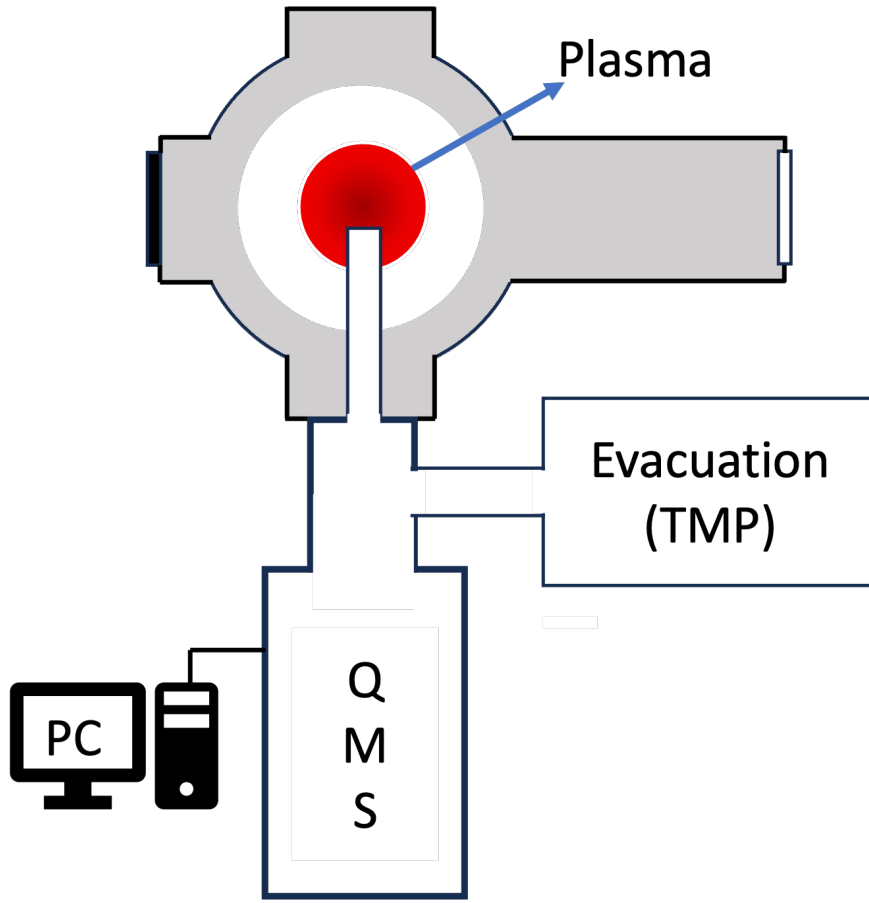


Figure 3.6: Schematic of plasma ion energy distribution measurement using QMS with Bessel box energy analyzer.

the electrical potential of the orifice was grounded. In this measurement, the m/z value that can transmit the quadrupole was adjusted at 40 to detect Ar^+ . A Bessel-box type energy analyzer was placed in front of the quadrupole in QMS. The Bessel-box type energy analyzer can transmit Ar^+ with a specific kinetic energy. From the ion energy that was swept and transmitted by the energy analyzer, we obtained the energy spectrum of Ar^+ . It was assumed that the ion energy corresponding to the peak of the energy spectrum gave us the plasma potential. This was because the kinetic energy of ions passing through

the orifice of the QMS chamber was determined by the difference between the plasma potential and the electrical ground. There were two mechanisms for the broadening of the ion energy spectrum. One was the spatial distribution of the plasma potential and the other was the charge exchange collision between Ar and Ar^+ inside the sheath. The influence of the latter one was too significant if the Ar pressure was higher than 10 Pa.

3.7 Laser Mie Scattering

It was impossible to detect the location and the spatial distribution of nanoparticles trapped in CCP by observing the plasma with naked eyes. Since the in-situ observation of the location of nanoparticles was vital to optimize the gas pressure, the discharge power of magnetron sputtering, and the discharge power of CCP, we injected a cw laser beam at a wavelength of 532 nm into the region between the magnetron sputtering and the bottom electrodes, as shown in figure 3.7. The power of the laser beam was 0.5 W, and the shape of the laser beam was arranged to be planar using two cylindrical lenses. The planar laser beam passed through the cylindrical axis of the discharge system. The laser beam was scattered by nanoparticles via the Mie scattering process [50]. We captured the image of the scattered laser light from the right angle using an electron multiplying charge-coupled device camera (Princeton Instruments Photon Max 512).

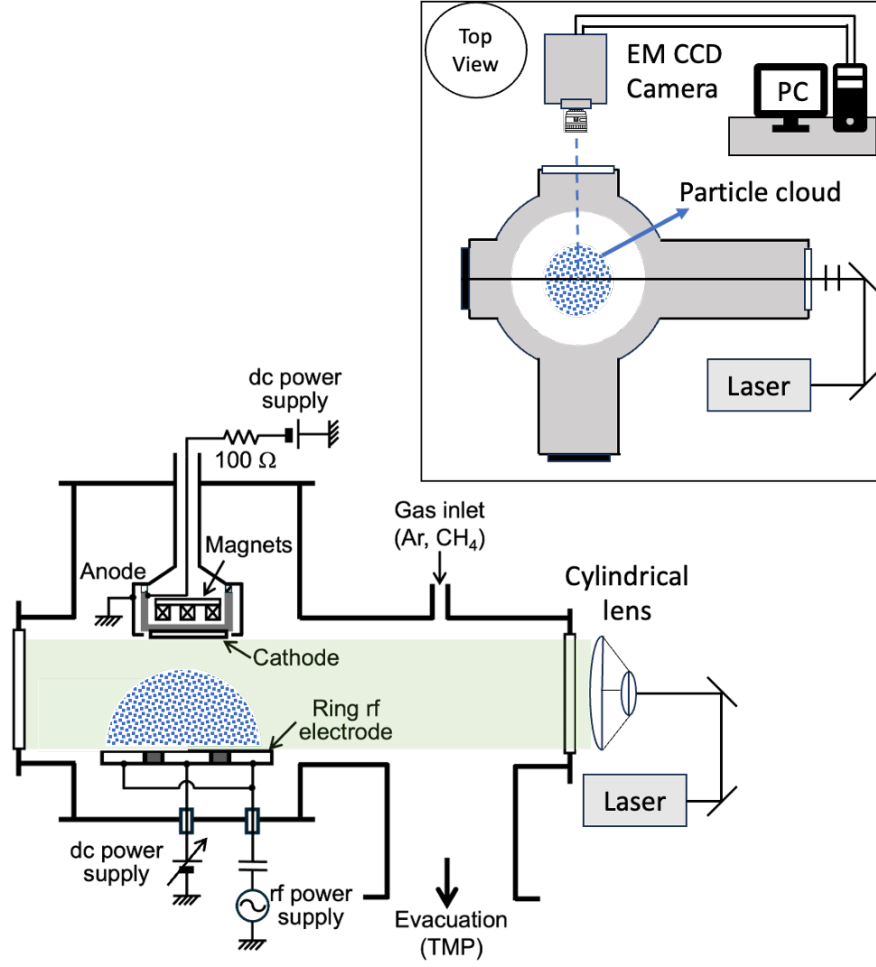


Figure 3.7: Schematic of Laser mie scattering to observe spatial distribution of nanoparticle cloud

3.8 Gas Temperature Measurement

Since the gas temperature was a key parameter to estimate the temperature of nanoparticles retained in the plasma, we measured the translational temperature of $Ar(4s[3/2]_2^o)$ (a metastable state of argon) by diode laser absorption spectroscopy [51]. A single-mode, cw diode laser beam was injected into CCP via a window attached on the side of the vacuum chamber, and the intensity of the

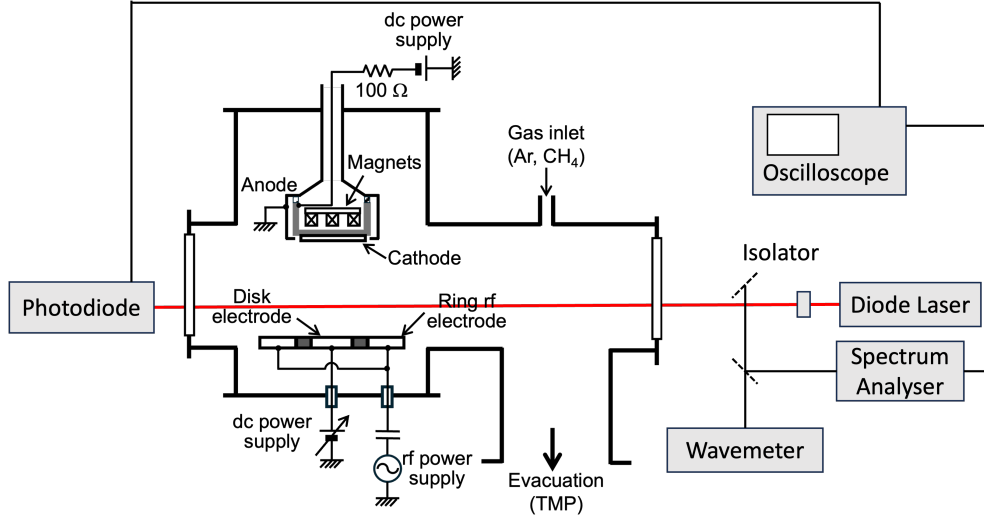


Figure 3.8: System for gas temperature measurement based on Doppler broadening of an argon transition line (the lower energy state is a metastable state)

diode laser beam transmitted through the plasma was measured using a silicon photodiode. Schematically illustrated in figure 3.8. The wavelength of the diode laser was adjusted using a wavemeter. The frequency of the diode laser beam was scanned around the center of the $4s[3/2]_2^o - 4p[3/2]_2$ transition line. The relative frequency of the diode laser beam was measured using a Fabry-Perot spectrum analyzer. When we plotted the transmitted laser light intensity as a function of the relative laser frequency, we observed a dip caused by the absorption. This gave us the absorption spectrum with the Doppler broadening. The gas temperature was deduced from the Doppler broadening width.

