

STUDY ON THE OSTWALD RIPENING PHENOMENON ON Fe SPUTTERED FILM ON SiO₂

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Nowadays the carbon nanotube (CNT) topic is in the spot of the scientific world. Many techniques have been developed for the production of single walled carbon nanotubes (SWCNTs) but, a standard method to produce long and high purity nanotubes has not been established. The main reason is the dependence of the carbon nanotubes on the catalyst particle on a substrate. The size and termination of the CNT will depend on the average particle size of the catalyst that is governed by the Ostwald ripening phenomenon.

This research focuses on the particle size distribution of the catalyst over the substrate and the relationship between time, temperature and thickness of the film to produce a desire particle size. The main interest was to determine the parameters and related equations that control the Fe particle growth and particle size distribution.

The study of the Fe particles on silicon oxide surface exhibited a pattern of growth of the Ostwald ripening type and may be used to develop carbon nanotubes. This based on the average particle growth which depends on time and thickness of the film as stated in the statistical analysis.

Resumen de Disertación Presentado a Escuela Graduada
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Requerimientos para el grado de Maestría en Ciencias

ESTUDIO DEL FENOMENO DE ENGROSAMIENTO DE OSTWALD DE PELICULAS DELGADAS DE Fe SOBRE SiO₂

Por

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Diciembre 2011

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Actualmente el mundo científico ha puesto el ojo sobre los nanotubos de carbono. Aunque muchos métodos han sido desarrollados para producir nanotubos de carbono, ninguno ha sido capaz de establecer una receta estándar para producir nanotubos de alta calidad y de un diámetro específico. El tamaño y la terminación de los nanotubos de carbono depende del catalizador y sustrato utilizado y el crecimiento de estos va estar regido por fenómeno de engrosamiento de Ostwald.

Esta investigación dedica su mayor esfuerzo a la distribución de las partículas de un sustrato para determinar el efecto que tiene el tiempo, la temperatura y el espesor de la muestra en crecimiento de la partícula promedio. La idea es determinar los parámetros que afectan o controlan las partículas de hierro (Fe) sobre un sustrato de óxido de silicio (SiO₂).

Este estudio provee un patrón de crecimiento en el comportamiento de las partículas de hierro sobre el sustrato que está basado en el fenómeno de engrosamiento de Ostwald el cual puede utilizarse para crecer nanotubos de carbono de un diámetro específico. Esto está basado en el crecimiento de la partícula promedio que depende directamente del espesor de la muestra y al tiempo expuesto a calor según estudios estadísticos.

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*This thesis is dedicated to my parents Iván Rosa and Carmen Molina for their love,
inspiration, support and encouragement to pursue life challenges.*

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LIST OF ABBREVIATIONS

OR	Ostwald ripening
LSW	Lifshitz, Slyozov and Wagner
CNTs	Carbon nanotubes
HRTEM	High Resolution Transmission Electron Microscope
MWCNT	Multiwall carbon nanotubes
SWNT	Single wall carbon nanotube
(n, m)	Chiral indices
CVD	Chemical vapor deposition
PSD	Particle size distribution
R^*	Critical particle radius
LS	Lifshitz and Slyozov
R	Radius
t	Time
ρ	Re-normalize radius
MLSW	Mean Lifshitz, Slyozov and Wagner
AFM	Atomic Force Microscope
SPIP	Scanning Probe Image Processor
SPM	Scanning Probe Microscope
D	Diameter

K	Correction factor
W_r	Real width
W_m	Measured width
h	Tip surface distance
β	Feature slope angle
nm	Nanometers
$K(Q)$	Coarsening rate
$D(0)$	Initial diameter
$D(t)$	Diameter at time t
$R(0)$	Initial radius
$R(t)$	Radius at time t
G_{LSW}	Diffusion limited ripening
$^{\circ}C$	Celsius degrees
min	Minutes
H_0	Null hypothesis
H_a	Alternative hypothesis

LIST OF SYMBOLS

C	Carbon
Ni	Nickel
Co	Cobalt
Fe	Iron
HgO	Mercuric Oxide
SiO ₂	Silicon Dioxide
Si	Silicone
Ar	Argon
CH ₄	Methane
C ₂ H ₆	Ethane
HC ₂ H	Acetylene
C ₂ H ₄	Ethylene
C ₆ H ₅ CH ₃	Toluene
OH	Hydroxide
H ₂	Hydrogen
O ₂	Oxygen

CHAPTER 1

INTRODUCTION

In 1900 scientist Whilhelm Ostwald expressed that the solubility of small HgO particles depends on their radii.[1]Further studies on this observation lead to the name of Ostwald ripening (OR) in honor of his contribution. This phenomenon is explained as the local coarsening that occurs at the expense of small neighboring particles,[2, 3] as a result the average particle size distribution curve move towards the larger sizes.It was postulated that the bigger particles grow because of the condensation of the material diffused in the matrix due to the small particles evaporating in the process. So the bigger particles will absorb the small particles dissolving them during the process following the conservation of mass law.Scientists Gibbs-Thompson suggests in their studies that matter diffuses from high range of curvature to regions of lower curvature range[4].

The Ostwald ripening phenomenon is associated to the diffusion process that occurs in the last stage of the first phase of transformation. The mixture is not thermodynamically in equilibrium when the particles are very small. Eventually the particle tends towards equilibrium by reducing the gradient of its chemical potential. The phenomenon can be observed in figure 1.1 as time increases the bigger particles absorb the smaller particles. This phenomenon occurs widely in fields of physics, materials science and, other subjects providing applications to metallic, ceramic and, nanostructured materials in the engineering world.

In this investigation the Ostwald ripening phenomenon will be monitored to observe the behavior of the Fe particles over SiO₂ substrate in order to predict a pattern of growth. Available statistical models will be used to calculate the particle size distribution using most common OR theories.

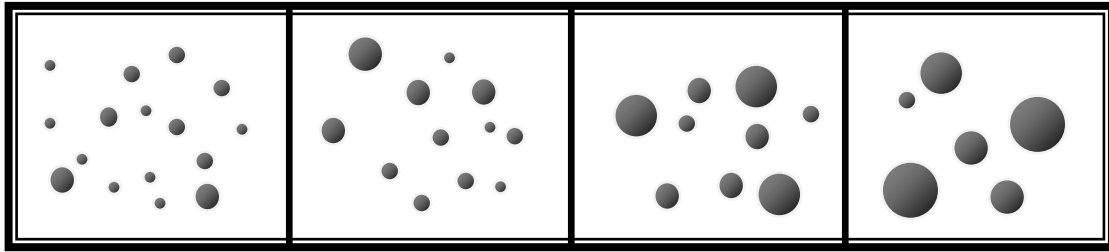


Figure 1.1:Diagram of the particles transformation due to Ostwald ripening phenomenon

1. Literature Review

Since the discovery more than fifty years ago of the Ostwald ripening phenomenon, scientists have tried to model the changes of the particle size distribution in different materials and systems. The phenomenon arises from a binary mixture cooled from a disordered phase into a two metastable region in which the components condense into small droplets.[5] Locally the bigger droplets grow by consuming neighboring small droplets. The OR phenomenon has a wide range of applications among metallic, ceramic, polymer, semiconductor, and nanostructured systems.[4]

Although many years have passed since the discovery of the Ostwald ripening phenomenon only qualitative explanation of it exists. Some scientists have made quantitative approximations and the first one was published by researchers Lifshitz, Slyozov, and Wagner. The theory is known as “LSW” for the contribution of each investigator. The LSW theory states a zero volume fraction in which the interaction among particles is far away. A major problem encountered in the theory is the assumption that the particle coarsening rate is independent of its surrounding. The LSW theory lacks understanding of the close proximity among particles distributed through the microstructure and the interaction that arises among them. Based on the

limitations of the LSW theory scientist started to work with the LSW equations to create a non zero volume fraction for the particle size distribution.

In the literature many names can be seen proposing theories derived from LSW principle, but for two dimensional systems J. Marqusee[6] was the first one to achieve a theory. In his theory, Marqusee derived a growth law for a particle in the presence of other particles. The growth law considers the minority phase as spherical particles of radius R surrounded by the majority phase that broadens in response to local interactions.[7] The Marqusee theory was eventually extended and generalized by other researchers such as Zhen, Gunton, and, Ardell[4, 8]. These theories are used to model the Ostwald ripening phenomenon in two dimensions using analytic and numerical methods and are based on statistically averaged diffusion interaction of a particle with its surrounding. Actually a fully satisfactory approach that describes the coarsening at finite volume fraction has not been found. The previous information will be used to delineate a foundation to compare the dependency of the growth rate upon any parameter established.

1.2 Objectives

The main goal for this investigation is to establish a relationship between the particle size distribution and the dependence of the average particle upon parameters such as time, temperature and thickness of the film. These parameters are used as a way to control the particle size distribution in order to obtain a pattern of growth. Multiple levels will be employed in the parameters to quantify the effect on the average particle.

The overall idea is to relate the behavior of the catalyst particles to known ripening theories in order to predict the diameter of carbon nanotubes. The catalyst particle size is linked to the diameter of the carbon nanotubes. Smaller CNT diameters necessary for the growth of

desired Single Wall CNT's are linked to the presence of smaller catalyst particles, Iron was sputtered over silica to observe the Ostwald ripening phenomenon to fulfill the objectives of this investigation.

1.2.1 Specific Objectives

1. Calculate the average particle size.
2. Create curves of particle size distribution for all samples and check the interaction between parameters using Anova statistical model.
3. Establish a relationship between the particle growth rate and the available parameters.
4. Used available Ostwald ripening theories to predict the behavior of the average particle size.

1. Thesis structure

Chapter 2 summarizes the theory of the Ostwald ripening (OR) phenomenon and some basic principles of carbon nanotubes. All the detail information regarding OR effect in the average particle is properly described in this chapter. In Chapter 3, the methodology and the experimental procedure are discussed such as sample fabrication, involved parameters and equipment used. The chapter details each of the steps for the sample preparation and all the components required to create nanoparticles. Chapter 4 presents the experimental data, the data analysis and the discussion of the results in context with the available literature. Finally the conclusions are provided in Chapter 5.

CHAPTER 2

THEORETICAL BACKGROUND

2.1 Carbon Nanotubes

Since the discovery of the carbon nanotubes (CNTs) the scientific community has been observing cautiously the development of it, due to promising applications in the nano and macroscopic scale. In 1991 scientist Sumio Iijima observed a microtubule graphitic structure using a High Resolution Transmission Electron Microscopy (HRTEM).[9] This observation led to the discovery of what today is called multiwall carbon nanotubes (MWCNT) and the naissance of the CNT field.

Carbon nanotubes exist in many variations and can exhibit a variety of properties. The previously mentioned MWNTs is one distinction and it is made of a bunch of single walled carbon nanotubes (SWNTs) of increasing diameter concentrically positioned one with respect to the other. The SWNT is composed of a rectangular graphene sheet folded to produce a hollow tube. It can also be described as an elongated fullerene, a carbon allotrope discovered by Kroto in 1985[10]. A hexagonal net is created with a carbon atom meeting three wires that form the sheet. The common carbon nanotube structure can be seen in Fig. 2.1. The SWNT exhibits chirality, in which the C atoms are positioned with respect to each other depending on the orientation of the graphene sheet. The difference in structure can be characterized by two chiral indices, (n, m) where $n \geq m$. [11] The indices can be interpreted as a chiral vector, the axis in which the graphene sheet will be rolled. These chiral vectors provide three different types of SWNT from the same sheet of graphene. The most common shapes are armchair and zig-zag nanotubes, if the graphene sheet in the direction $(n, 0)$ is rotated 90° the new direction will be (n, n) instead of

having zig-zag nanotubes, armchair nanotubes will grow. The other SWNT are called chiral CNT due to the chirality in the axis (n, m) , where $n \neq m$ and $m \neq 0$. The difference in SWNTs is shown in Fig. 2.2 and the chirality can be seen upon the same graphene sheet.

The electrical and mechanical properties of CNTs promise a bright future in the nano world. Carbon nanotubes are known as the strongest material available today[12] with 100 times the tensile strength of steel of the same diameter.[13] The thermal and electronic conductance will depend on the orientation of the CNTs[14]. This converts the CNTs in a material that can be conducting on one side and insulating in the other direction. These properties make CNTs a desire material but the complexity in the production of high quality and low cost nanotubes is a barrier among scientist. It is also known that CNTs has a similar behavior of the asbestos causing cell death. These are some of the barriers that CNT field has encounter but new advances in the production are trying to overcome the difficulty to produce high quality nanotubes at a reasonable price.

A standard recipe to produce CNTs has not yet been established but, several methods have been proposed for the growing of carbon nanotubes. Three common methods are used for the production of CNT;s namely arc-discharge, laser ablation and chemical vapor deposition (CVD). The arc discharge method was discovered by Iijima[9] who in an effort to produce fullerenes produced the first CNT instead. In the arc discharge process the carbon in the negative electrode sublimates because of the high discharge temperature.[7]To produce CNTs using laser ablation, the laser vaporize a graphite target in an inert atmosphere on the reactor and so the nanotubes grow on the cooler surface as the vaporized carbon condenses. In the CVD process a substrate with metal catalyst particles is inserted in a reactor at high temperature and in an

atmosphere of a mixture of an inert gas, hydrogen and a carbon containing gas. The CVD process will be further discussed in detailed in the methodology section (chapter 3).

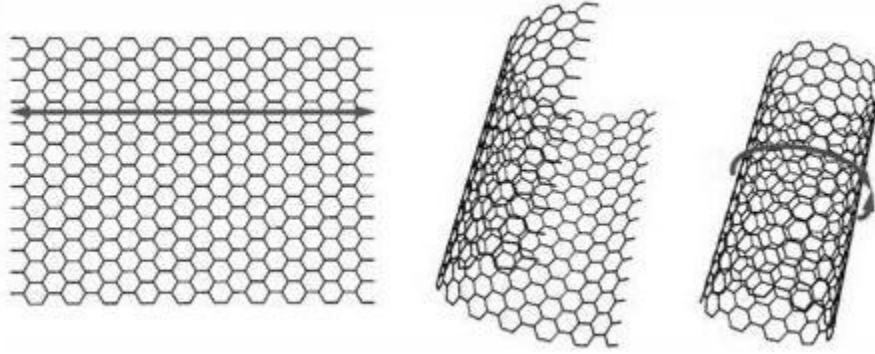


Figure 2.1: From left to right a graphene sheet is folded to create a SWNT.[15]

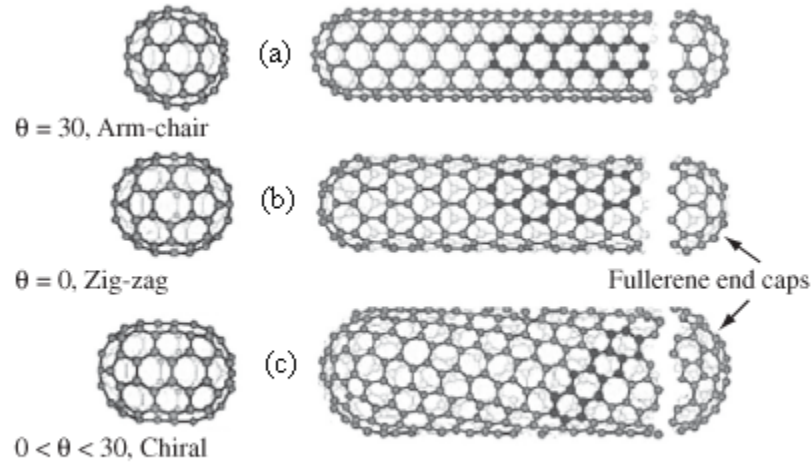


Figure 2.2: Schematic of the SWNTs and chiral vectors acting on the graphene sheet. (a) An armchair nanotube is created by folding the graphene sheet in chiral vector (n, n) . (b) The second illustration is the zig-zag nanotube and the chiral vector direction is $(n, 0)$ which can be obtained by rotating the graphene sheet 90° . (c) The last SWNT is called chiral nanotube, because the chiral vector is (n, m) where $n \neq m$ and $m \neq 0$. The θ represents the chiral angle for each chiral vector. Adapted from reference[16, 17].