3.9 Nanoparticle Analysis Techniques

For the analysis of nanoparticles both with and without the shell film deposition, we used scanning electron microscope (SEM) and transmission electron microscopes (TEM). The images obtained from SEM analysis gave us the details of irregular surface morphology. The particle size, the size of core and the thickness of the shell were measured from the images obtained using TEM. The atomic compositions of the core and shell parts were analyzed by energy dispersion spectroscopy (EDS) built into TEM. We used a double tilt heating holder for checking the robustness of the shell against the core melting. In this heating system, the sample was heated together with the holder, hence, there is the possibility of difference in actual particle temperature of the sample position on the target. In order to analyze the crystalline structure of the tin core, we observed electron diffraction pattern.

4 Results

4.1 Production, retention and transport of tin nanoparticles

Tin nanoparticles were synthesized successfully in the gas phase of the high-pressure magnetron sputtering. As reported in literature [41,52], the region where nanoparticles were present was sensitive to the discharge power. The particle cloud distribution obtained from laser light scattering is shown in the figure 4.1(a), which is the image of laser Mie scattering when the disk electrode is electrically grounded. The thermophoretic forces pulled the particles away from the bright region of the magnetron sputtering discharge, where the gas temperature could be higher than that in the outside region. We performed the trial and error experiments at the available operating range: rf powers for CCP from 10 W to 100 W and dc powers for the magnetron sputtering from 10 W to 40 W. We found that the effective discharges for the current experimental configuration happened at the powers 25 - 40 W and 40 - 60 W for the magnetron sputtering and CCP, respectively. The trial experiments also include the changes in pressure from lowest 0.5 Pa to 130 Pa and found the effective operating pressure from 40 Pa to 120 Pa. The time for methane gas to deposit the shell film was decided at 180s after trial experiments from 60 s to 300 s. The retention of nanoparticles

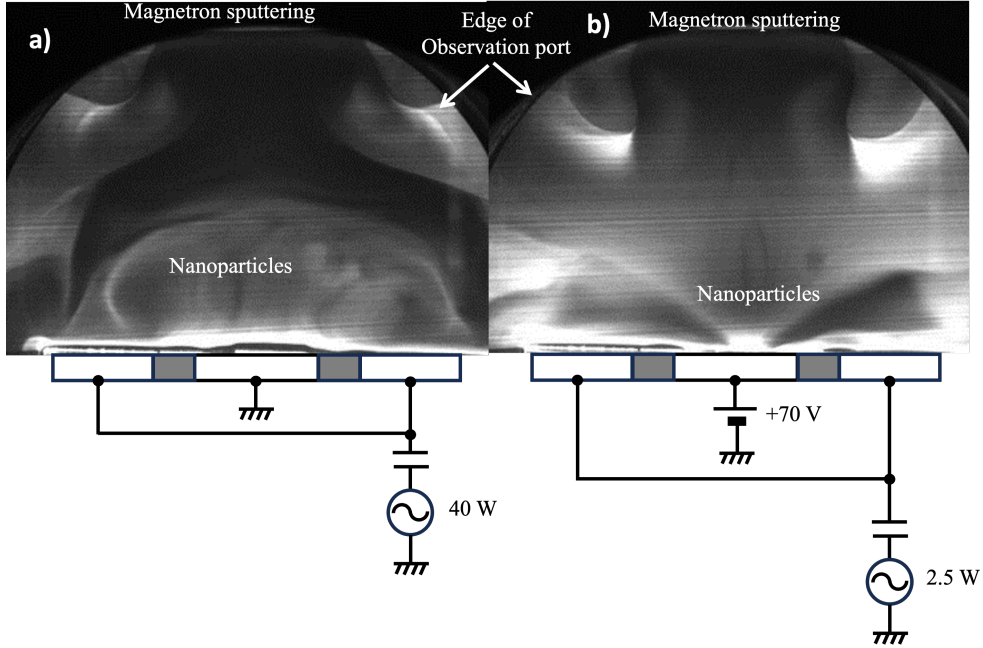


Figure 4.1: Image of scattered laser light. a) was observed when the disk electrode was electrically grounded. When we applied positive bias potential of +70 V with respect to the ground, we observed the scattered light image shown in (b).

above the bottom ring electrode was observed, as shown in figure 4.1 (a). There was a dark region between the electrode surface and the cloud of nanoparticles. The dark region means the region without nanoparticles. The separation between the electrode surface and the cloud of nanoparticles was caused by the balance between the downward gravitational force and the upward electrostatic force, as described in section 2.7. The situation shown in figure 4.1 (a) was kept for an adjusted time of 120 - 600 s, and after that, we introduced methane into the vacuum chamber to deposit amorphous carbon film around tin nanoparticles. This led to the formation of the shell around the liquid tin core droplets sustained above the bottom ring electrode.

4.2 Collection of nanoparticles

Floating Potential

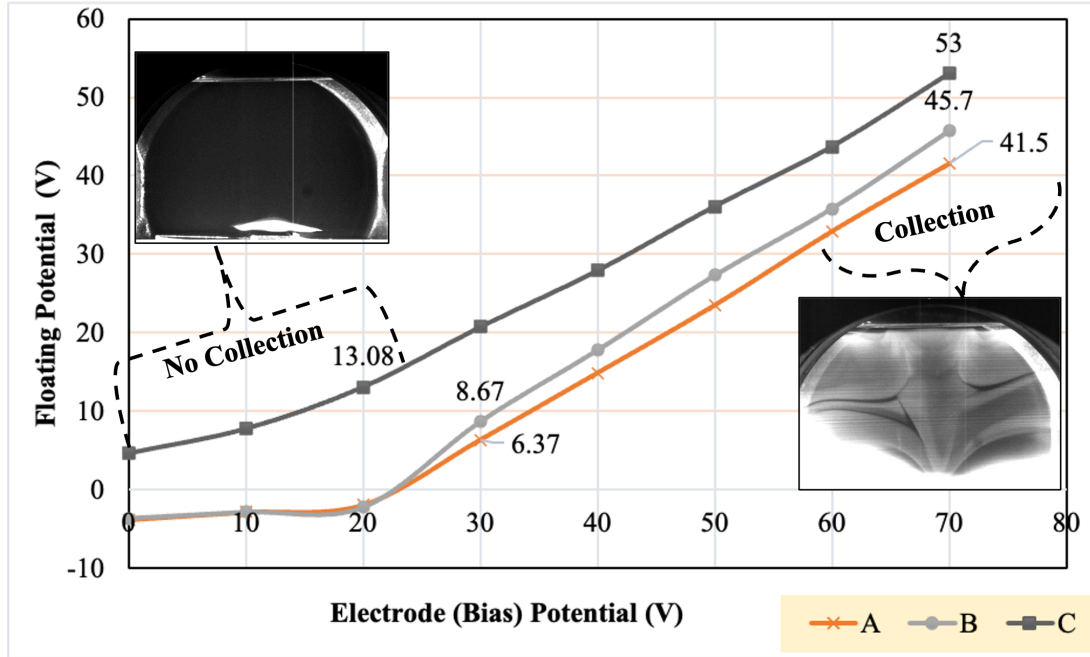


Figure 4.2: Change in V_f against increase in the potential of the disk electrode. [(A) dc 25 W, rf 2.5 W, (B) dc 25 W, rf 0 W, and (C) dc 0 W, rf 2.5 W]

Prior to the experiments to collect core-shell nanoparticles, the floating potential was measured as a function of the dc bias potential applied to the disk electrode. Figure 4.2 shows the relationship between the floating potential and the dc bias potential applied to the disk electrode. It can be observed that, at positive bias potentials between 10 and 20 V, there was no significant change in the floating potential. However, when the bias potential was adjusted between 30 and 70 V, we observed the increase in the floating potential. This indicates the rise in plasma potential. The positively biased disk electrode attracted the

electrons in the plasma. In this situation, the plasma potential increases with the bias potential to realize the confinement of electrons. Since the difference between the plasma and floating potentials is basically fixed at a value that is determined by the electron temperature, according to the standard Bohm sheath theory.

Plasma Potential

Figure 4.3 shows the ion energy distributions obtained using QMS. The ion energy corresponding to the peak in the ion energy distribution was assumed to be the plasma potential. The vertical axis shows the intensity of the ion current. As shown in figure 4.3, at disk electrode dc bias voltage (V_B) is 0 V, the plasma potential was ≈ 7 V. Switching the V_B from 10 to 70 V resulted in the increase in the plasma potentials from ≈ 9 to 35 V. The plasma potentials obtained by multiple measurements of ion energy distribution is plotted in figure 4.4 as a function of the disk electrode potential. The ion energy distribution measured using QMS was affected by the electrode potentials in QMS. The measurement ambiguity related to the electrode potentials inside QMS is represented using the error bars. The CCP power was 2.5 W, which was the rf power when collecting nanoparticles by applying the dc bias voltage to disk electrode. The plasma potential increased with the electrode potential, which has a similarity with the floating potentials shown in figure 4.2. The increase in the plasma potential, as well as the floating potential, is understood by the transport of a substantial amount of electrons towards the electrode. However, the plasma potential was lower than the electrode potential when the electrode potential was higher than + 20 V.

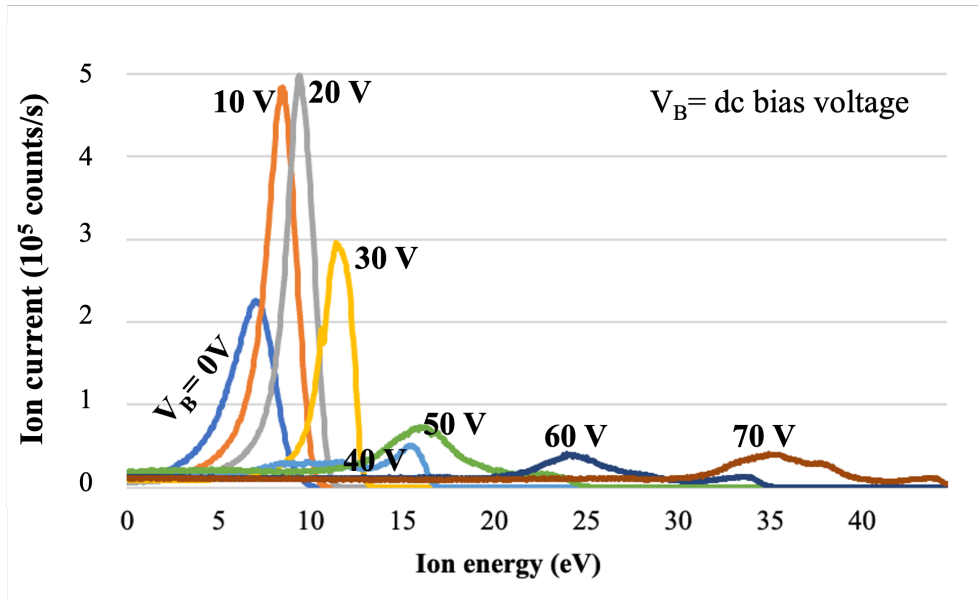


Figure 4.3: Ion energy distributions observed at various potentials applied to the disk electrode

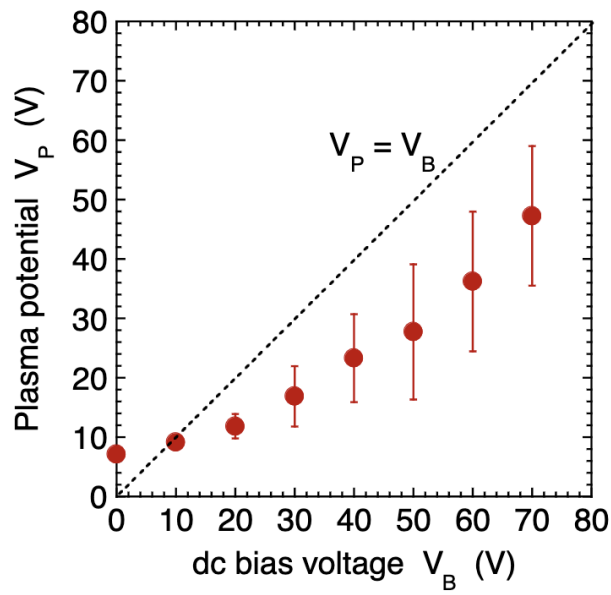


Figure 4.4: Relationship between the plasma potential and the potential applied to the disk electrode

Transport of nanoparticles

We succeeded in transporting nanoparticles to the substrate placed above the disk electrode by applying the dc bias voltage. As shown in figure 4.1(b), when a dc bias voltage of +70 V was applied to the disk electrode, the cloud of nanoparticles was pulled towards the disk electrode, and the cloud of nanoparticles touched with the electrode surface. The successful transport of nanoparticles toward the disk electrode was owing to the fact that the plasma potential was higher than the electrode potential when we applied the bias potentials higher than 20 V, as shown in figure 4.4. Figure 4.5 shows the temporal variation of the images of the scattered laser light, which was obtained by the sequential frames of a movie. The interval between the succeeding image is ≈ 1 s. A bias voltage of +70 V was applied to the disk electrode in figure 4.5(b). As can be seen from figure 4.5, during the transport of nanoparticles toward the disk electrode, we observed the gathering of nanoparticles from the outside of the dense nanoparticle cloud. The possible reason could be that, in the outside of the dense particle cloud, the distribution of nanoparticles before applying the bias voltage was determined by the balance among the gravitational, electrostatic, and thermophoretic forces. The positive bias voltage applied to the disk electrode changed the potential distribution at a long distance from the electrode slightly, resulting in the change in the nanoparticle distribution. A part of nanoparticles in the outside region of the dense particle cloud was probably captured by the electric field lines, and they are transported to the disk electrode.

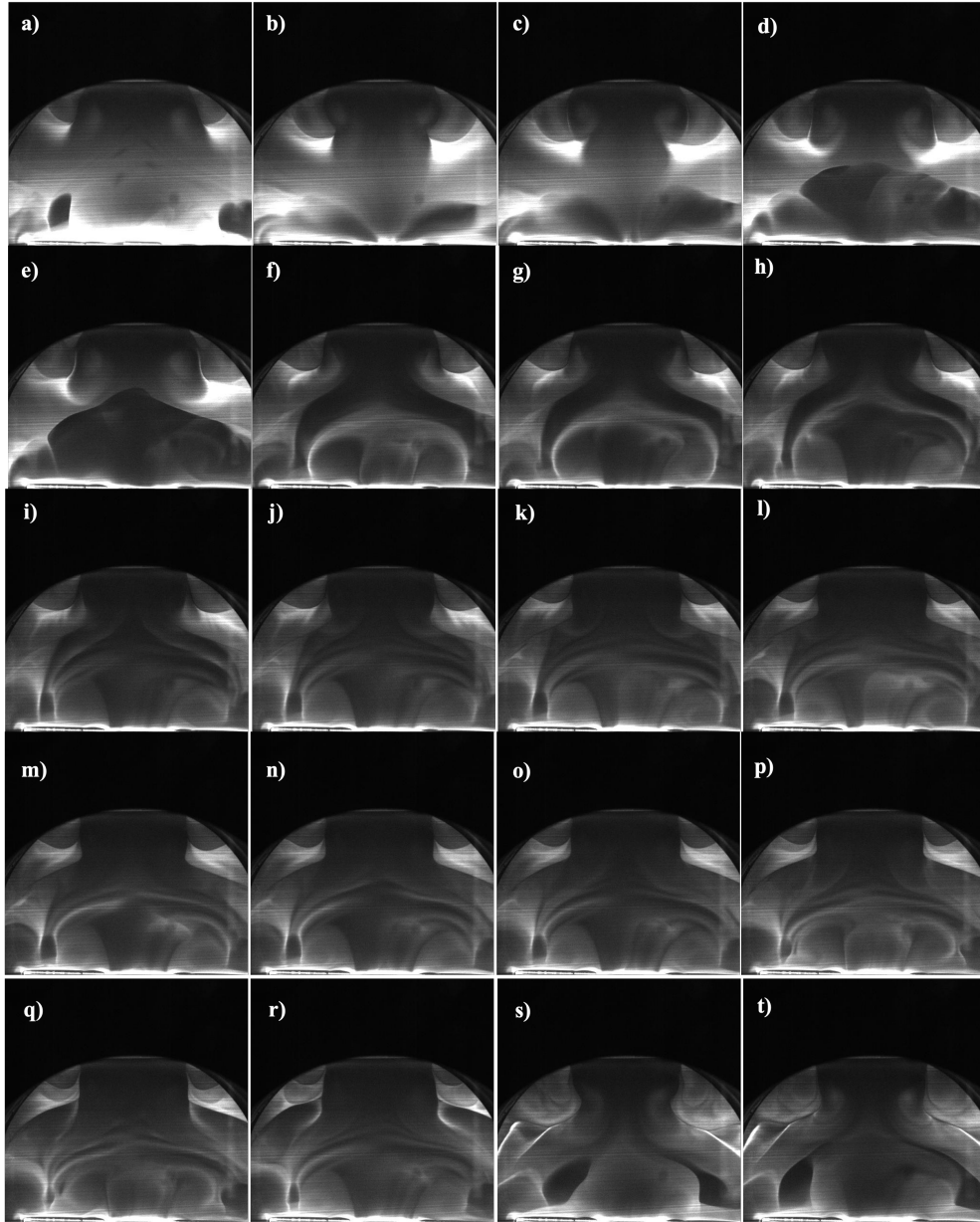


Figure 4.5: Images of the scattered laser light when a dc bias potential of $+70$ V was applied to the disk electrode. The images were obtained by the succeeding frames of a movie, and the interval of the frames was 1 s. The dc bias voltage was applied at (b)

4.3 Measurement of gas temperature

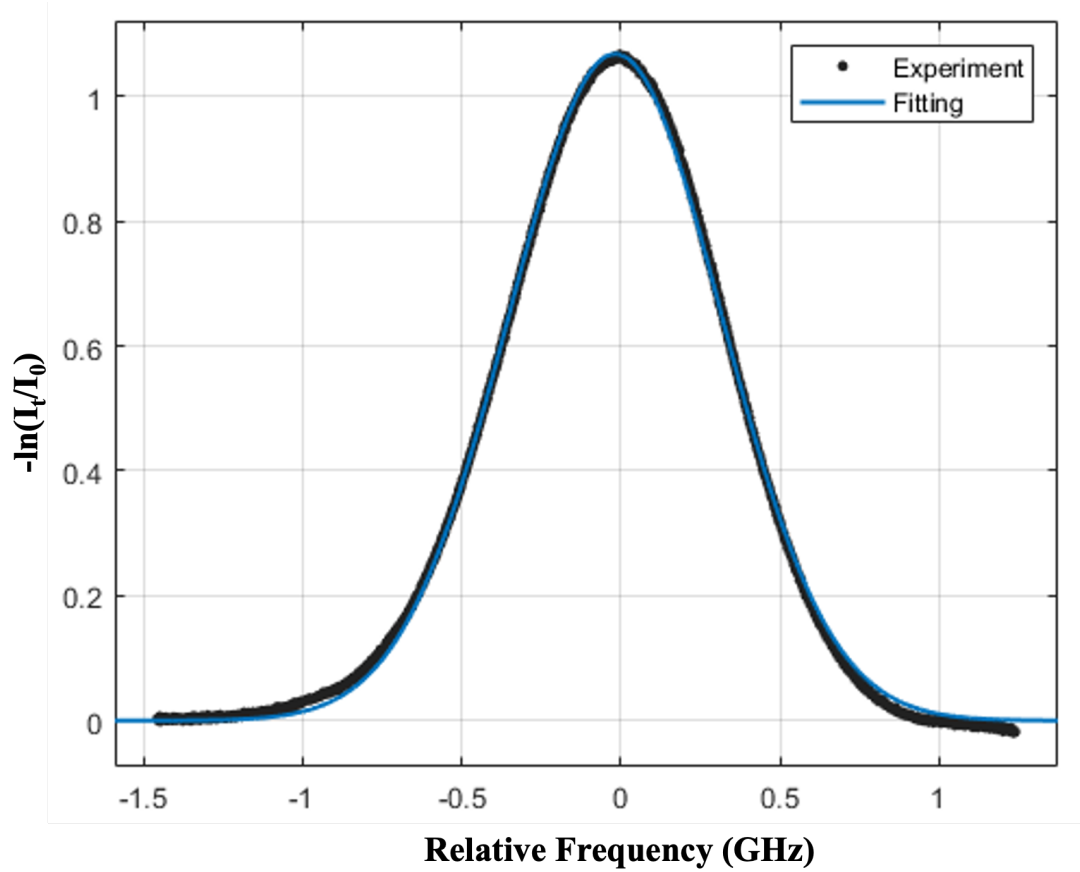


Figure 4.6: Absorption spectra of argon metastable state at the pressure 80 Pa, rf power 10 W