2.1.1 SWNTs Catalyst

The production of single walled carbon nanotubes normally carried out at high temperatures using techniques such as arc discharge, laser ablation and CVD with an ultra small metal catalyst to produce single wall tubes. The CVD technique promises a bright future because of the ability of mass production and the better control of the production parameters and hence chirality. Parameters such as the catalyst, the carbon source, the supporting material of the catalyst and the temperature need to be carefully controlled for the production of SWNT.[18] Catalyst such as Ni, Co, Fe or mixtures of them are among the most used to obtain high quality SWNTs. The mechanism is based on the ability of the metal to dissolve carbon particles into the substrate, therefore allowing graphitization of carbon. The catalyst particle becomes saturated with C atoms before the CNT growth starts but it is not known if the catalyst needs to be filled with carbon atoms at the surface to nucleate growth.

Catalyst can be placed on a substrate surface to promote the growth of the CNTs. A catalyst placed over a substrate can exhibit two different types of growth mechanisms. The growth will depend on the interaction between the catalyst and the substrate, if the bond between them is strong the catalyst will remain attached to the substrate and the CNT will grow out from the catalyst particle.[19] This mechanism is known as “root” growth in which the catalyst will remain on the substrate. On the other hand if the interaction is weak, the nucleated CNT will attach to the substrate while the metal particle will detach from the substrate and elevate at the top of the CNT.[19] This mechanism is known as “top” growth and fig 2.3 will show a schematic of the growth mechanism. The adhesion strength between the CNT and the substrate is very important because a weak interaction among them will lead to detachment of the carbon nanotube.

On recent studies Teresa de los Arcos[20] indicated that controlled catalyst oxidation will promote a better quality CNTs. The role played by oxygen or oxidative species on the working gas can have an extremely positive influence on the growth and on the inhibition of catalyst deactivation.[20] Catalytic oxide particles have shown a better performance in the growth of CNT than the metallic substrate by itself.[21]

The constitution and the size of the catalyst particle are important parameters for CNT growth. The diameter of the catalysts has been reported to be slightly larger than the CNTs grown, typically 1.1-1.6 times the CNT diameter.[22] The main importance of the catalyst is that SWNTs nucleate and grow from the catalyst particle.[17] It is great importance to study the catalyst behavior in order to create better and longer CNTs due to the dependency of this parameter to grow nanotubes.

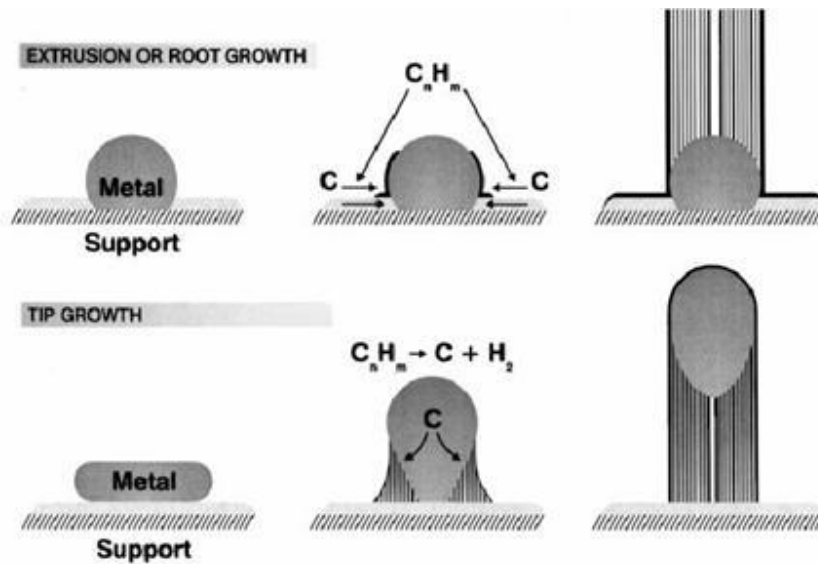


Figure 2.3: Schematic of the growth mechanisms of CNT when the metal catalyst is mounted over a substrate.[23, 24]

2.2 Introduction to Ostwald Ripening Phenomenon

Ostwald ripening is a process related to the coarsening of one phase dispersed in the matrix of another.[25] When a binary mixture is cooled from the disordered phase into the two-phase metastable region the minority component condenses into spherical droplets.[4] This phenomenon born his name by experiments of scientist Wilhelm Ostwald[26] in which he observed that the solubility of particles of HgO depends on their radii. The small particles exhibit a large geometric curvature and more free energy per unit mass than large particles that have small curvature and so the average particle tends to grow at expense of the small particle. The larger particles absorb solute atoms that are released into the matrix by the small particles that dissolved in the system. Locally the bigger droplets grow by consuming the smaller neighboring droplets (see figure 2.4 & 2.5).

On average the particles will grow in radius $R(t)$ as time passes and the number of particles will decrease based on “the big one will consume the small one”. The driving force for this process is the reduction of the total surface free energy. The excess surface energy is responsible for the evolution of the particle size distribution (PSD), which it is described as coarsening. This large surface area is responsible for an unstable mixture which means that the first stage (original PSD) it is not in thermodynamic equilibrium. During the process of coarsening the critical particle radius (R^*) is monitored. According to the theory, locally particles with lower radius than the critical radius will shrink while particles with bigger radius will grow. Solute atoms flow through the matrix from the smaller particles to the bigger particles causing the average radius of the system to increase. This can occur at any stage of the precipitation process and it is described by Gibbs-Thompson [7] . The final evolution of the PSD

will be a single precipitated particle that will contain the entire volume in the second phase of the binary mixture.

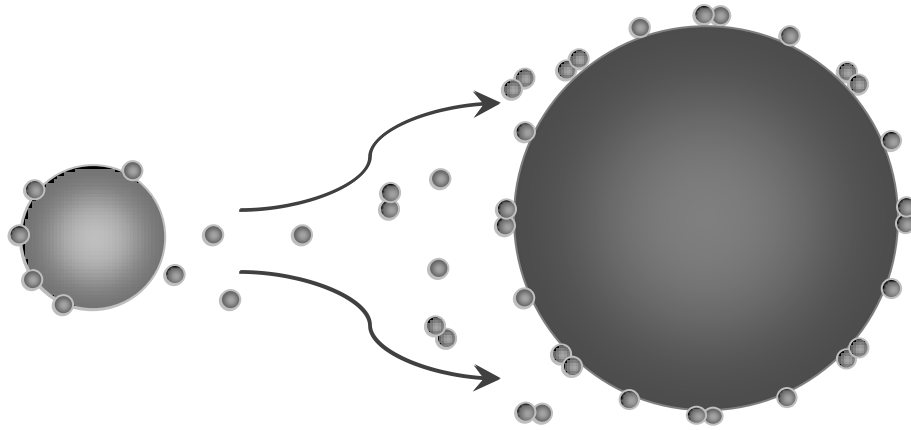


Figure 2.4: The schematic show the small in the left donating solute atoms to the matrix that absorb by the bigger atom making it bigger.

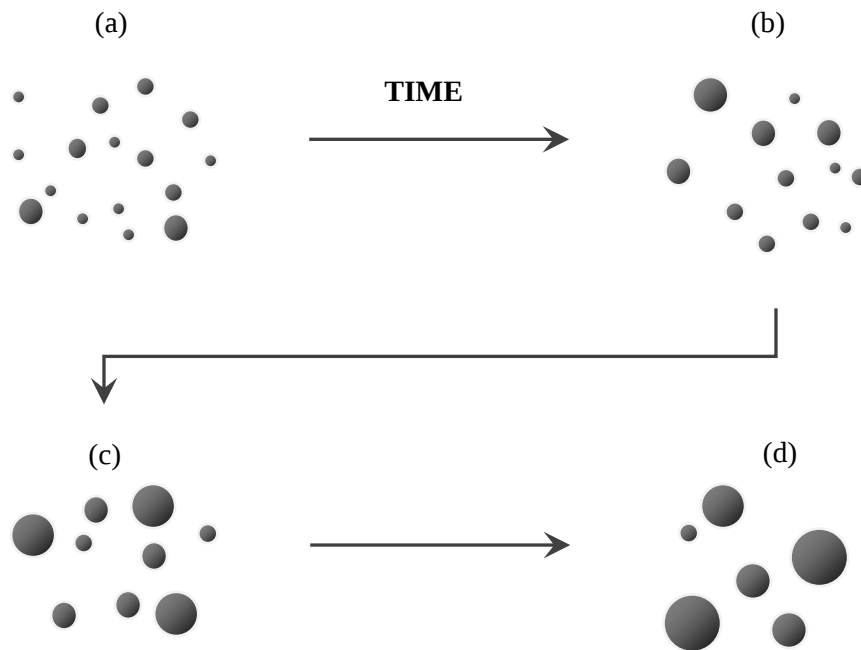


Figure 2.5: The particle size distribution can be observed through time from the left corner (a) to the bottom corner (d). The bigger particle will absorb the small particles as a result of the solute atoms released into the matrix and so the small particles dissolved in the system.

2.2.1 Coarsening Theory and Available Models

Since the discovery of the Ostwald Ripening (OR), scientists attempted to obtain a quantitative explanation of this phenomenon. Many scientist like Greenwood[27] and Asimov[28] developed quantitative theories that were based on unrealistic assumptions for the diffusion field in the matrix. After almost 50 years of no development, Lifshitz[29], Slyozov[29] and Wagner[30] came up with a quantitative prediction of the long-time behavior of the coarsening system. Lifshitz andSlyozov (LS) developed a method to predict the behavior of the coarsening system without recourse to a numerical solution and Wagner wrote a paper relating the LS work to known systems. Nowadays the contribution is known as “LSW” theory.

The LSW theory proposed a zero volume fraction by means of an ideal case. From the theory three equations govern the particle size distribution, in which the continuity equation is the first one and state as follow,

$$\frac{\partial F(R, t)}{\partial t} + \frac{\partial}{\partial R} \left[\frac{dR}{dt} F(R, t) \right] = 0 \quad (1)$$

where R and t are the particle radius and the coarsening time. The second equation describes the growth rate of the particle. It relates the radius of the particle with the critical radius of the system. In which the critical radius R^* is provisionally stable and it has zero grow rate. The equation known as the mean kinetic field state ruled the previous mentioned growth rate,

$$\frac{dR}{dt} = \frac{1}{R} \left(\frac{1}{R^*} - \frac{1}{R} \right) \quad (2)$$

The last equation stated by the LSW theory is for mass conservation for the coarsening system. In which it only retains its validity for a zero volume fraction. The cube of the average length scale of particle increases linearly with time has shown to remain strong by numerous experiments, even for cases where the assumption of a zero volume fraction of particles is seriously violated.[1] The particle size distribution equation for the diffusion is as follows,

$$G_{LSW}(\rho) = \begin{cases} \frac{4}{9}\rho^2 \left(\frac{3}{3+\rho}\right)^{7/3} \left(\frac{3}{3+2\rho}\right)^{11/3} e^{\left(\frac{-\rho}{1.5-\rho}\right)}, & (0 \leq \rho < 3/2) \\ 0, & (\rho \geq 3/2) \end{cases} \quad (3)$$

The particle re-normalized radius is $\rho = \frac{R}{R^*}$, which is not dependent of time. Where the variable ρ compares the instantaneous particle size to the entire population's increasing size.[1]

Soon after the publication of the LSW papers many experimentalist rushed to test the veracity of the theory. Even though the experiments confirmed the prediction of the coarsening behavior they noticed that the major problem of the LSW theory was the mean field nature of the kinetic equation. In the latter, the approximation assumes that a particle's coarsening rate is independent of its surrounding.[7] The LSW theory became far away from the realistic scenario in which the systems exhibit a non zero volume fraction. In real systems, a finite, non zero volume fraction is distributed through the microstructure. Most of the particles remain a close proximity and many interactions arise among them. Scientist knowing the limitations of this equation started to develop equations for a non zero volume fraction using principles of the LSW theory.

2.2.2 Mean Field Theory

The naissance of the LSW theory revolutionized the study of the Ostwald ripening among the scientific community. The non-zero volume fraction was an issue to be resolved to ensure the veracity of the model. Ardell[31] was among the first one to modify the LSW theory for a non zero volume fraction of the disperse phase. He considered the influence of the nearest neighbor on the grow rate of the particles. The theory known as MLSW state a non zero volume based on diffusion controlled coarsening and a modification of the kinetic equation. It shows the PSD broadened in response to the local interaction, and the coarsening rate increased with the increasing volume fraction. Although this model overestimate the influence of the volume fraction.

Less after Tsumuraya and Miyata[32] make a variation on Ardell work using a series of different kinetic coarsening interaction laws. Their work is known as “T-M” model and it defines an appropriate radius of influence surrounding each particle. They explored six-mean field interactions to predict the growth rate of the interacting particles. The model share common approximation with Ardell work and so exhibit similar traits in the kinetic prediction for the microstructure evolution.

Eventually Brailsfords and Wynblatt[33] developed the effective medium theory based on LSW work. They obtained the theoretical growth rates of particles and a broadened PSD relative to the LSW model. They established an implicit relationship between the coarsening rate and the volume fraction. Then a concept of statistical “field cell” was introduced by Marsh and Glickman[34]. In their work they obtained the coarsening rate constant based on particles acting around each size class undergoing coarsening. These methods are all based on Laplace’s

equation as the quasi-static approximation for the time dependent diffusion field.[1] They rely on finding self-consistent global microstructure constraints that provide a cut-off distance to terminate mass diffusion at some appropriate distance from a particle centered in a otherwise infinite Laplacian field.[1]

Other researchers such as Marquees and Ross[6] show that Poisson's equation is more appropriate than Laplace's equation for deriving the kinetic expression. They found the maximum particle radius expected in effective media at different volume fractions, the relationship between the coarsening rate and the volume fraction.

All mean-field theories stated that a nonzero volume fraction of the particles does not alter the temporal coarsening exponent in the kinetic law from the LSW mean field theory. Although all the previous mentioned models comply with non-zero volume fraction no available model has been achieved closer to reality.