Figure 4.6 is an example for the absorption spectrum of the $4s[3/2]_2^o - 4p[3/2]_2$ transition of argon, which was observed at an argon pressure of 80 Pa and a CCP power of 10 W. The horizontal axis is the relative laser frequency where the origin is the centre of the transition line. The vertical axis is given by the neutral logarithm of the transmission, which is proportional to the spectral line shape function. According to the Lambert-Beer law, the intensity of the laser

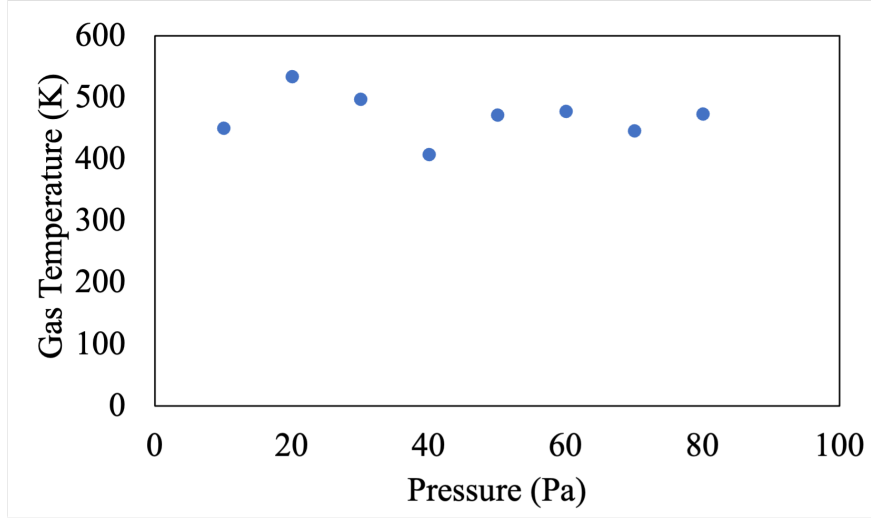


Figure 4.7: Gas temperature as a function of discharge pressure of CCP

beam passing through the plasma is given by $I_t(\nu) = I_0 \exp(-\alpha(\nu)l)$, where $\alpha(\nu)$ is the absorption coefficient and l is the absorption length. Transmission (T) is defined as by

$$T = \frac{I_t(\nu)}{I_0(\nu)} = \exp(-\alpha(\nu)l). \quad (4.1)$$

The absorption coefficient $\alpha(\nu)$ is given by

$$\alpha(\nu) = \frac{h\nu B_{12}}{c} \left(N_1 - \frac{g_1}{g_2} N_2 \right) g(\nu) \simeq \frac{A_{21} c^2}{8\pi \nu^2} \frac{g_2}{g_1} N_1 g(\nu), \quad (4.2)$$

where h is the Plank constant, ν is the laser frequency, c is the speed of light, B_{12} is the Einstein's B coefficient for absorption, N_1 and N_2 are the populations of the lower and upper energy states, respectively, g_1 and g_2 are the statistical weights of the lower and upper energy states, respectively, and A_{21} is the transition probability. The spectral line shape function $g(\nu)$ is governed by the Doppler broadening, and it is given by

$$g(\nu) = \frac{1}{\Delta\nu_d} \sqrt{\frac{\ln 2}{\pi}} \exp\left(-\frac{\ln 2(\nu - \nu_0)^2}{\Delta\nu_d^2}\right), \quad (4.3)$$

where ν_0 is the line center frequency of the transition line, and $\Delta\nu_d$ is the Doppler broadening width, which is the half width at half maximum of absorption spectrum, and it is given by

$$\Delta\nu_d = \nu_0 \sqrt{\ln 2} \sqrt{\frac{2kT}{m_{\text{ar}}c^2}}, \quad (4.4)$$

where m_{ar} is the atomic mass of argon and T is the gas temperature. The black curve in figure 4.7 is the experimental result, and the blue curve is the fitting using Eq.(4.1). From the fitting shown in figure 4.7, we deduced a gas temperature of 440 K. Figure 4.13 shows the gas temperature as a function of the gas pressure. It was observed that the gas temperature was roughly independent of the gas pressure.

4.4 Surface morphologies of nanoparticles

This section gives the observations of synthesized nanopartilces (with and without shells) using SEM and TEM. The discharge conditions and corresponding SEM and TEM images are shown in Table 4.1, figures 4.8 and 4.9. The plasma conditions are falling approximately 25 W for the power of magnetron sputtering and 40-60 W for the power of CCP. From the SEM pictures shown in figure 4.8, changes in particle size and different surface morphology are observed. The retention time and the gas pressure were found to have greater influence on the morphology than remaining parameters. Particle diameters were in the range of 200 - 400 nm. It must be impossible to distinguish the core and shell of the nanoparticles in the SEM images, since the penetration depth of the electron

Table 4.1: Discharge conditions

Figure	Sputtering Power (W)	RF Power (W)	Pressure (Pa)	Retention Time (s)
a)	25	50	75	600
b)	25	40	70	300
c)	25	40	100	180
d)	25	60	100	180
e)	25	60	70	180
f)	25	60	120	180

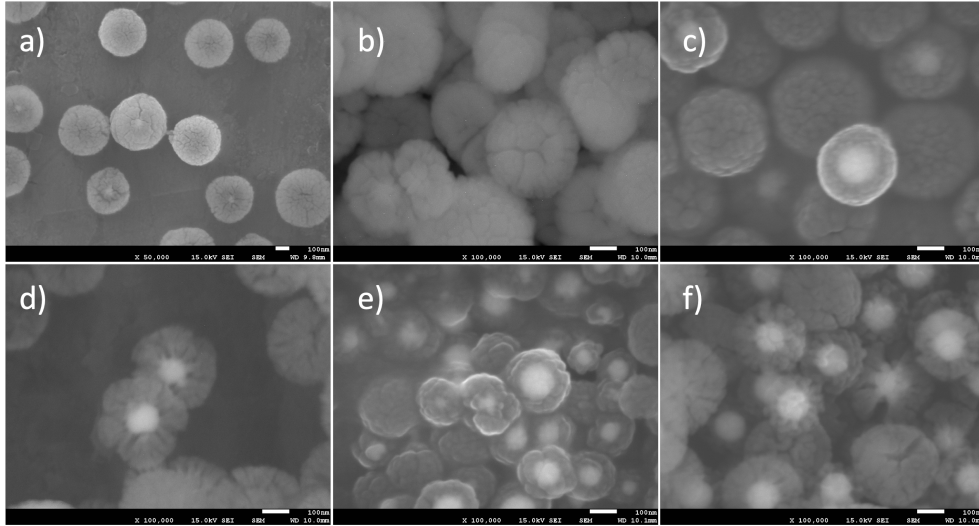


Figure 4.8: SEM surface morphology of particles for at the conditions in table 4.1

beam was shorter than the thickness of the shell at the electron energy (30 keV). However, the reason for observing the "egg-like" images of nanoparticles shown in figure 4.8 is that the penetration depth is long enough to observe cores.

The inside structures of the core-shell nanoparticles were observed clearly by

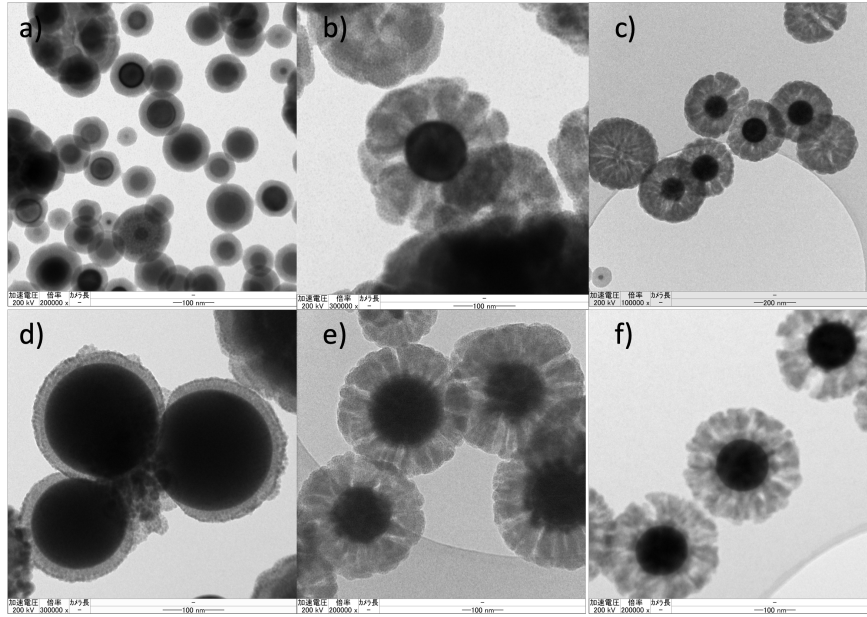


Figure 4.9: TEM core-shell images for the conditions given in table 4.1

TEM, as shown in figure 4.9. The energies of the electron beams in TEMs we used were higher than 200 keV. The perfectly spherical cores in the TEM images gives the proof that the tin core was melted, and the melted cores were surrounded by shells with a uniform film thickness. A clear interface was observed between the core and the shell. This may be due to the fact that the solubility of atomic carbon into liquid tin is close to zero at around the melting temperature [54]. The arrival of carbonic species at the surface of liquid tin dominantly results in the deposition to form an amorphous carbon film.