CHAPTER 3

METHODOLOGY

This section provides the methodology used to describe the particle behavior as a function of different parameters such as time, temperature and thickness of the substrate. It also includes information of the adequate materials to successfully fulfill the objective of the research. Through the chapter all the equipment used for the investigation will be properly described. Fig 3.1 shows a flowchart of the steps followed during the experimental work.

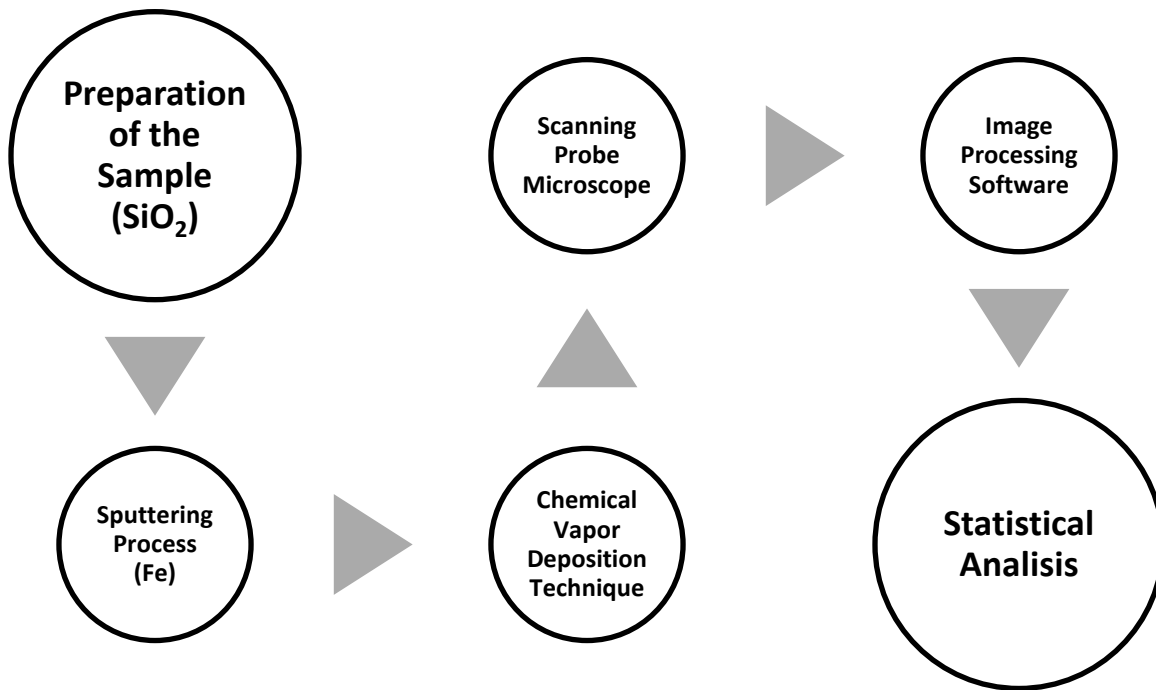


Figure 3.1: Flowchart of the experimental procedure followed.

3.1 Materials

3.1.1 Substrate

The substrate used was a silicon wafer that has a silicon dioxide coating of about 10nm growth by thermal oxidation. SiO_2 has tetrahedral crystalline different structures that can be polymorphs or amorphous. The glass consists of a non-repeating network of tetrahedra, where all the oxygen atoms connect to neighboring tetrahedral. Silica is most used for electrical applications as insulators with high chemical stability. Figure 3.2 shows a picture of the silica wafer used. The dimensions of the wafer are 3" diameter with a thickness of $655\mu\text{m}$ coated with oxide.

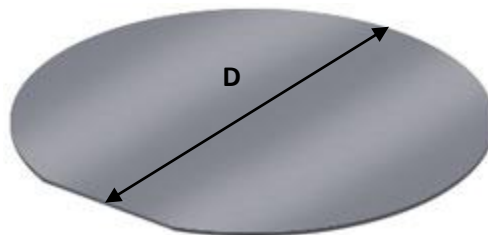


Figure 3.2:Picture of the Si wafer with an oxide coating of about 10 nm

3.1.2 Ion Beam Sputtering

Sputtering is a deposition process, which physically removes a target material by bombarding it with gaseous ions of Ar^+ under a voltage field of 2-10 kV. The ions collide with the target, and atoms and molecules are ejected from the target and propelled to the sample. The ion beam sputtering allows the deposition of ultra thin films by controlling the plasma current and voltage [35]. The film deposited is of uniform thickness and smooth with no substructure. This technique is widely used to provide electrically conduction surfaces for high resolution electron microscopy.

A model IBS/e ion beam (Fig.3.3) sputtering apparatus was used to deposit the catalyst over the substrate. Iron (Fe) was used as target and the deposition ratio was monitored using an oscillating quartz crystal. A mask was used to deposit three different thicknesses over the silica wafer. The thickness of the film is controlled accurately (in Angstroms) by the deposition parameters and it is independently measured with a quartz microbalance. The wafer was divided into center, bottom and top with the highest amount of Fe in the center of the sample and Fig.3.4 shows the distribution deposition on the sample.



Figure 3.3:IBS/e Ion Beam Sputtering apparatus

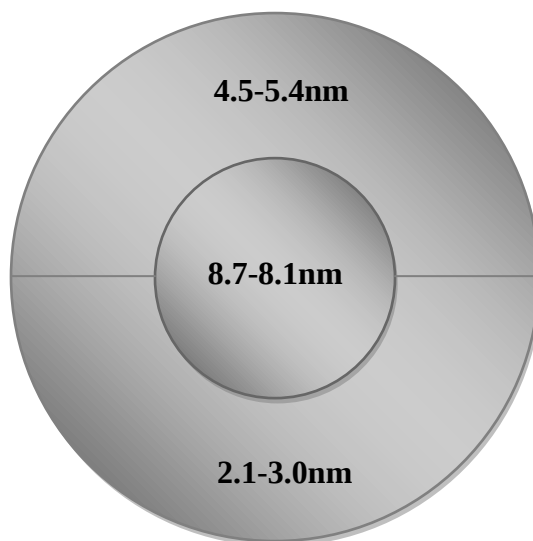


Figure 3.4: Illustration of the thickness distribution of Fe over the substrate. A mask was put over the substrate to cover the different areas in order to obtain different thicknesses over the sample. The thickness was monitored using a quartz microbalance.

3.1.3 Chemical Vapor Deposition

Chemical vapor deposition is called to a group of processes that involve depositing a solid material from a gaseous phase. In the process precursor gases are delivered in a reaction chamber that will decompose when contacting the substrate cause by an energy source. The process produces a solid phase in the substrate and Fig. 3.5 exhibit a schematic of the components of the CVD.

For the production of CNTs a carbon source in the gas phase is introduced in the reaction chamber that has an energy source in this case a tube furnace to transfer energy to the carbon molecule. The energy source will crack the molecule into reactive atomic carbon that diffuses

into the substrate. With thermal annealing over the catalyst the nucleation process starts creating clusters on the substrate from which nanotubes will grow.

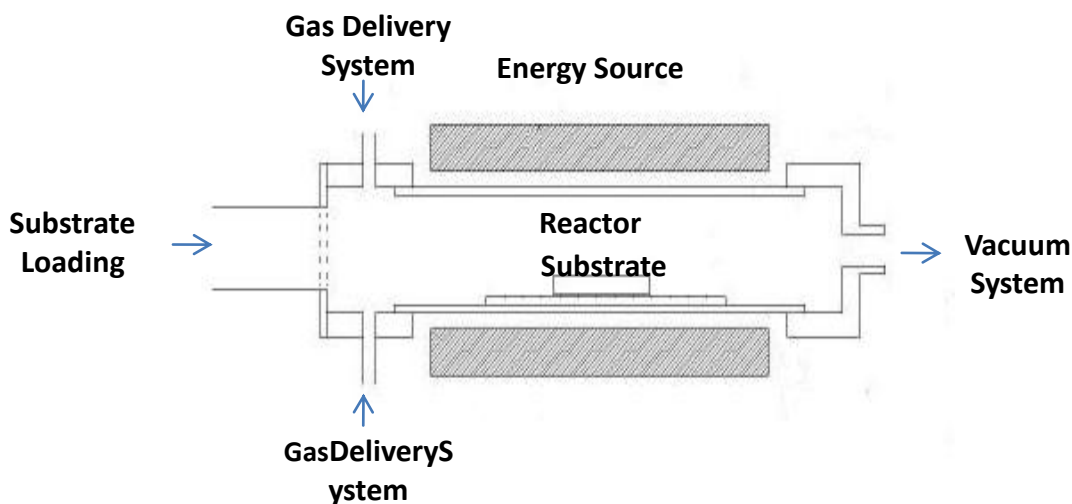


Figure 3.5: Schematic of the components of the CVD. From left the sample enters the reactor chamber using a rapid insertion device when the tube furnace is at the desired temperature. While the function of the vacuum is to remove all pre-existent gaseous species.

3.1.3.1 Precursor gases

Hydrocarbon such as methane (CH_4), ethane (C_2H_6), acetylene (HC_2H), ethylene (C_2H_4), and toluene ($\text{C}_6\text{H}_5\text{CH}_3$) are used as carbon precursors. The chemical reaction between the carbon source and the substrate produces OH. This reduces the formation of soot combustion chemistry inhibiting the formation of side-products, resulting on a cleaner synthesis process. The dangling bonds are removed to create high purity SWNTs.

A vacuum process is used to prevent oxidation of the carbon in which a continuous inert gas flows. Hydrogen (H_2) or Argon (Ar) is used to reduce the Oxygen (O_2) content in the CVD environment. The process is responsible of removing all the gaseous species other than those required for the reaction deposition.

3.1.3.2 Tube Furnace

A horizontal tube furnace held at 825°C and 700°C was used to heat the samples in a time interval of 4, 8 and 16 min. An atmosphere of $\text{Ar}+H_2$ was used to prevent contamination of the samples. The samples entered the reactor chamber using a rapid insertion device to induce rapid heating rates, avoiding growth anomalies during heating to the desired temperature. The tube furnace provides a controlled environment for the samples allowing the growth of the Fe particles on the substrate. The furnace used for the experiment was a Lindberg/Blue M* 1100°C [36] shown in Fig. 3.6 and Fig 3.7 shows the rapid insertion device utilized to deliver the samples into the oven.



Figure 3.6:Lindberg/Blue M* 1100°C Tube Furnace

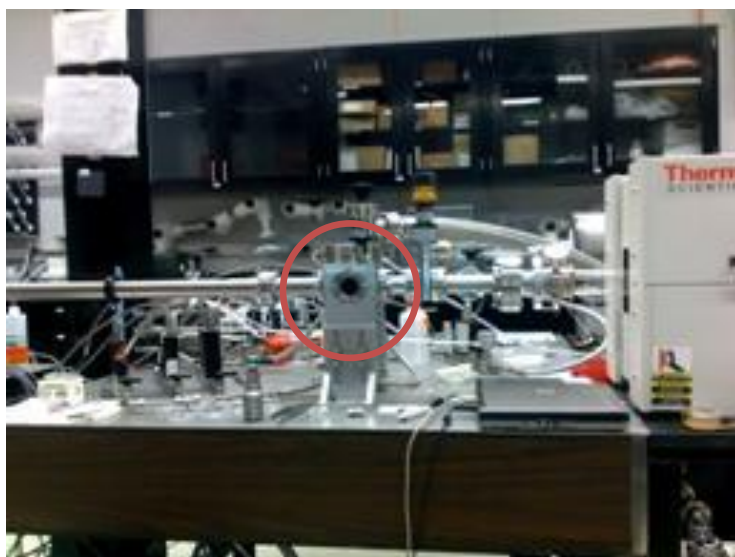


Figure 3.7: The rapid insertion device is marked with a red circle. The sample is loaded in the device and delivered into the reaction chamber using quartz boat. The system is responsible to load and extract the sample from the tube furnace.

3.1.4 Scanning Probe Microscope

A VEECO Dimension 5000[37] scanning probe shown in Fig. 3.8 was used to obtain a surface image of each sample. The idea was to use the atomic force microscopy (AFM) to acquire pictures in the nanoscale resolution to observe particle growth on each sample. One sample was analyzed before the rapid insertion annealing to show the absence of substructures (Volmer-Weber effect) on the deposited films. In the annealed samples, the scan provides mapping of the particles along the sample for the time interval previously mentioned. The pictures taken from the AFM will be used to quantify the particles along the sample and to calculate the average particle and distribution size in each sample. The equipment monitored the particle size distribution by gathering information of each time in a nanoscale picture of the surface of the substrate. In order to characterize the particles and follow its behavior, SPIP software was used. The latter will be discussed in detail at the end of this chapter.



Figure 3.8:SPM VEECO Dimension 5000

3.1.4.1 Atomic Force Microscope

The atomic force microscope (AFM) was invented in 1986 by Binnig, Quate and Gerber. The mechanism consists of a sharp tip moving over the surface of the sample that scans it to produce an image. The scanning process is conducted by a high resolution piezoelectric scanner which delicately moves the tip in a raster pattern with respect to the sample. The end radius of the tip ranges from 2 to 20nm and it applies a constant force over the sample. With the interaction between the surface of the sample and the tip an image is produced using a reflecting laser beam on top of the tip that converts into a split photodiode detector. The sample is raster while monitoring the change in the cantilever deflection with the detector. A feedback loop maintains a constant cantilever deflection by vertically moving the scanner to maintain a constant photodetector difference signal. A topographic image of the surface is produced by the x, y and z coordinates stored from the tip movement over the sample. Figure 3.9 shows an example of the AFM mechanism and components.

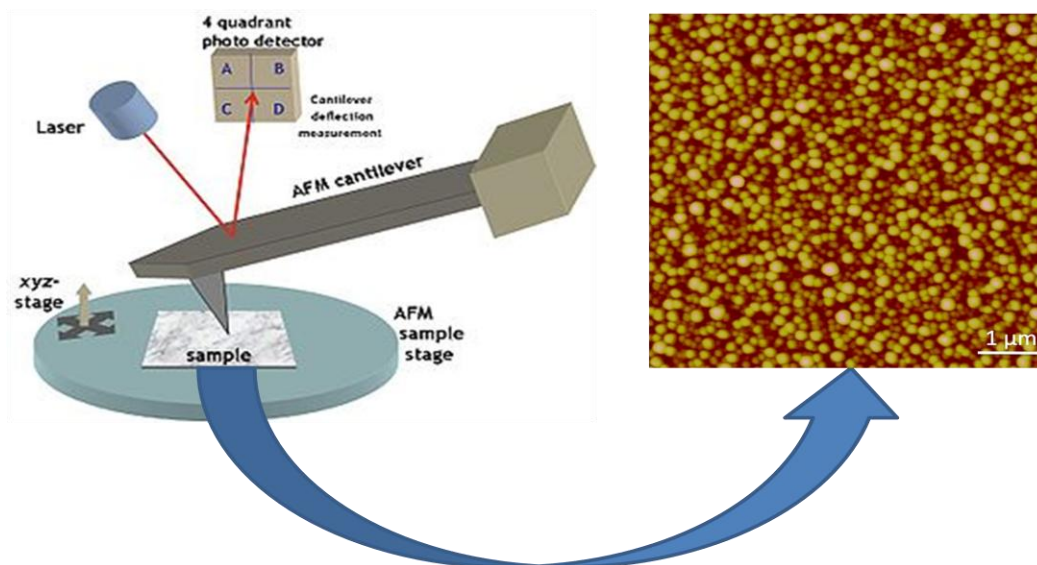


Figure 3.9: Schematic of the AFM mechanism in which the sample is rastered by the tip that is monitored using a laser that reflects over cantilever beam into the photodiode detector to produce an image of the surface as the one seen on right.

3.1.5 Image Processing Software for Microscopy

The Scanning Probe Image Processor better known as SPIP[38] is a windows software with features for image processing and analysis. It is one of the most useful software for images obtained in the scanning probe microscope. The software supports a wide variety of microscopes and their file formats including Scanning Probe Microscopes (SPM). It is featured with correction tools to create an accurate surface image and automated analysis techniques to help users in the visualization of the images.

The software was used during this investigation to measure the catalyst particles diameter and particle size distribution using the particles and pore analysis feature. The images obtained from the SPM were analyzed observing the particle size distribution along a time frame of 4, 8, and 16 minutes. The software measured the particles by creating a grid of pixels in which in the center of it has the image point to create the shape of the particle. The pixels causes the particles

to be bigger than they are but the program allows contour smoothing to soften the particle perimeter with the following relation (see Fig. 3.10):

$$P \approx \pi \times D(4)$$

Each image was processed using the Watershed-disperse feature in which the particles are measured using a flood technique that allows accurate measurement of conglomerated particles. Fig. 3.11 shows the Watershed Feature technique. Although two watershed methods can be applied to analyze the samples, the dispersed feature was used instead of the packed feature to provide a more accurate measurement of the particles. The contour mean height was used to measure the radius of the particle from z direction based on what is shown in figure 3.10 and compare it to the in-plane (x-y) measurements. Appendix A will provide schematics and information of the detection, post processing and filters used to obtain the particle measurements.

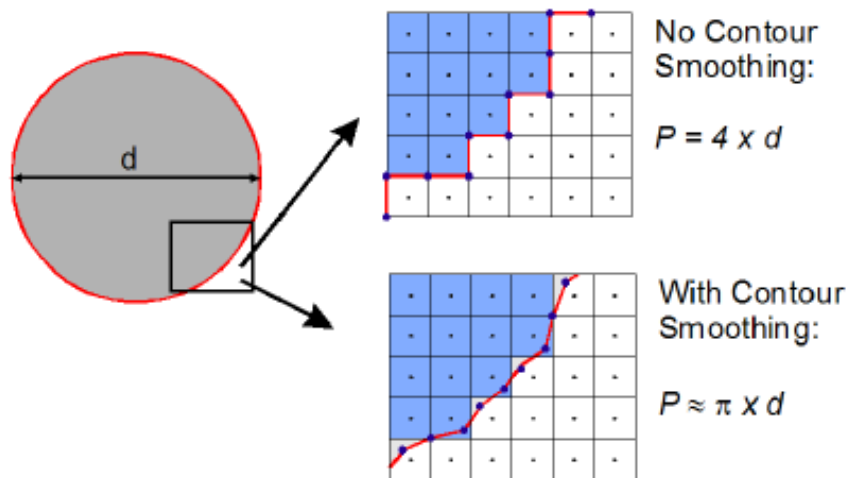


Figure 3.10: Schematic of the contour smoothing system for circular particles

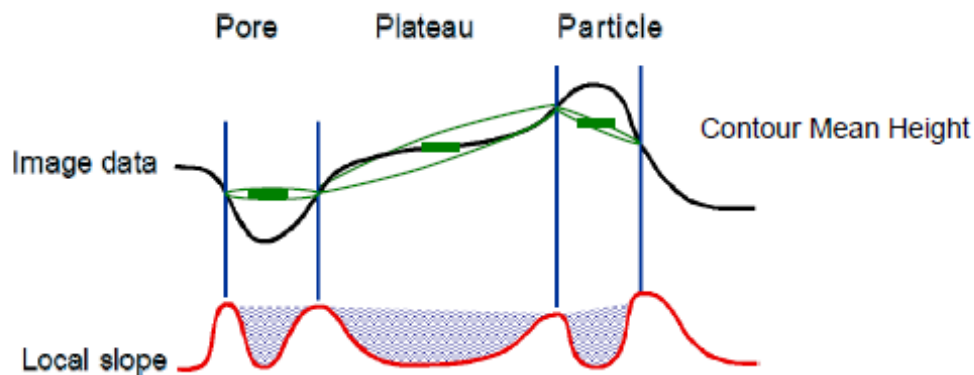


Figure 3.11:Illustration of the flood method used in the Watershed Disperse feature to detect particles, pores and plateau in which the contour mean height represents the radius of the particle.

The area measured by the AFM was $5\mu\text{m} \times 5\mu\text{m}$. Pictures of the detection method can be seen in the Figure 3.12 showing the sample with and without the detection method to see the accuracy of the software in the determination of the particle size.

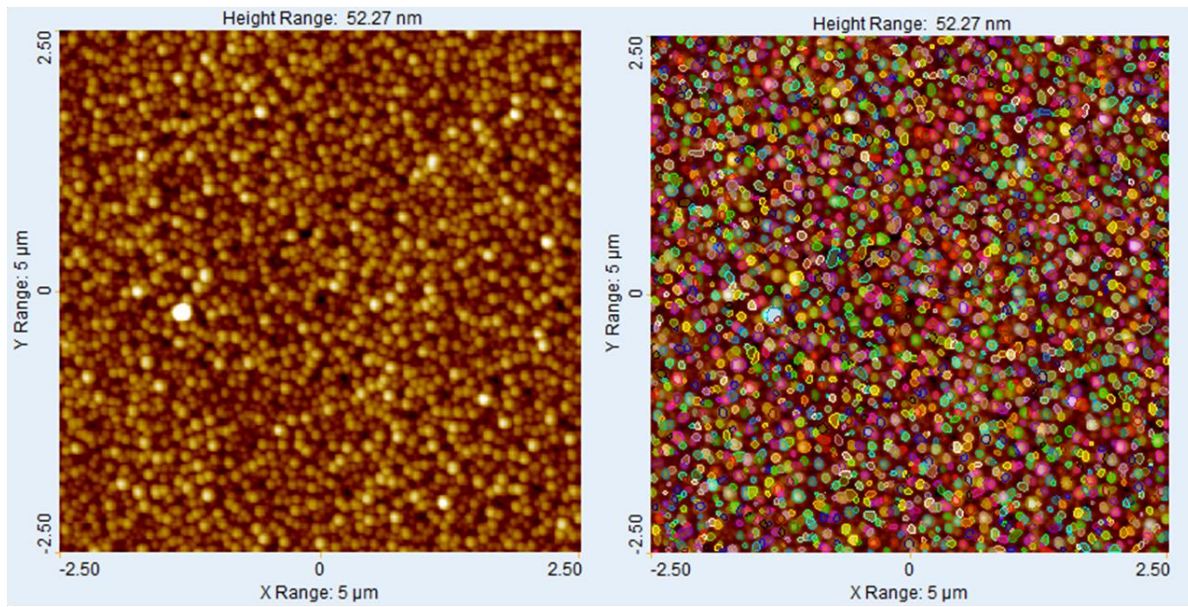


Figure 3.12:Particles detected using the Watershed Disperse feature.

3.1.6 Statistic Software

Minitab software was used for the analysis of data with a variety of statistic application. The general linear model was used to observe the dependence of the parameters such as time thickness and temperature on the average particle diameter. The interaction between the parameters was monitored to observe if, it has an effect in the growth of the average particle.

The nested method used the average particle diameter as a response that depends on factors such as time, thickness, and temperature and sample variation. The general linear model analyze the factors in hierarchy in which samples will be on the top with 2 levels and so the others will be on the bottom with 3 levels for a response that will be the average diameter. The method will give as an output the p-value in which the value must be less than the level of significance ($\alpha = 0.1$). All the levels were fixed and the analysis of variance was performed. The results from this test will be further discussed in the next chapter. A schematic of the design of experiment test will be shown in Fig. 3.13

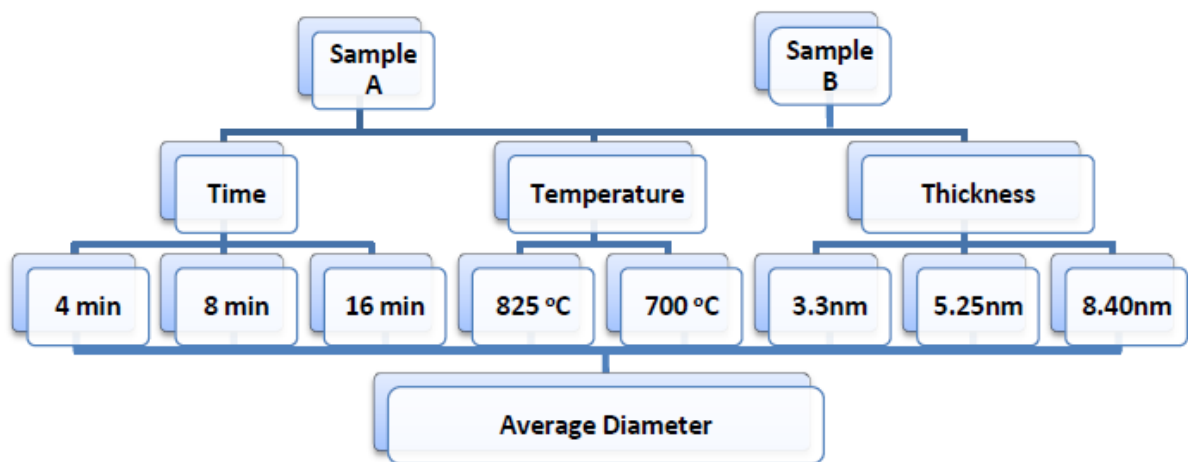


Figure 3.13: Hierarchy of the General Linear Model.

3.2 Experimental Procedure

The samples were made of silicon wafers coated with an oxide surface thickness of 10nm by thermal oxidation process. A mask was placed over the substrate to control the amount of iron (Fe) to be deposited on the wafer. The mask, divided into three sections, was used to prevent unwanted deposition on the samples. At first a 10Å coating was deposited using a South Bay IBS/e sputter with a Fe target with a mask on top and bottom covered by a mask. Then the top mask was removed and 7Å was deposited as for the bottom area the mask was removed and the remainder amount was deposited. The Fe sputtered over the substrate SiO₂ was monitored using a quartz crystal. After deposition, a chemical vapor deposition (CVD) was used with argon (Ar) and hydrogen (H₂) as gaseous media to prevent oxidation. The reaction chamber placed at the middle of a tube furnace was held at either 825°C or 700°C. The samples were placed into the furnace using a rapid insertion mechanism to minimize particle development during heating and to observe the true growth rate of the particles at the temperature. A time interval of 4, 8 and 16 minutes was used to grow the iron nanoparticles over the substrate. Then each sample was analyzed using a scanning probe microscope VEECO Dimension 5000 to obtain images of the sample. In which the atomic force microscopy raster the surface of the sample with a 10nm and 20 nm tip to provide an image of the sample. Pictures for each section of the samples were taken and analyzed using SPIPsoftware with the particles and pore analysis section. The software provides the average particle size required for the Minitab analysis. The Ostwald ripening phenomenon will be confirmed based on the changes of the particle size distribution and the average particle size. The results will be discussed with the available ripening models to corroborate their accuracy under these experimental conditions. A schematic of the previous discussed process is shown in Fig. 3.14

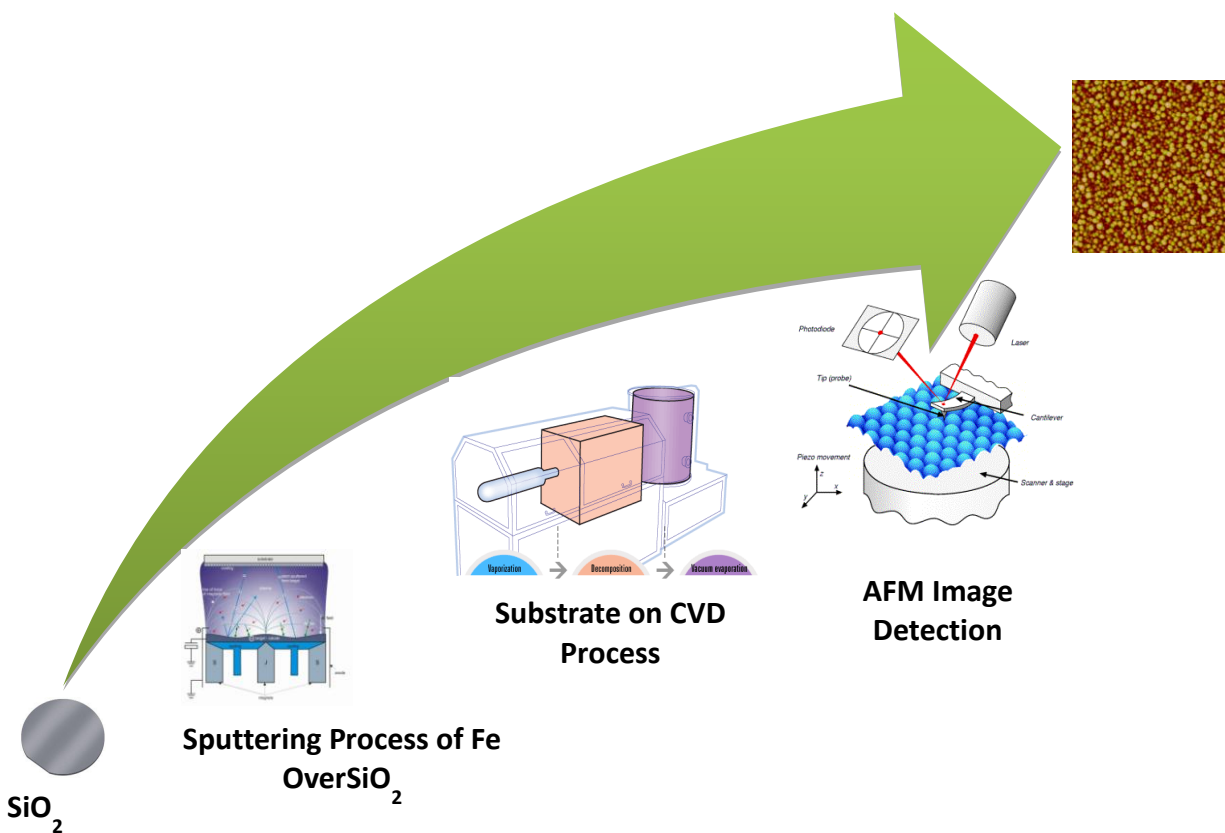


Figure 3.14: From left to right the process used to observe the particle size distribution in the Ostwald ripening phenomenon.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Particle Size Distribution

The outcome of the previous experimental procedure led to a pattern of growth of the iron (Fe) particles over the SiO₂ substrate. Each particle was measured individually and the mean was calculated for each sample to observe the growth rate of the average particle. Based on these calculations Tables 4.1 to 4.4 were created to monitor the behavior of the average particle subjected to different deposition and synthesis parameters. Tables 4.1 & 4.2 exhibit the particle size distribution obtained from in-plane measurements. These were compared with the results obtained without the addition of the AFM tip radius, as seen in Tables 4.3 & 4.4. The idea behind the measurement is to have a more realistic value of the average diameter of the particle. When the particle average diameter and particle size distribution are obtained from the in-plane measurements there is an effect of the AFM tip diameter on the measurements. As part of this investigation a correction is made to eliminate the effect of the tip diameter on the particle size measurement. In order to have a better understanding of the particle distribution it is important to remember that in each sample an average of 2500 particles were measured in an area of 5 μ x5 μ . This population will show the development of the average particle size as time and temperature increases between samples. The particles were monitored in three stages of time and two of temperatures to follow their growth and its dependency upon a parameter. Also the variation of thickness in samples was monitored very carefully to measure the effect of the Ostwald ripening phenomenon.