Further comparisons of nanoparticles with (figure 4.10(a) and 4.11(a)) and without (figures 4.10(b) and 4.11(b)) shell films are shown in figures 4.10 and 4.11, which were obtained using SEM and TEM, respectively. The nanoparticles without the shell deposition had uneven surfaces with significant porosity, in comparison with particles having carbon film deposited.

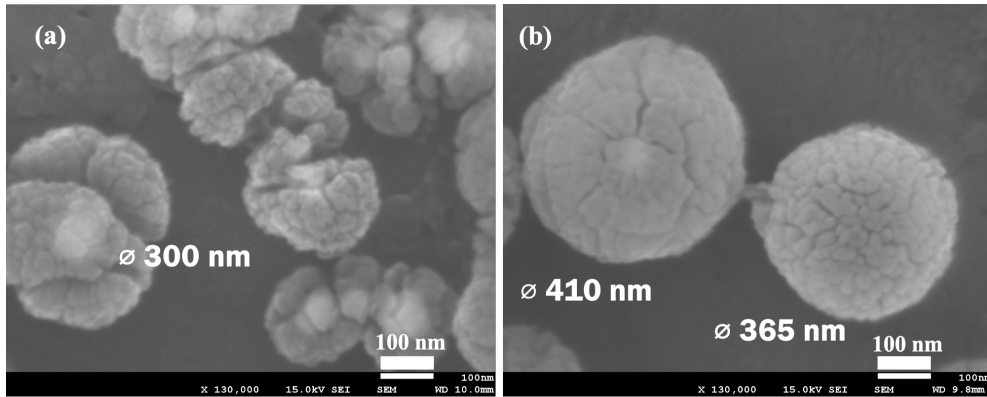


Figure 4.10: SEM images of a) without and b) with shell film deposition

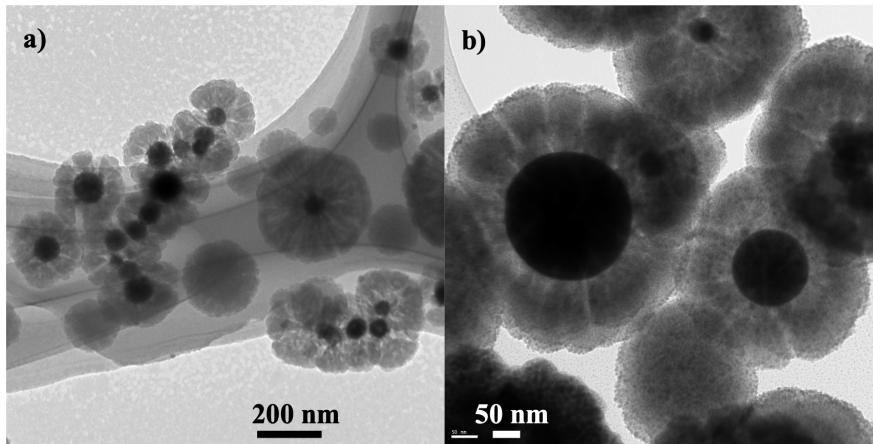


Figure 4.11: TEM Images of a) without and b) with shell film deposition

4.5 Particle size and atomic composition analysis

Particle size analysis

The size of tin core of core-shell nanoparticles is plotted in figure 4.12 as a function of the duration of retention of tin nanoparticles above the bottom ring (rf) electrode. The plots show the average diameter, and the error bars show the

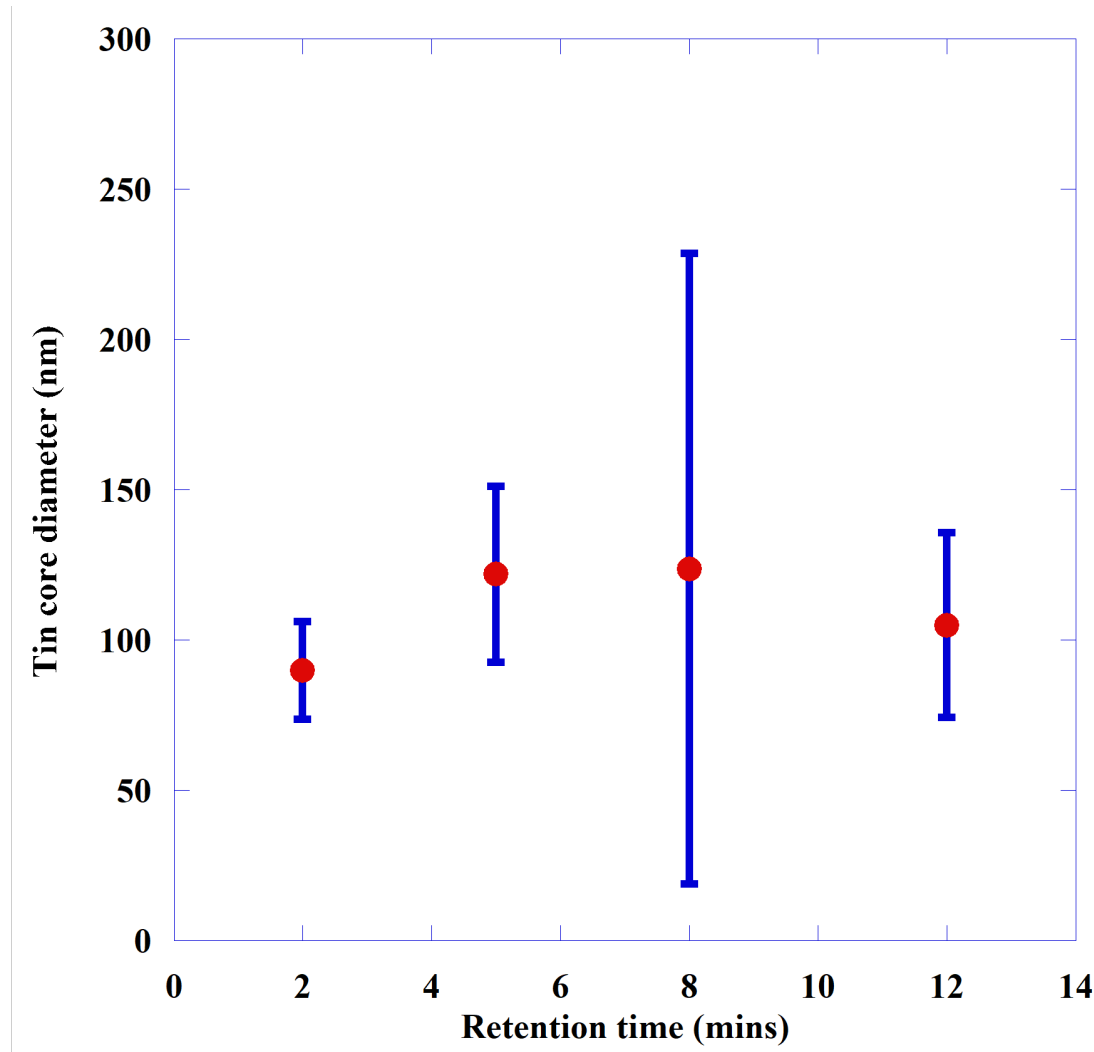


Figure 4.12: Tin(Sn) core diameter in core-shell nanoparticles as a function of retention time.

standard deviation. As shown in the figure, the diameter of tin core of core-shell nanoparticles was roughly 100 nm, and it was independent of the retention duration. Considering the growth model reported by Watanabe et al. [40], suggests the saturation of the nanoparticle growth before 2 s. As described in Section 2.6, it is expected that the growth of the tin core particle size in coreshell particles

discussed in current research is saturated at similar time of 2 s after the initiation of the discharge at the similar particle density in the order of 10^9 cm^{-3} . Therefore, the saturation of the nanoparticle size shown in figure 4.12 is reasonable. The large error bars shown in figure 4.12 indicates that the particle diameters had a significant distribution. This result is consistent with the literature [41], which shows that the synthesis of monodisperse nanoparticles is difficult using magnetron sputtering with significant spatial distribution. On the other hand, we obtained no systematic data on the relationship between the thickness of the shell film and the discharge condition of CCP (the plasma density and the partial pressure of methane). In addition, no clear correlation was found between the structure of amorphous carbon films and the retention period in the plasma after the completion of the deposition.

Atomic composition analysis

Figures 4.13(a) and 4.13(b) show the atomic compositions observed along the chords passing through the core and shell parts, respectively. Note that the atomic composition observed along the chord passing through the core includes the information of the shell. It is also noted that this analysis was just qualitative, and the absolute values of the atomic compositions shown in figure 4.13 was not trustable. This was because the x-ray emitted from the core was attenuated during the propagation through the shell. In addition, the atomic composition of carbon was probably enhanced by the contamination. Figure 4.13 suggests that the oxidation of the core was less significant than that of the shell. Another remarkable point was the detection of tin along the chord passing through the shell. The shell was deposited after stopping the magnetron sputtering, but tin was admixed into the amorphous carbon film.