Table 4.1: PSD measured in Plane at 825°C

Ave. Dia. (nm)	Thickness (nm)	Time (min)
60.38	8.1	16
60.42	8.1	16
58.51	8.7	8
56.99	8.7	8
57.21	8.1	4
54.95	8.1	4
55.86	5.1	16
57.34	5.1	16
32.5	5.4	8
31.39	5.4	8
20.83	5.4	4
20.97	5.4	4
43.23	3.3	16
42.01	3.3	16
26.44	3.3	8
24.62	3.3	8
19.39	3.3	4
17.92	3.3	4

Table 4.2: PSD measured in Plane at 700°C

Ave. Dia. (nm)	Thickness (nm)	Time (min)
41.14	5.4	16
41.86	5.4	16
22.05	5.1	8
23.44	5.1	8
14.55	4.5	4
12.92	4.5	4
37.77	3.0	16
37.77	3.0	16
18.26	3.0	8
18.17	3.0	8
9.64	2.1	4
8.16	2.1	4

4.1.1 Clusters Formation and Particles Distribution

The cluster formation is an irreversible process in which nucleation evolve smoothly from a diatom to several hundred configurations. Nucleation process involves the formation of clusters that entirely depends on energy instability in the parent state. Low temperatures provide a driving force toward equilibrium while high temperature creates instability in the cluster formation. Clusters form because of solute species mobility, monomers eventually bond to each other and form small aggregates that can grow or dissolve depending on their free energy. Once they have reached the critical size, the thermodynamics driving force induces further growth by capturing surrounding monomers. Basically particles will decompose into the matrix and a neighbor particle absorbs the solute atoms disperse through the matrix. This happens because of the concentration gradient, i.e. the smaller ones will dissolve and the bigger ones grow correspondingly. Isolated nuclei surrounded by such concentration gradient, progressively accretes atoms from its surroundings. Gibbs-Thompson[39] established the feature of growth to the effect of surface curvature. Particles will diffuse from high range of curvature to regions of lower curvature range.

As previous shown Table 4.1 to 4.4 demonstrates how the growth of the particles undergoes clusters formation and supports Gibbs-Thompson studies. In a time frame of 16 minutes particles evolve and show increment in size as time passes. The average particle is measured to follow the pattern of growth. Even though the average particle was measured using two systems (in plane and height) it is clear that particles grow as time passes. This growth evolution depends on the balance between thermodynamics and kinetic growth factors. The factors of growth of the average particle size will depend on several factors such as nucleation

rate, components diffusion, enthalpy and free energy.[1, 40] In terms of temperature particles exposed to the higher temperature grow bigger than the particles exposed to lower temperature.

At long times the size of the particle reach equilibrium or its maximum size. Smaller particles have more energy than larger ones as particles evolve through the process the total energy is reduced. In the process a quasi-equilibrium govern the growth rate, a significant fraction of particles are still undergoing formation as other grow. This affects the size distribution in terms of accuracy while establishing a pattern of growth for the particles studied.

The particle size distribution is dependent on temperature, time and thickness of the sample and each table shows discrepancies between the average particle diameter values. These discrepancies demonstrate some relationship between the parameters and the size distribution. This will be further discussed using an ANOVA statistical analysis to the previous particle population to observe the interaction among the parameters.

4.1.2 Average Particle Correction

Atomic force microscopy is a reliable instrument for investigations at the nanoscale but, the interaction of the tip and the sample causes an over estimation on the size of the particles. The tip shape causes the picture to differ from the real object and it increases the real size. During the scanning process the tip moves along an equipotential surface instead of the sample surface. In the scanning process, the tip radius is added to the surface of the particle when measured. In such case the path of the tip is broadened or narrowed with respect the shape of the particles and introduces a significant deviation. The distance between the real surface and the measured surface varies between several nanometers to a few tens of nanometers, which could be a relative large value in this investigation.

To reduce the over estimation a method called “blind reconstruction” [41, 42] is used to recover the real surface of the particles. The measurement method determines the lowest oscillation amplitude of the tip due to the resolution and acceptable level of noise.[43-57] Although this method reduced the value to near the real size, it is important to emphasize that tip-sample distance estimation is difficult, due to a problem with defining the permanent contact point (0nm distance). This has been discussed in several papers.[41, 58]

To make a correction analysis to the previous in-plane diameter values the equations used for round objects are;

$$W_r = W_m - K$$

Where K is the correction value, which is subtracted to the measured width (W_m) and so gives the real width (W_r) that is represented in Fig. 4.1. For the correction factor K the equation state as follow:

$$K = 2((r + h) \sin \beta)$$

The variables used for the calculations are the tip curvature radius (r), the tip-surface distance (h) and β the feature slope angle. For the calculation of β the following subtraction was made;

$$\beta = \alpha - 90^\circ$$

$$\beta = 25^\circ - 90^\circ = 65^\circ$$

In which α represents the tip cone angle that was equal to 25 degrees. Refer to Fig 4.1 to observe the variables involved in the tip correction.

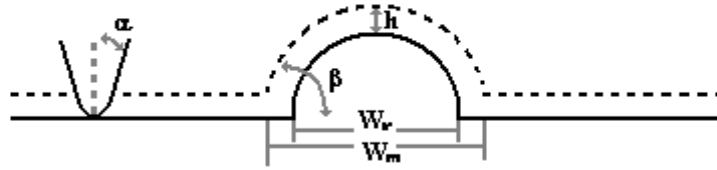


Figure 4.1: Added tip value and variables involved in the correction formulae

Using this method Table 4.3 and Table 4.4 was generated to observe the pattern of growth based on elimination of the over estimation. Observing the values it can be seen the same pattern of growth so it is clear that the tip correction only eliminates the addition of the tip radius to the diameter of the particles. To better understand the growth behavior, the values are plotted and compared in the next section to determine the trend of the particles.

Table 4.3: PSD Tip Correction at 825°C

Ave. Dia. (nm)	Thickness (nm)	Time (min)
44.36	8.1	16
45.22	8.1	16
43.64	8.7	8
42.93	8.7	8
41.03	8.1	4
38.90	8.1	4
41.44	5.1	16
43.64	5.1	16
18.31	5.4	8
18.14	5.4	8
9.56	5.4	4
9.75	5.4	4
30.76	3.3	16
29.45	3.3	16
15.97	3.3	8
14.36	3.3	8
8.67	3.3	4
7.33	3.3	4

Table 4.4: PSD Tip Correction 700°C

Ave. Dia. (nm)	Thickness (nm)	Time (min)
30.11	5.4	16
30.78	5.4	16
11.98	5.1	8
13.22	5.1	8
4.11	4.5	4
2.63	4.5	4
26.22	3.0	16
27.03	3.0	16
8.47	3.0	8
8.42	3.0	8
0.95	2.1	4
0.48	2.1	4

4.1.3 Plots of the Particle Size Distribution

The following section provides plots of the previous data collection. In order to have a better understanding of the development of the particles each plot provide information of the time and temperature in the furnace based on the thickness of the sample. The discussion of the plots will be made individually and a final review will be made in the next chapter.

At first, the particles were measured using the in-plane method which was the default measuring system of the SPIP program. There are replicas of the same thickness sample to confirm the pattern of growth to establish a better analysis.

To normalize the data the AFM tip radius was eliminated using equations 4.1, 4.2 and 4.3 to observe the real behavior of the particles. This method provides a more accurate value for the particle size distribution in order to obtain information of the growth process of the particles based on Ostwald Ripening phenomenon.

To have a better understanding of the particle size distribution each plot will be discussed individually to attribute the dependency of growth to any of the parameters or a combination them. All the gather information will be discussed in detail based on LSW model and statistical data to correlate experimental findings with theoretical models.

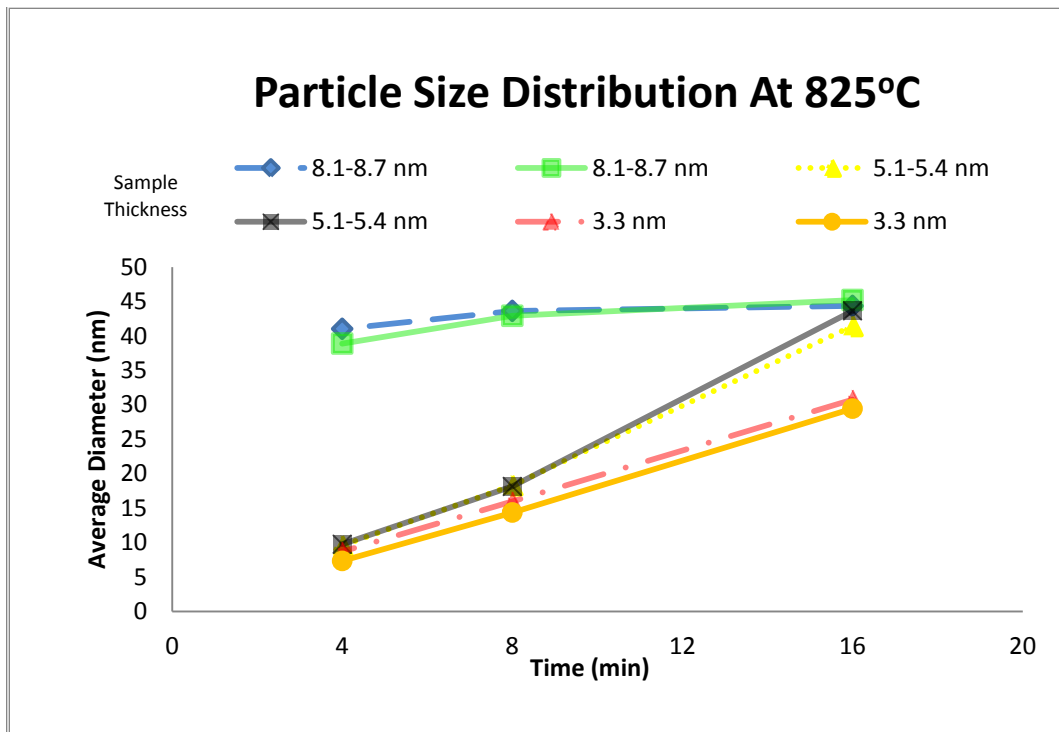


Figure 4.2: Growth distribution of the average particle in terms of oven time exposure at 825°C.

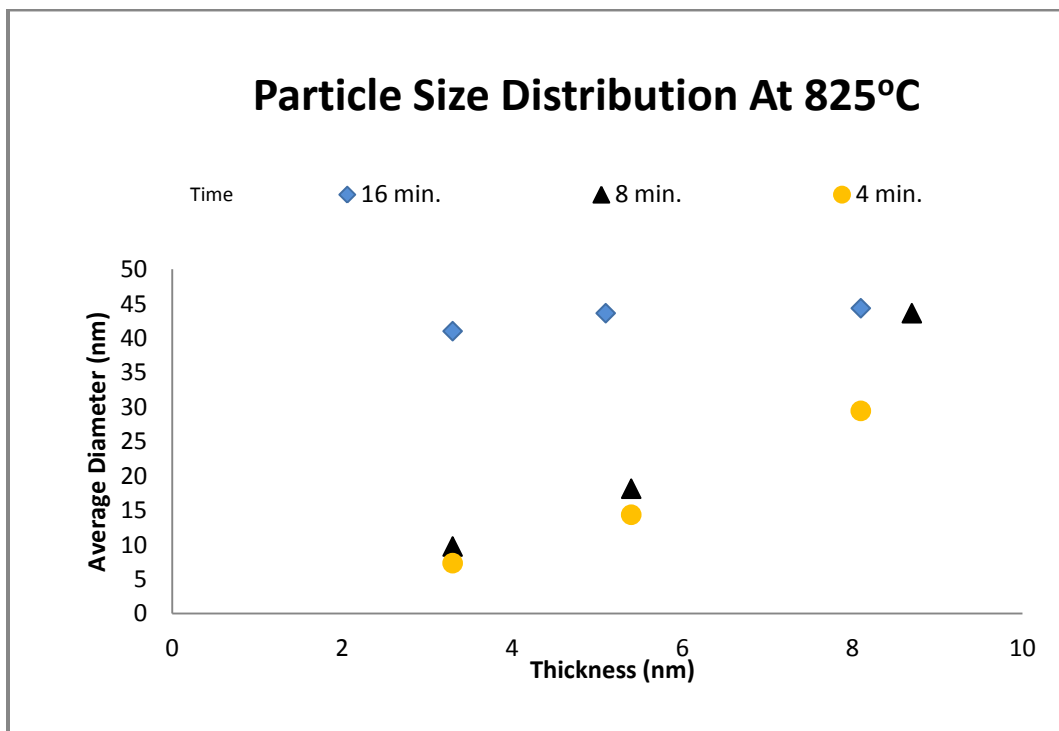


Figure 4.3: Overall growth of the average particle in terms of sample thickness at 825°C.

The Figures 4.2 and 4.3 show that as time increases, the average particle size increases, however, at high temperatures, the growth rate is strongly dependent on the initial sputtered thickness of the film. There seems to be an energy associated with the film thickness that affects primarily the nucleation process of the particles. At 825°C, smaller particles in the range of 5-10nm are detected after 4 min of annealing in thinner films (3-5nm thick), while in thicker films (over 8nm thickness) the nucleation is poor and the particles grow readily (to 40nm in diameter) without competition. This is attributed to radius of curvature, particles have absorb all neighboring small particles that allow them to continue growing process in which the surface energy is as lower as possible. At this point there are not much solute atoms dispersed through the matrix and the distance between particles are so far that the growth process starts to reach equilibrium.

The next Figures 4.4 & 4.5 shows that the temperature has an impact on the overall growth of the average particle size. Particles grow smaller at lower temperature range however; the same pattern of growth is seen when comparing graph results. The growth rate is strongly dependent on the initial sputtered thickness of the film but also on time exposure to temperature.