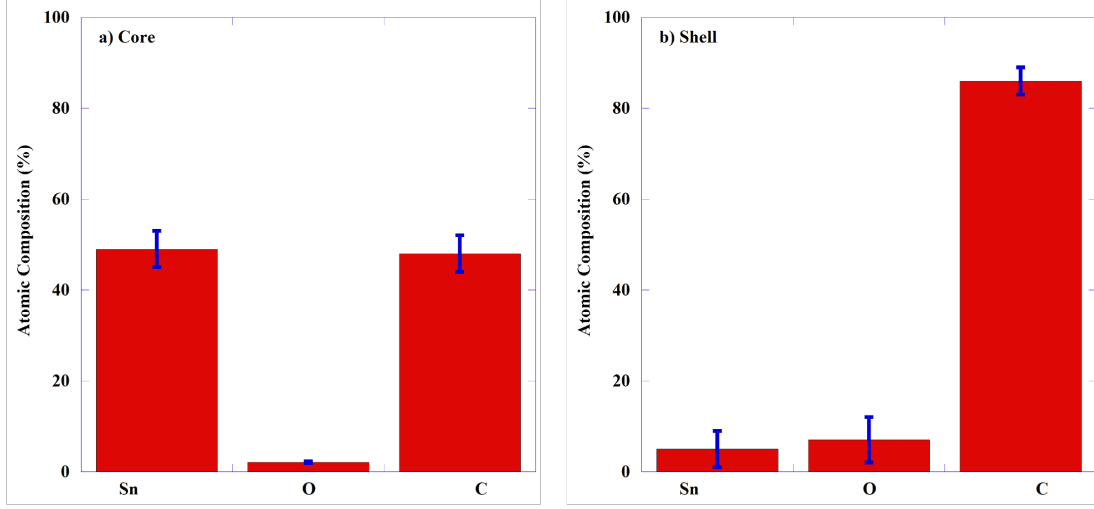


Figure 4.13: Atomic composition of core-shell nanoparticles (a) through the core.
(b) through the shell

4.6 Melting of Core against Heating

Core-shell type PCMs are effective if the core is melted without breaking the shell film. In order to inspect this, we employed a sample holder with a heating system in the TEM observation, and examined the electron diffraction patterns at various sample temperatures. Nothing happened at the melting point of metal tin in the TEM image, even though we observed the change in the electron diffraction pattern, as shown in figure 4.15. The experimental condition is shown in the line (f) of Table 4.1 for both figures 4.14 and 4.15, and electron diffraction patterns at 200 and 238 °C are shown in figure 4.15(a) and 4.15(b), respectively. The change in the electron diffraction pattern from a polycrystalline to amorphous indicated the melting of core at 238 °C. No change in the TEM image is reasonable since the volume expansion of tin at the melting is 3.6 %, corresponding to the length expansion of just 1 %. The leak of liquid tin from the core was not observed. We did not detect the breakdown of the shell film, indicating that the shell was

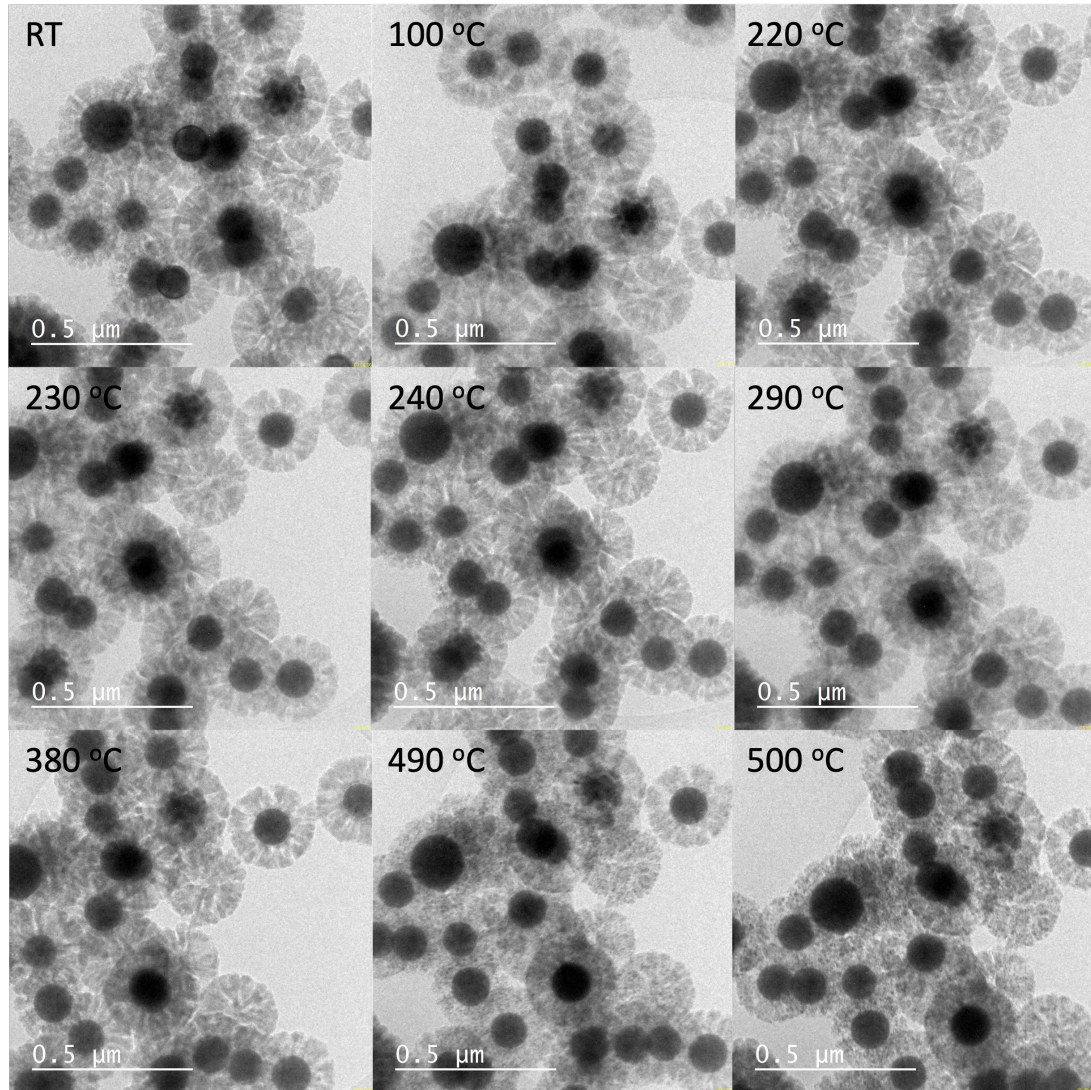


Figure 4.14: TEM images while heating the core-shell nanoparticles from room temperature (RT) to 500 °C

robust against the volume expansion of the core at the melting, even if the shell had a porous structure. We detected no change in the TEM image up to 300 °C. However, we observed the appearance of small dots in the shell when the sample was heated above 380 °C, as shown in figure 4.14. According to the low transmis-

sion of the electron beam, the dots were tin particles with small sizes. We will discuss the mechanism of this unpreferable phenomena in the next chapter. The electron diffraction pattern shown in figure 4.15(a) was understood by the lattice parameters of β tin [55]. We calculated the radius of the fringes correspond-

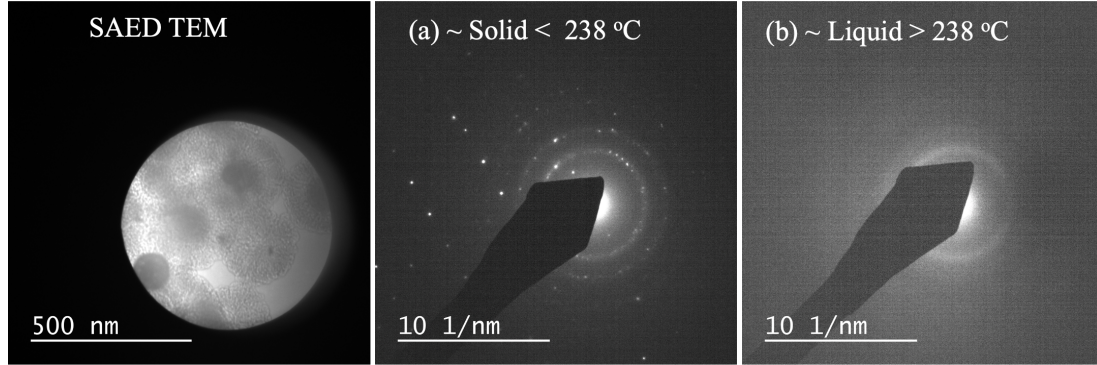


Figure 4.15: SAED patterns of core-shell nanoparticles (a) 200°C and (b) 238°C.

ing to the lattice parameter (d spacing) of β -tin, considering the disappearance rule. The fringes with corresponding (hkl) planes are represented in figure 4.16. On the other hand, we observed the disappearance of the spots in the electron diffraction pattern when the sample temperature was 238 °C, as shown in figure 4.15(b). Considering the fact that the melting temperature of metal tin is 232 °C, the disappearance of the polycrystalline structure is considered to be caused by the melting. The melting at the melting point of metal tin indicates that the oxidation of tin core was not significant. This was supported by the fact that the electron diffraction pattern of β tin was observed before the melting, as shown in figure 4.15(a). In other words, the amorphous carbon shell was sufficiently protective from the oxidation of the tin core. When the sample was cooled down below the melting point of metal tin, we observed the reappearance of the spots in the electron diffraction pattern, indicating the consolidation of the core tin.