Analyses of the films annealed at 700°C also show the above trend. As the thermal energy available is limited, the difference in the particle size with thickness that can be attributed mainly to the film thickness, that is, nucleation at 2.1-3nm thickness film is higher than the nucleation at the 4.5-5.4nm thin film thickness.

Particles double size in time intervals of 4 minutes at the any temperature this due the concentration gradient caused by the thermodynamic demand but only for thicknesses smaller than 5.4nm. In contrast the thickness bigger than 5.4 nm exhibit poor nucleation because particles rapidly absorb neighboring solute atoms making a big gap among particles that prevents the continuous growth.

In order to obtain smaller particles, the thickness of the sputtered film should fluctuate between 2.1-5.0nm less than 6 minutes for both temperatures. The temperature has a smaller impact on the particle size distribution when compared to sample thickness and time exposure. Figure 4.6 and 4.7 shows the distribution of the particles in terms of film thickness and time exposure and a correlation can be made. The bigger particles can be observed for sputtered films bigger than 5.4nm at long periods of temperature exposures contrary the smaller particle are obtained from the smallest thickness of the films and time intervals. The main role in particle size distribution is attributed to two factors sample thickness and time exposure. The comparison of the plots shows the existence of a pattern of growth that entirely depends on the environment that surrounds it.

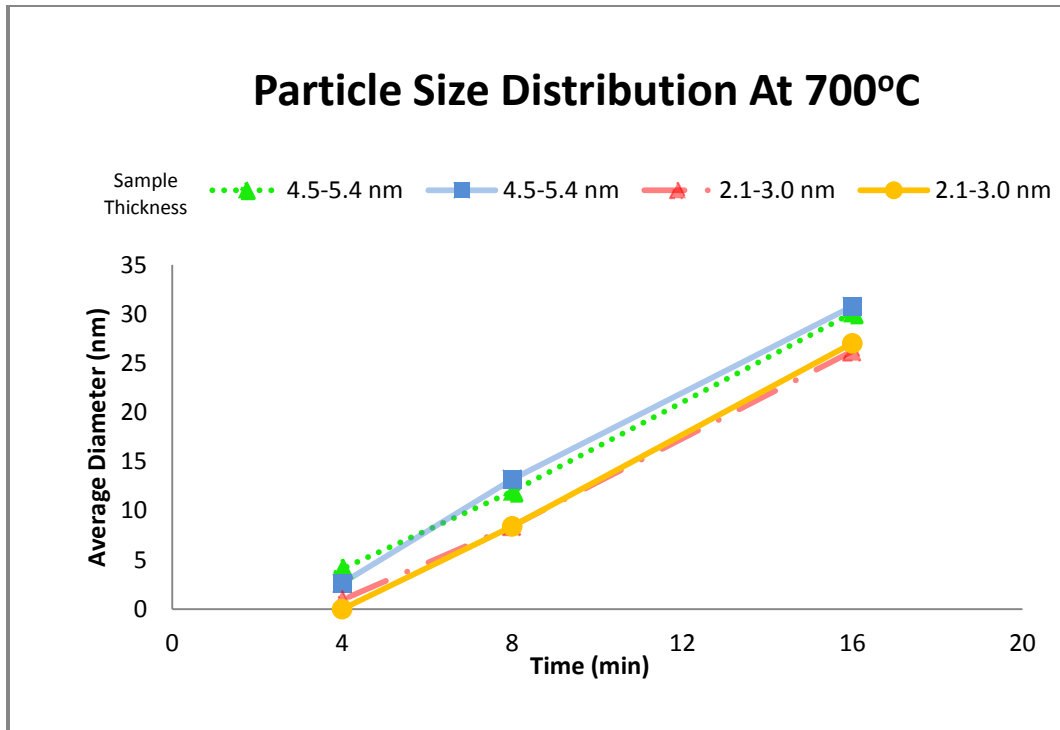


Figure 4.4: Growth distribution of the average particle in terms of oven time exposure at 700°C.

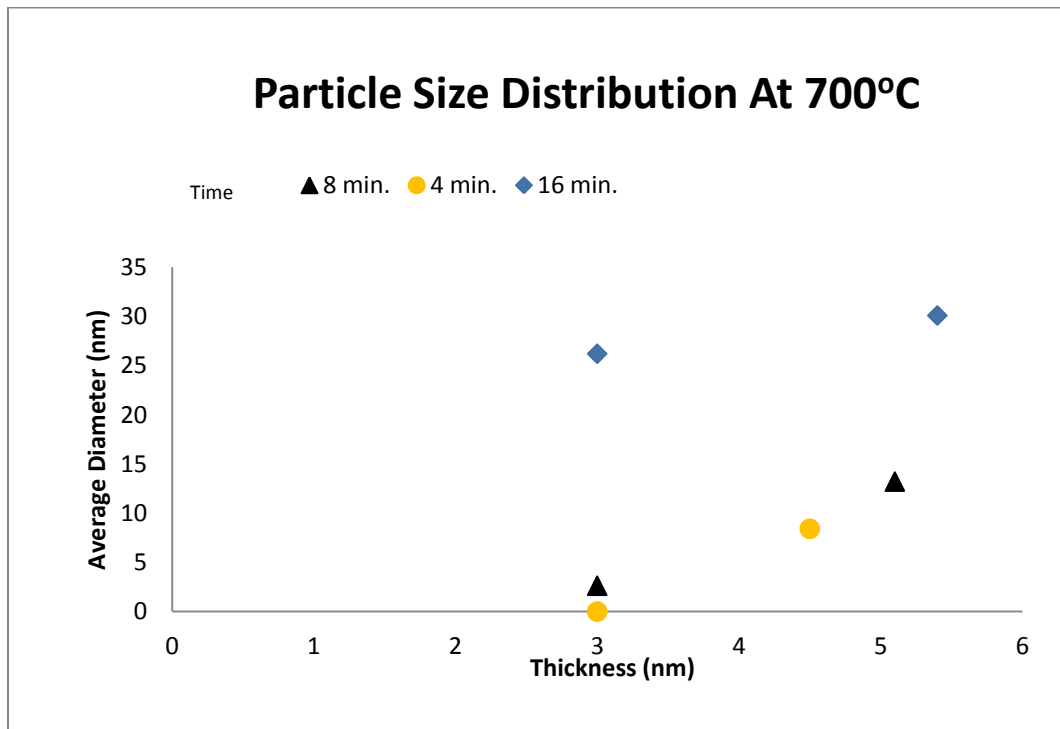


Figure 4.5: Overall growth of the average particle in terms of sample thickness at 700°C.

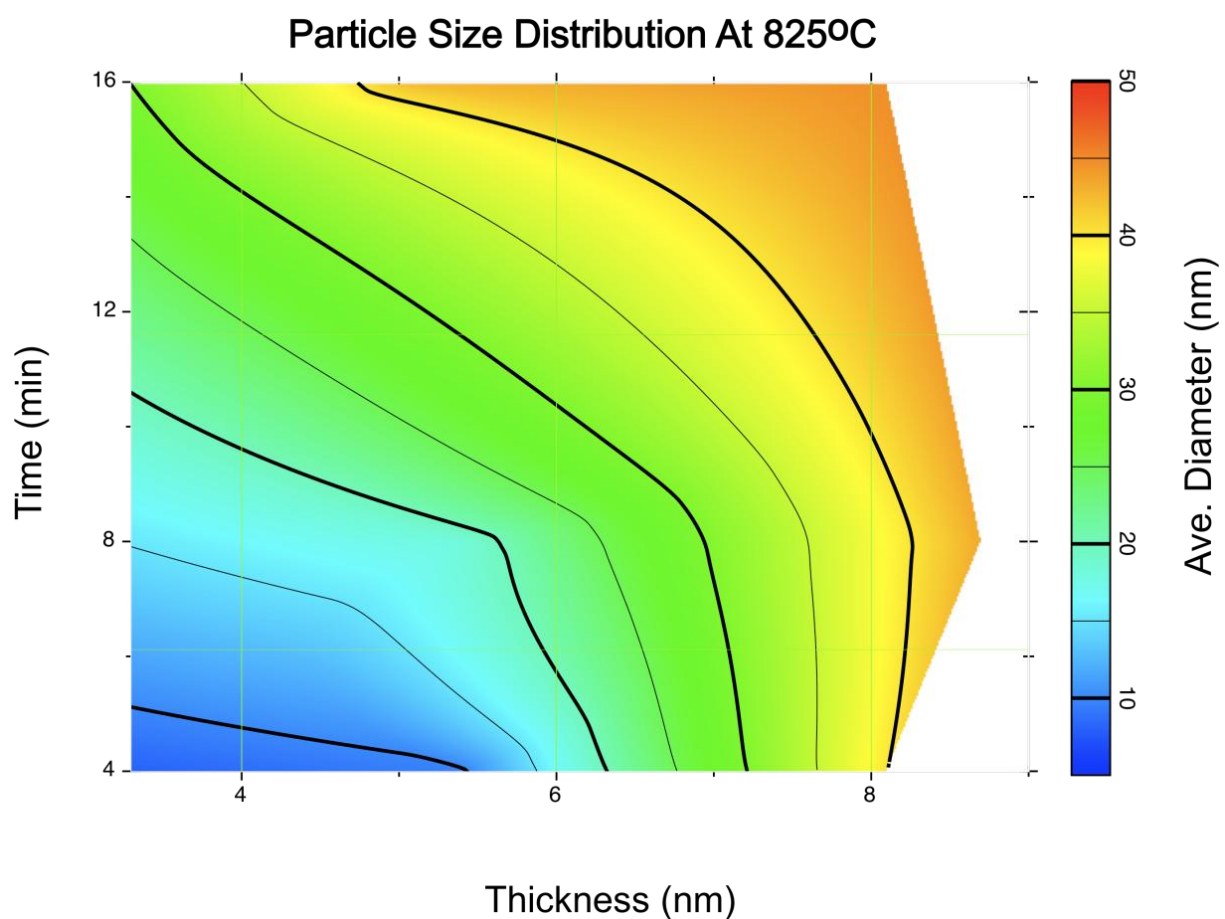


Figure 4.6: Particle size distribution contour at 825°C

Figures 4.6 and 4.7 shows the iso-contour of the average particle diameter as a function of annealing time and initial sputtered film thickness at 825°C and 700°C respectively. It is important to note that if the average particle size were independent of film thickness the iso-contours should be parallel to the x-axis. Any deviation from the horizontal can be attributed to a thickness effect. On the other hand, the observed near vertical lines are a measure of the initial diameter obtained during nucleation (critical nuclei size).

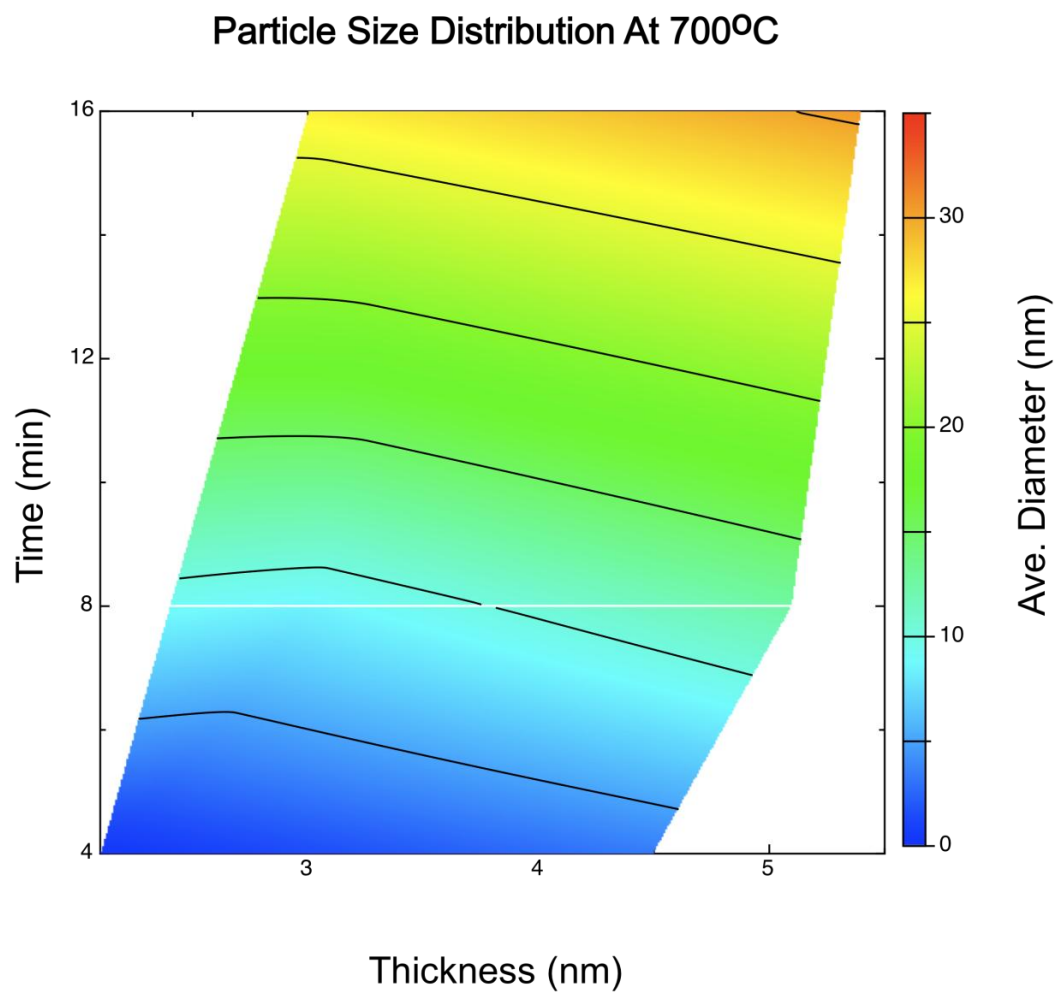


Figure 4.7:Particle size distribution contour at 700°C

4.2 Coarsening Rate

The growth rate of a particle is controlled by the volume diffusion that is related to radius of the particle itself and the system critical particle or average particle. The average particle is a provisionally stable in size and curvature with respect to the matrix in which the growth process is attributed to the difference in curvature between the critical particle and the particle of interest. Atoms flow from regions of high to low curvature. This process is established in LSW kinetics in order to predict the growth rate and population dynamics of a single particle interacting with an infinite collection of neighbors set an infinite distance away. For a three dimensional diffusion controlled process, the LSW theory predicts the following behavior:

$$\bar{R}^n(t) - \bar{R}^n(0) = K(Q)t \quad (5)$$

Where $K(Q)$ represents the coarsening rate of the population. This coarsening rate is determined out of the cube of the average length scale of particles increasing linearly with time. It implies that the average length scale of the system increases as the cube-root of the annealing time change rapidly until the phase separation increase causing them to slow down.

In this investigation, the coarsening rate was observed as a function of annealing time from 4-16 minutes and it was obtained from the slope of the figures 4.2 and 4.4. It can be seen that at lower temperatures (700°C), the average diameter of the particle changes linearly with time that is according to the equation:

$$D(t) = D(0) + K(Q)t. \quad (6)$$

Where $K(Q)$ is the linear coarsening rate and $D(0)$ is the initial nucleation diameter. As the observed lines are nearly parallel, it implies that the coarsening rate i.e. Oswald ripening rate is nearly constant and independent of the sputtered film thickness. A coarsening rate of 2.2nm per min was measured in these samples. The initial diameter $D(0)$ was found to change from 0.9nm for thicknesses of 2-3nm to 3.3nm for thicknesses of 4-5nm.

As the temperature increases to 825°C, the linear behavior is repeated by the smaller sputtered thickness (3.3nm) with a growth rate of 1.85nm per min. The figure 4.2 also indicates that the initial diameter $D(0)$ formed before the sample reached the uniform temperature of 825°C.

The above results indicate energy associated with the deposition of thin films, the thinner the film, the higher energy enhances the nucleation process.

At higher sputtered thickness, the curve cannot be fitted by a straight line and the diameters obtained are at the very high end of our measurements. This can be explained by a lack of nucleation and the small number of nuclei present grows without competition.

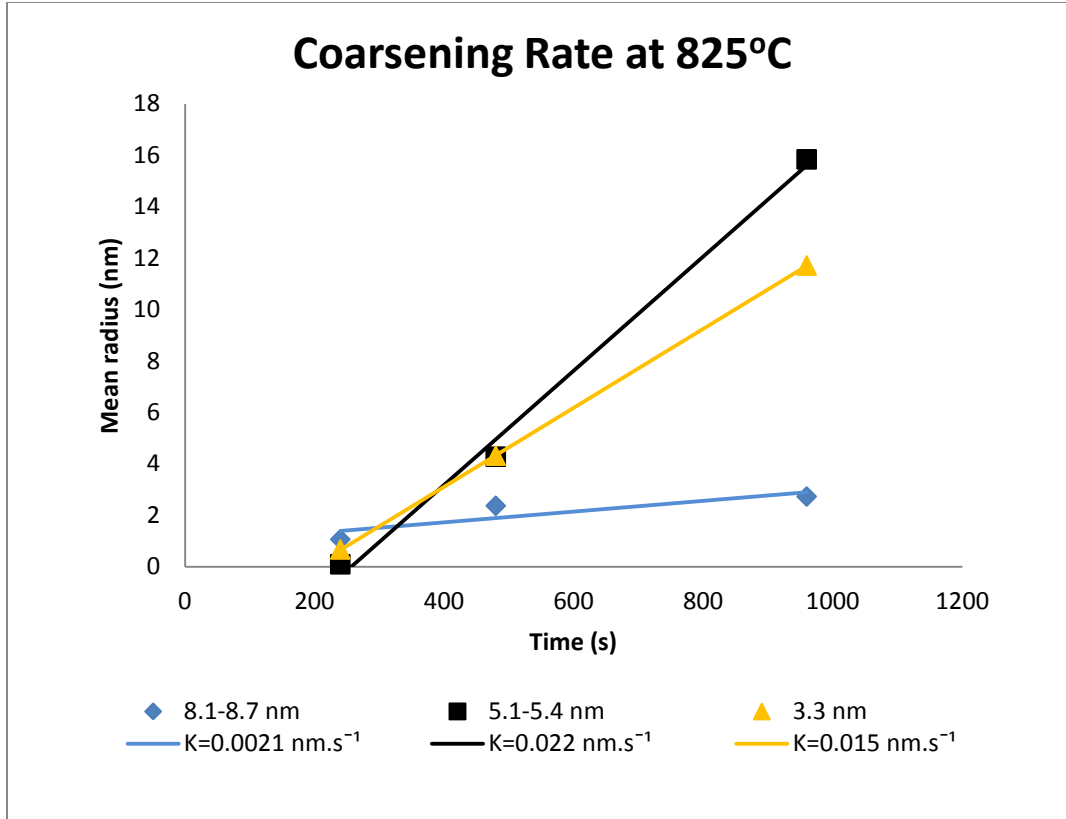
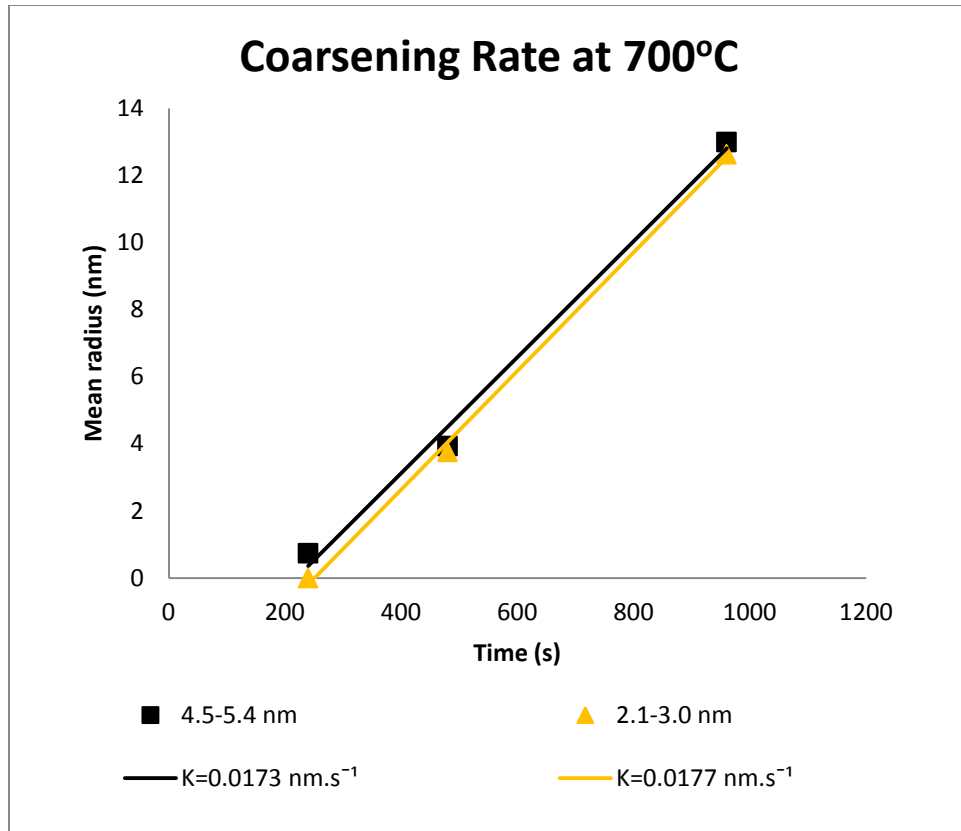


Figure 4.8:Coarsening rate of the population at 825°C

The temperature has also an effect on the coarsening rate. Smaller temperature provides a good environment for the formation of a large number of nuclei in thinner films.

In summary, our results indicate that there are two energies associated with each of the samples. The thermal energy provided by the annealing temperature and the thickness energy possibly provided by internal stresses and/or surface tension associated with film deposition. The latter enhances nucleation at lower temperatures and the rate of coarsening is higher than the rate in three dimensional systems. At high temperature and large film thickness, the energy associated with the film deposition is very small, nucleation is poor but growth is very fast, so that the nuclei grow without competition.



Graph 4.9:Coarsening rate of the population at 700°C

4.3 Ostwald Ripening LSW Model

The Ostwald ripening phenomenon can be modeled using LSW approximation for particle size distribution. In which spherical droplets are expected to nucleate and growth in radius as function of time while their number decrease. The bigger particles grow at expense of the smaller ones. The smaller particles diffuse through the matrix by donating solute atoms into the matrix until dissolve and so bigger atoms swallow those atoms that make them grow. As time evolve the total number of particle decreases and the average particle radius increases while the volume fraction does not change.

In order to demonstrate the veracity of the theory experimental analysis was performed to observe and compare the particle size distribution with LSW model. With the data obtained out of the experiments to fulfill the particle size distribution equation;

$$G_{LSW}(\rho) = \begin{cases} \frac{4}{9}\rho^2 \left(\frac{3}{3+\rho}\right)^{7/3} \left(\frac{3}{3+2\rho}\right)^{11/3} e^{\left(\frac{-\rho}{1.5-\rho}\right)}, & (0 \leq \rho < 3/2) \\ 0, & (\rho \geq 3/2) \end{cases} \quad (7)$$

In which ρ represents the critical particle radius of the population. These theories have some limitation in volume fraction. In the experiment because it a real system there is nonzero volume fraction of particles and the proximity among particles is very close but the theory can be used to observe the particle size distribution.

To observe the discrepancy among experiments and theory the data obtained was graph to study the dependency of the critical radius on time, temperature and film thickness between ranges of re-normalized radius from 0-1.5 for a diffusion-limited ripening process.

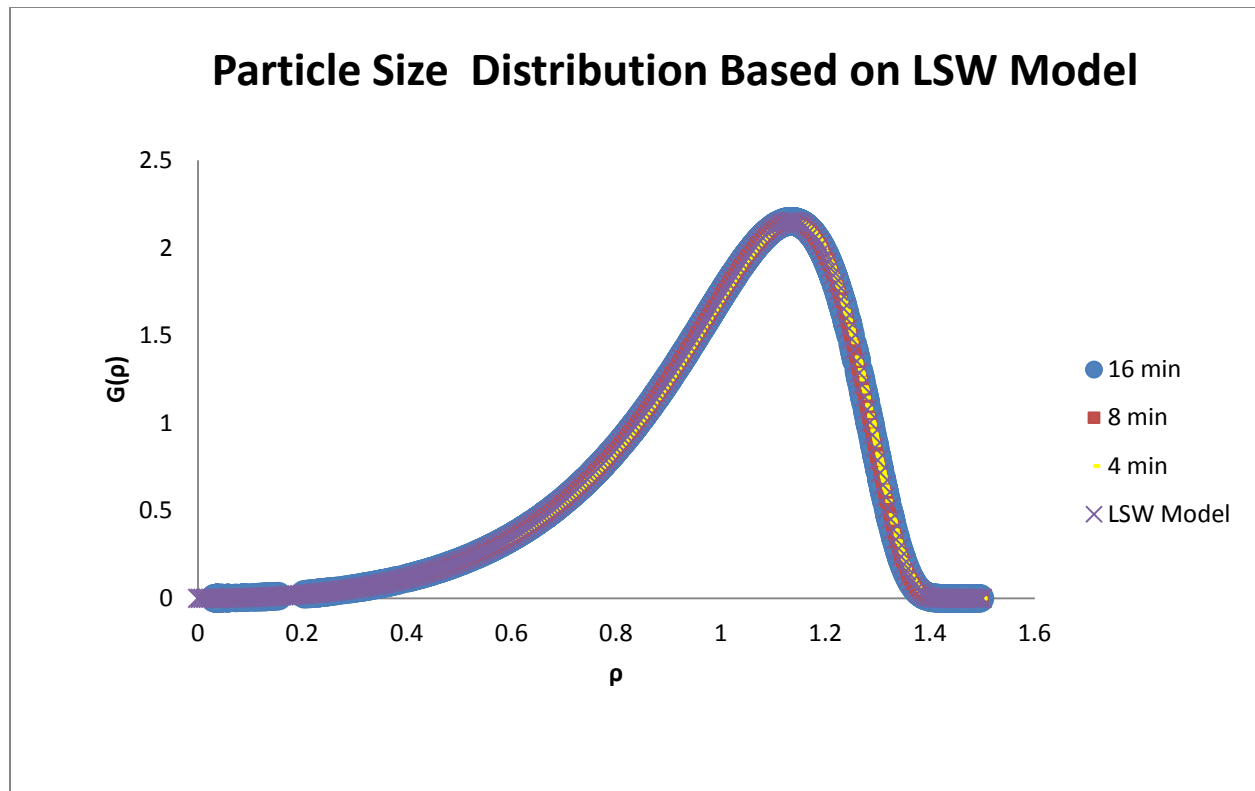


Figure 4.10:Representation of the particle size distribution at different time's intervals and comparison with LSW model.

The representation of figure 4.10 shows overlapping among PSD and it is expected due the constrain limitation of the equation. It compares the instantaneous particle size with the entire population ripening process. Normalized particles bigger than 1.5 tends to 0 and the representation will show a small portion of the system but, it confirms that the particle size distribution is lined with the Ostwald ripening phenomenon and it shows the asymmetry of the particle size distribution which is characteristic of the Ostwald ripening phenomenon. To have a better representation of the system histograms of the particle size distribution were created to observe the development of the average critical particle.

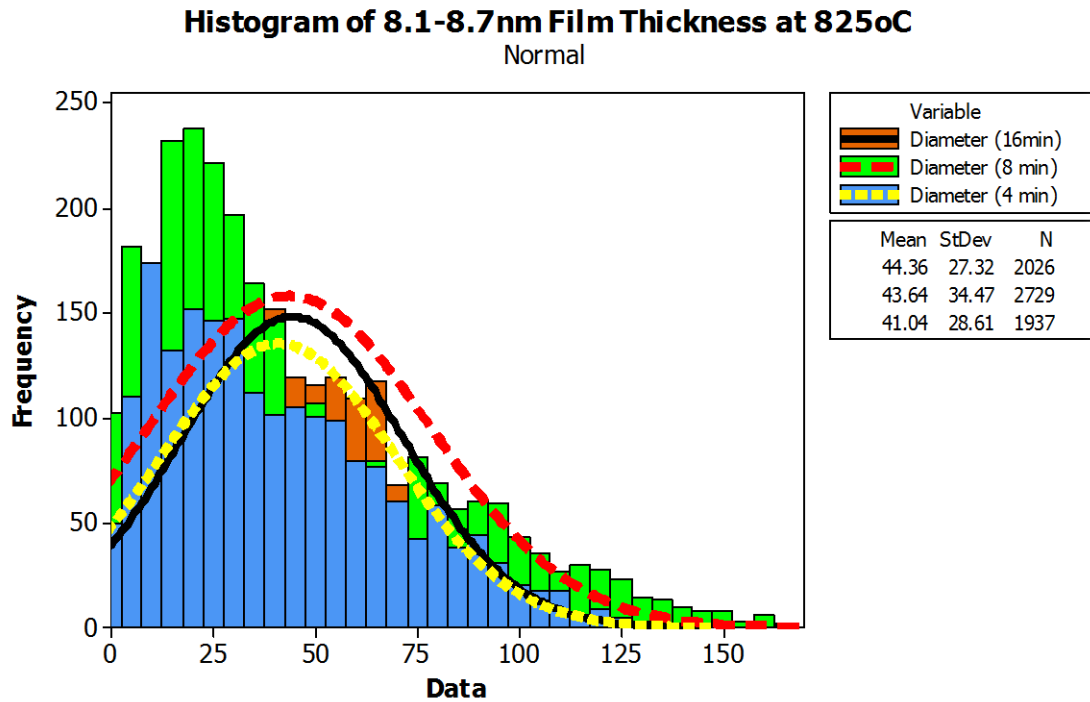


Figure 4.11: Histogram of the particle size distribution at 825°C for a period of 16 minutes over film thicknesses of 8.1-87nm.