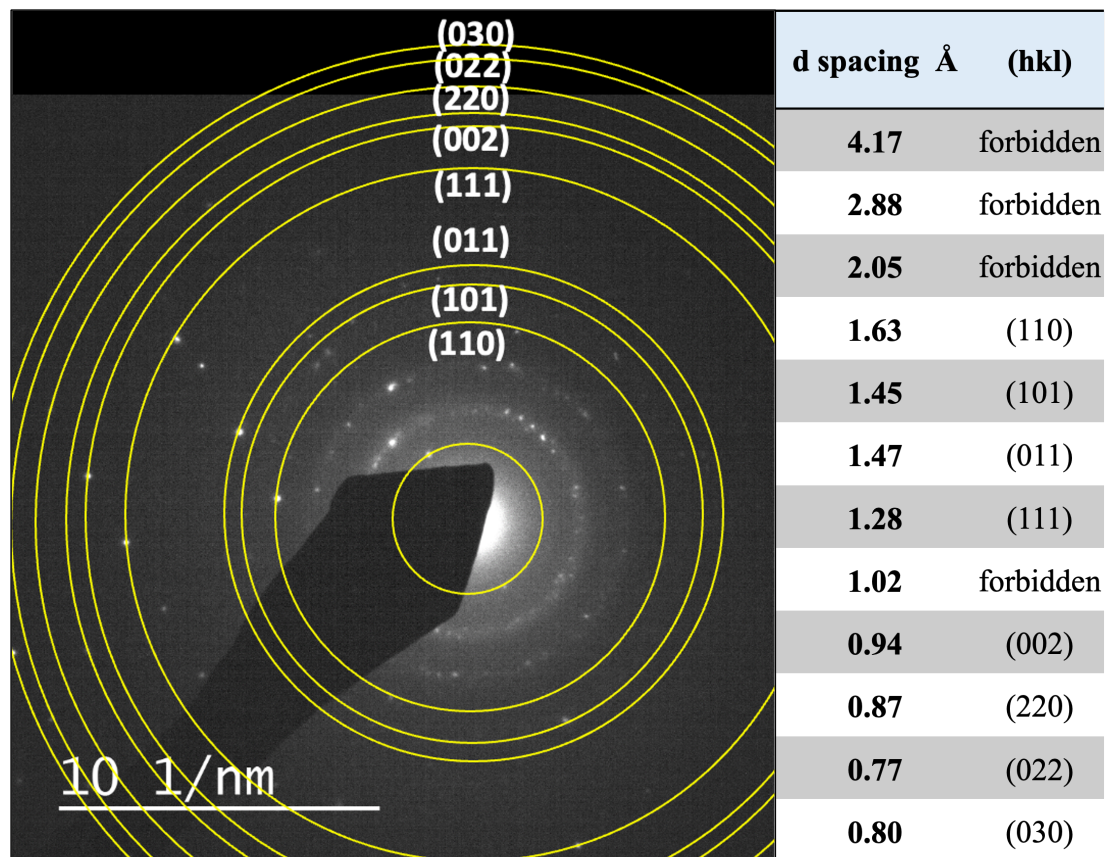


Figure 4.16: Measured lattice parameter (dspacing) with corresponding (hkl)

5 Discussion

5.1 Influence of Drag Force due to CH_4

Injection

Drag force due CH_4 injection was an issue in this process development for obtaining core-shell nanoparticles. The robust shell film is needed to withstand the melting of core, but the introduction of CH_4 into the chamber without losing existing nanoparticles was very difficult. At the moment when the CH_4 was released, the particle cloud was swept towards the walls of the chamber. It was necessary to release CH_4 slowly so that there was less impact on the melted tin particle cloud sustained above the bottom electrode. From the discussions on the forces acting on nanoparticles in Section 2.7, the vertical forces (gravitational force and, electrostatic force) are balanced, but the question arises about forces in horizontal direction. The force due to the gas injection is unclear, but if it is acting in horizontal direction, it could have significant trouble while retaining the particles above the sheath. However, the injection time is very small, hence the need for the drag force control can be small interval of time.

5.2 Estimation of Particle Temperature

The most important point of the present synthesis method is the deposition of shell films around melted cores. The spherical cores shown in figures 4.7 and 4.9 reveal that tin nanoparticles were melted when they were retained in CCP. To confirm the melting, we estimated the temperature of nanoparticles based on the heat transfer theory reported in literature [56]. The temperature of nanoparticles retained in CCP is determined by the balance between the heating and cooling powers such that $q_H = q_R + q_K$, where q_H is the heating energy flux deposited onto the nanoparticle, and q_R and q_K are the cooling energy fluxes due to radiation and conduction, respectively.

The heating energy flux is governed by ion bombardment in the argon plasma, and it is given by

$$q_H = n_i e (\varepsilon_i + V_f) \left(\frac{k_B T_i}{2\pi m_i} \right)^{1/2} \left[1 + \frac{e V_f}{k_B T_i} \right], \quad (5.1)$$

where the ion current obtained from the orbital motion limit theory [37] is assumed. V_f represents the difference between the plasma and floating potentials, n_i , T_i , and m_i are the density, the temperature, and the mass of argon ion, respectively, e is the charge of electron and ε_i is the recombination energy (ionization potential) of argon atom (15.8 eV). The energy flux of the radiation cooling is governed by the Stefan-Boltzmann law,

$$q_R = \sigma (\epsilon T_p^4 - a_c T_g^4) \quad (5.2)$$

where σ is the Stefan Boltzmann constant, ϵ and a_c are the emissivity and the absorptivity of the nanoparticle, respectively, T_g is the gas temperature, and T_p is the temperature of the nanoparticle. We assumed $\epsilon = a_c = 0.04$ in this work [57]. The energy flux of the conduction cooling is given by

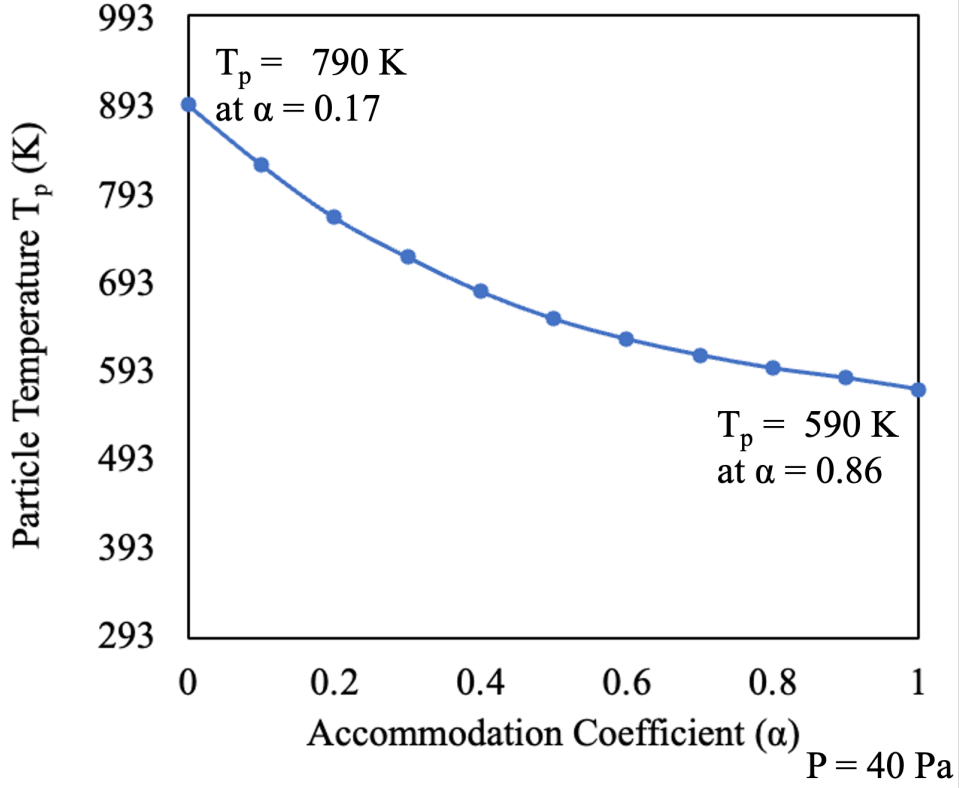


Figure 5.1: Particle temperature vs Accommodation coefficient (α)

$$q_K = \frac{\alpha}{16} \left(\frac{k+1}{k-1} \right) \frac{P}{\sqrt{T_g}} \left(\frac{8k_B}{\pi M} \right)^{\frac{1}{2}} (T_p - T_g), \quad (5.3)$$

where k is the heat capacity ratio, P is the argon pressure, and M is the mass of argon atom ($M \approx M_i$) and α is called the accommodation coefficient. The accommodation coefficient, α represents the degree of thermal equilibrium between the physisorbed argon and the nanoparticle surface. The value of α is sensitive to the surface condition of the nanoparticle. Piejak [58] suggested $\alpha = 0.86$, whereas Daugherty and Graves [56] reported the agreement between the experiment and the calculation by assuming $\alpha = 0.17$.

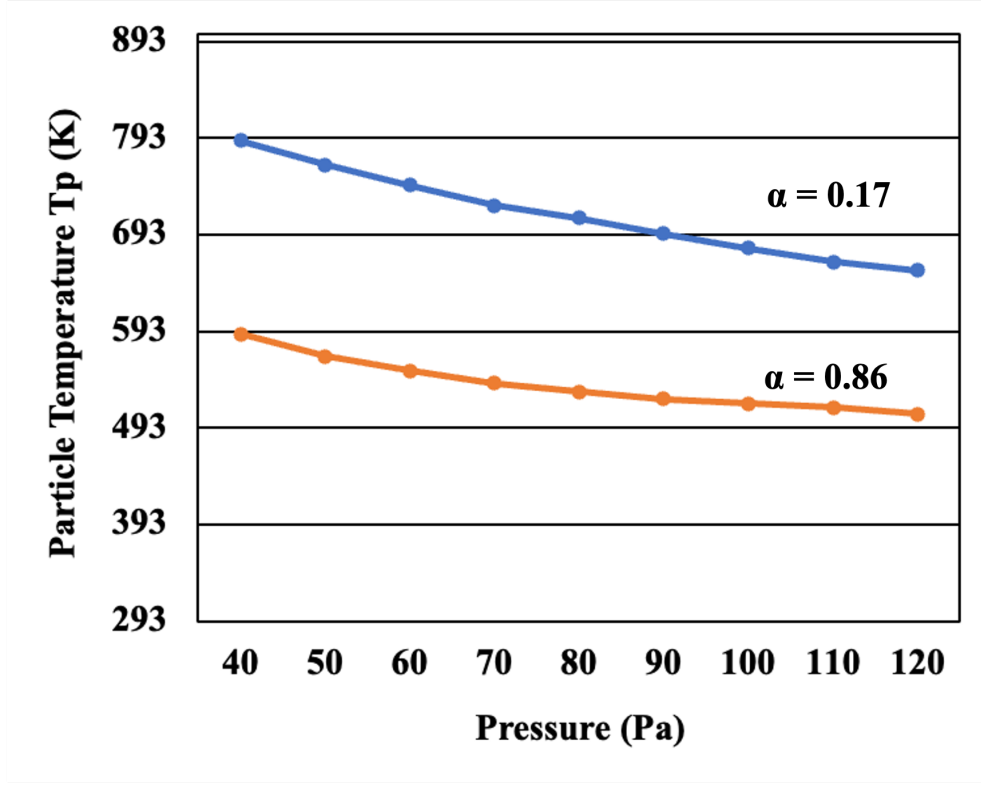


Figure 5.2: Particle temperature vs Plasma condition (Pressure)

We calculated the temperature of nanoparticle T_p by substituting $n_i = 3.4 \times 10^{15} \text{ m}^{-3}$, $V_f = 22.9 \text{ V}$, $T_g = 460 \text{ K}$ and $T_i = 500 \text{ K}$. The plasma density (n_i) and gas temperature (T_g) were the experimental values based on the measurement using the double probe and the diode laser absorption spectroscopy, respectively. $P = 40 \text{ Pa}$ was the experimental condition. Since we did not have the experimental data of T_i , we assumed it to be higher than the gas temperature slightly. The potential difference between the plasma and the nanoparticle is unknown, since it is expected that a sheath, which is approximated by the standard Bohm theory is not available around the nanoparticle. However, we assume $5.2kT_e/e = 22.9 \text{ V}$ here as a likely value for V_f . The particle temperature was calculated as shown in figure. 5.1 as a function of the accommodation coefficient at the gas pressure

$P = 40$ Pa. Figure 5.2 is the estimated particle temperature as a function of gas pressure. The particle temperature exceeded the melting point even if we assumed a large accommodation coefficient of $\alpha = 1$. The estimated gas temperatures exceeding the melting point of tin at all the values of α . It is sure that core-shell nanoparticles with spherical cores were obtained by the deposition of amorphous carbon films around liquid nanodroplets of tin.

5.3 Production mechanism of small Tin (Sn) particles

The experimental results indicate the robustness of the shell film against the volume expansion of the core at the melting. In addition, the shell film protects the core from the oxidation. A remaining problem of the synthesized core-shell nanoparticle is the appearance of small tin particles in the shell film when it is heated above 300 °C. We can suppose two possible mechanisms of this unpreferable phenomena: 1) the transport of liquid tin from the core to the shell and 2) the aggregation of tin atoms that are included in the shell film at the deposition.

We believe that mechanism 1) is unlikely according to the experimental results. We did not observe the flow of liquid tin through the porous structures in the real-time observation of the TEM image, and the small tin particles appeared at random places separated from the core. As shown in figure 4.14, we did not detect the decrease in the volume of the core even if the small tin particles appeared, suggesting the transport of liquid tin into the shell is negligible. In addition, the appearance of small tin particles was observed only when the sample was heated above 380 °C, even though the melting of core was detected at a temperature of 238 °C from the change in the electron diffraction pattern. Furthermore,

an extremely high pressure is necessary for the penetration of liquid tin into the porous structure of the shell film such as capillary rise scenario [59]. Schematically shown in figure 5.3. The required pressure to exert the force onto the pores in

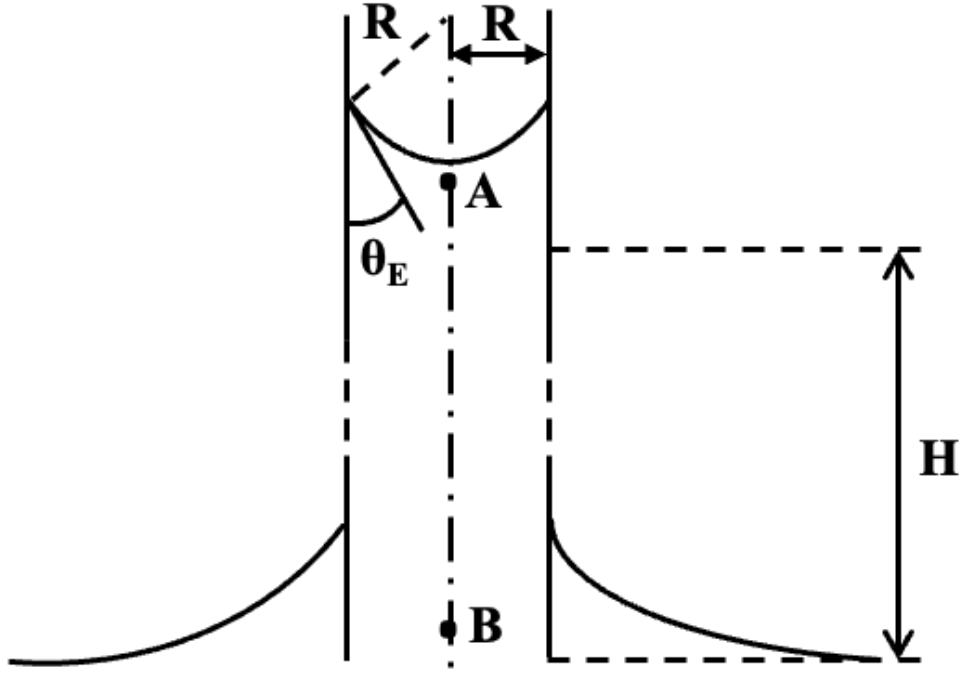


Figure 5.3: Hydrostatic pressure drop between point A and B

shell film or to call capillary rise can be calculated using the equation,

$$P = \frac{2\gamma \cos \theta}{R} \quad (5.4)$$

where $-\pi < \theta < \pi, \theta \neq 90$ and $-\frac{2\gamma}{R} < P < \frac{2\gamma}{R}$, γ is the surface tension of liquid tin (0.56 N/m [60]). The radius (R) of the porous structure considered as 5 nm. The contact angle (θ) between the porous structure wall and meniscus, which is assumed to be $\neq 90^\circ$. The pressure difference between A and B is

purely hydrostatic pressure. It can be observed that an extremely high pressure of 10^8 Pa is necessary for the penetration (capillary rise) of liquid tin into the porous structure in the shell. Such a high pressure is avoided in the present core-shell nanoparticle by depositing the shell around the melted core. Therefore, mechanism 2) seems more likely. As shown in figure 4.11, we detected tin in the atomic composition of the shell.

The mobility of tin in the shell may be enhanced by the heating, resulting in to coalesce to form the small particles. Note that the magnetron sputtering was stopped before injecting methane into CCP. Considering the short lifetime in the gas phase, atomic tin ejected from the sputtering target surely disappeared when methane was injected. The production of atomic tin from nanoparticles due to sputtering and evaporation is also impossible, since the kinetic energy of argon ion arriving at the surfaces of nanoparticles is about 20 eV and the nanoparticle temperature is much lower than the boiling point of tin. However, a longer lifetime would be possible for clusters located in the outside of the dense nanoparticle cloud. The positive bias voltage applied to the disk electrode collects nanoparticles even from the outside of the dense cloud, as shown in Fig. 4.5, resulting in the mixture into the amorphous carbon film.

5.4 How to improve the efficiency of particulate collection

Enhanced efficiency of cores-shell particles collection is necessary for the current process to adopt for large-scale production. As discussed in the earlier sections, this process need to supply the positive potential to the bottom disk electrode while transporting core-shell nanoparticles retained in CCP. Among the issues

involved, the tendency of plasma to raise its potential higher than the electrode potential is an issue to be considered in the design of the large-scale production system. Although this issue is relatively solved in the present work by placing the disk electrode inside the ring rf electrode, another design may be necessary in the large-scale production system. If an electrode for the collection is positioned in different geometry, the collection of nanoparticles by applying the positive bias potential would become difficult.

6 Summary

6.1 Conclusions

In this work, a method for synthesizing core-shell nanoparticles with liquid cores was developed and demonstrated. The method was composed of the nanoparticle generation, growth, the retention, the shell film deposition, and the transport of core-shell nanoparticles.

All the steps in the synthesis were completed in a single vacuum chamber. The dusty plasma allowed the liquid tin nanoparticles to remain suspended in the space, and it was possible to deposit amorphous carbon film uniformly around the liquid tin cores. The liquid cores are observed to have perfect spherical shape and the clear boundaries are observed between cores and shells. The perfect spherical cores with clear boundary reveals the melting of tin cores was covered with amorphous carbon film. The particle temperature was estimated based on heat transfer theory by substituting plasma parameters examined experimentally, and it was confirmed that the gas temperature at the deposition of the shell film was higher than the melting point of tin.

The robustness of the shell is examined by heating the core-shell nanoparticles using special TEM that has in-situ sample heating system. The change in the electron diffraction pattern from a polycrystalline β tin to amorphous indicates the melting of core at the melting point of metal tin. The amorphous carbon film

was sufficiently protective from the oxidation of the core, and it was also robust against the volume expansion of the core at the melting. The leakage of liquid tin through the porous shell is found to be negligible. A remaining problem was the appearance of tin particles with very small sizes in the shell if the core-shell nanoparticles were heated above 380°C.

6.2 Outlook

Enhancing the efficiency of particle transportation could lead to the process robustness. Then, the small tin particles observed after heating beyond melting point in the shell is probably originated from tin atoms admixed into the shell film at the deposition, but the mechanism can be further investigated. Additionally, testing the developed methodology for alternative combinations of core-shell materials can broaden the horizons of novel core-shell particles applicable for PCMs and others. The repetitive melting experiments in the order of 1000s is necessary for the practical use of core-shell nanodroplets. Negatively charged particles are able to be trapped against the negatively charged rf electrode, the design of the electrode (disk, ring) positions may have higher significance. The gas flow direction while introducing methane gas could be further analyzed.

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