The previous plot shows that the coarsening process starts before the 4 minutes because the average particle size is constant for the time interval of 16 minutes. From the period of 16 minutes the histogram shows a small difference in the average critical size of the particle. The critical particle only grows approximately 4 nm in time interval of 16 minutes although the observation of the trending of the particles in the system illustrate that particles are continuously changing.

There are not significant changes in the normal distribution and it is attributed to the poor coarsening rate process. The ripening process is poor during the time interval because the thermal energy applied to the system causes the coarsening to occur before the 4 minutes. In the

interval of 16 minutes it is seen a state of equilibrium in which particles are reaching its maximum size.

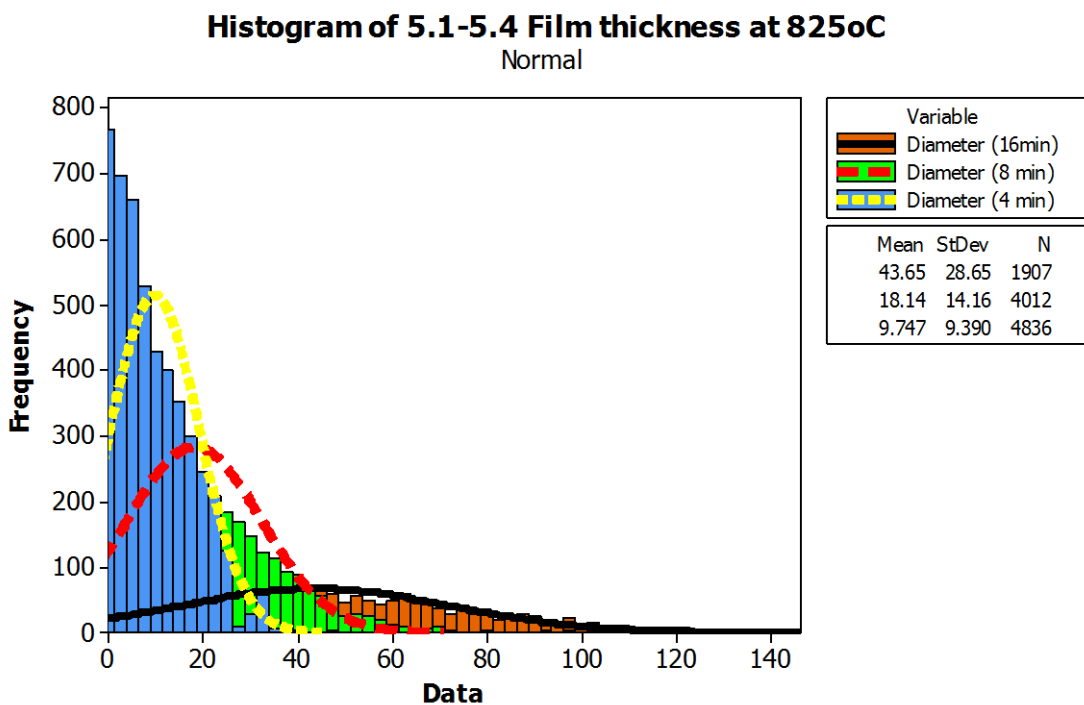


Figure 4.12: Histogram of the particle size distribution at 825°C for a period of 16 minutes over film thicknesses of 5.1-5.4nm.

The film thicknesses of 5.1 to 5.4 showed a different pattern when compared to higher film thicknesses. A controlled ripening process is seen in the plot. At 4 minutes interval it can be observed the beginning of the nucleation process. Particles start their growth process as time passes and Ostwald ripening phenomenon begins to govern the system. From 4 to 8 minutes the average particle doubles the size as the total number of particles decreases. For the last interval of time from 8 to 16 minutes the average particle continues the growth process. A continuous process of growth can be monitored throughout the sample as the total number of particles

diminishes. The plot shows that per time interval the critical particle can double in size (1.86-2.40) each 4 minutes and as time evolve the particles fit the normal distribution.

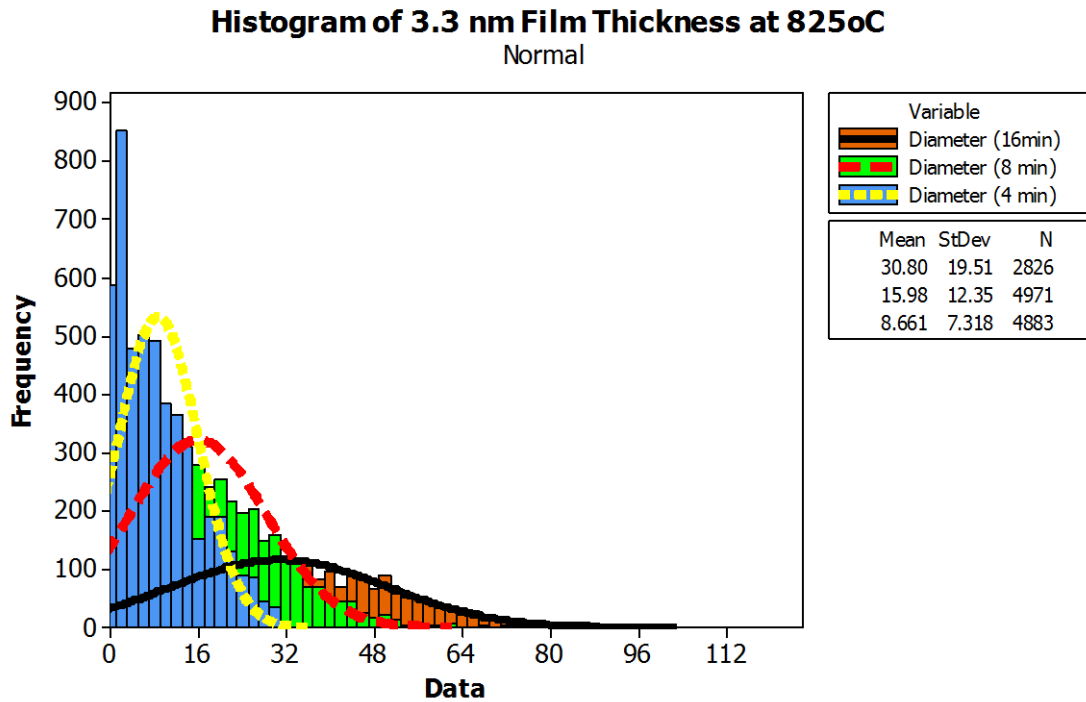


Figure 4.13: Histogram of the particle size distribution at 825°C for a period of 16 minutes over a film thickness of 3.3nm.

The lower film thickness of 3.3nm exhibits a similar behavior as the 5.1-5.4 film thicknesses. Particles nucleate in the first stage of the process and as time passes they grow until equilibrium position in which the critical particle has consumed the majority of the its neighbors and it has reached a maximum size. This must be associated to the film thickness that causes a rich nucleation process and a continuous coarsening rate.

Equal to the previous system the particles can double size from time interval form 4 to 8 minutes the average particle size difference was of 1.84 and for the last interval was 1.92. From this

observation it can be state that in the first stage of the process from 4-8 minutes the particles rapidly consume neighboring particles while for the last stage the growth process became slow because it was needed twice the time to double the size of the average particle.

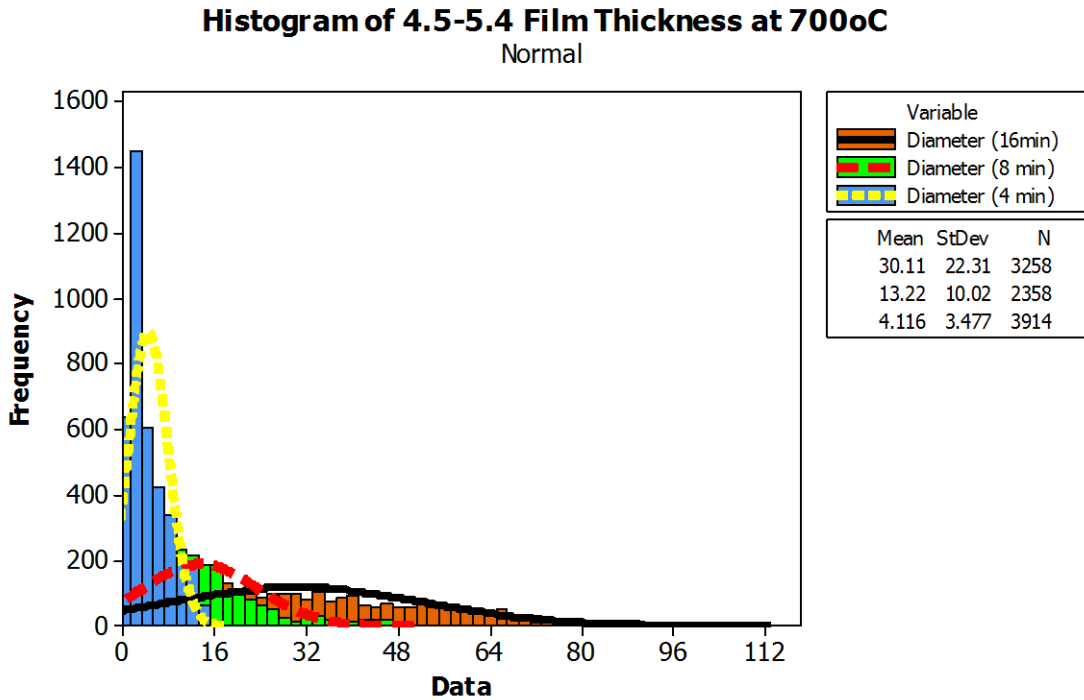


Figure 4.14: Histogram of the particle size distribution at 700°C for a period of 16 minutes over a film thickness of 4.5-5.4nm.

The difference in temperature causes particles to grow slowly and smaller when compared to 825°C temperature sample. The particle size distribution exhibit the previous mention pattern, as time evolve the critical particle grow as stated in OR phenomenon.

The 700°C temperature provides less thermal energy to the sample which allows the temperature to be reached before the nucleation process begin. This is an indication that particles are not only dependent on the thickness of the sample but also on temperature to determine their critical size.

For smaller thicknesses as shown in figure 4.15 it is seen a smaller particle size distribution through the process and it can be compared to the maximum thickness in which large particles can produced due to poor nucleation. Lower thicknesses need to be handle with care because it can produce a large density of particles that will coarsen at a higher coarsening rate than in 3D samples, following the OR phenomenon.

As seen throughout all the samples it exist an interaction of the sample thickness with the time and temperature that rules the system in terms of particle size distribution. The final PSD is attributed to the combination of the previous mentioned parameters and next section will provide detail information with the statistical test.

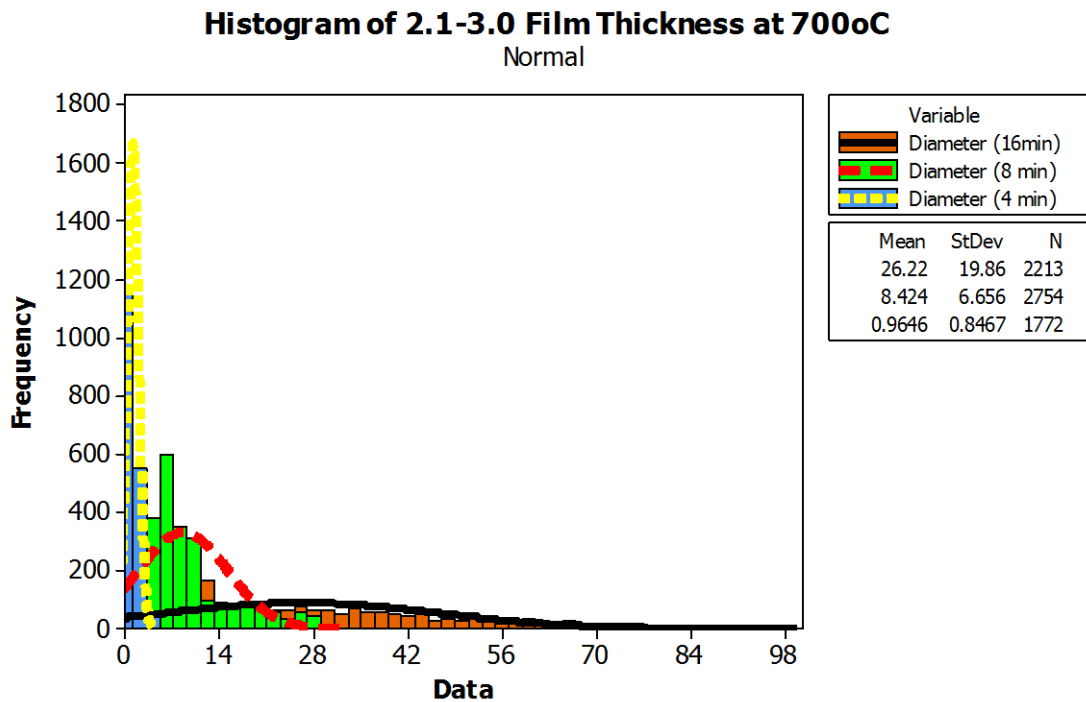


Figure 4.15: Histogram of the particle size distribution at 700°C for a period of 16 minutes over film thicknesses of 2.1-3.3nm.

4.4 ANOVA Statistical Analysis

As part of this investigation it was required to analyze the data in table 3 and 4 to observe any difference among the data obtain with respect the average diameter. During the statistical test the dependent variable was identified as the average diameter and the factors or independent variables were time, temperature, film thickness and samples. A null hypothesis (H_0) was generated to test the effect of the factors over the critical average diameter. It was state that sample A which is the output of the samples at 825°C is equal to sample B that represent the output of samples at 700°C. In which the hypothesis test is known as a statistical procedure that is designated to test a claim[59-61]. The alternative hypothesis H_a is the counter part of H_0 in which is stated that sample A is bigger than sample B in terms of diameter. The essence of this statistical test is to confirm that there is enough evidence to support a decision.

In order to state a good conclusion of the statistical analysis sample replicas were evaluated and sample thicknesses were averaged and fixed to obtain the best results. The test was conducted and the output was the following:

General Linear Model: Average Diameter versus Thickness, Time, Temperature and Sample

Factor	Type	Levels	Values
Thickness	fixed	3	3.30, 5.25, 8.40
Time	fixed	3	4, 8, 16
Temperature	fixed	2	700, 825

Analysis of Variance for Average Diameter, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Thickness	2	3262.5	1949.4	974.7	42.70	0.000
Time	2	2665.1	2529.3	1264.7	55.40	0.000
Temperature	1	290.2	28.1	28.1	1.23	0.278
Error	23	525.1	525.1	22.8		
Total	29	6744.1				

At first the null hypothesis was rejected because the statistical test F proves there is difference among the samples. The P-value demonstrate how strong the evidence is against the claim.[59] The P-value must lie between 0 and 1 and the bigger the P-value the less the factor contribute to the response. As seen in the statistical test the P-values shown that mostly affect the average diameter are the sample thickness and the time exposure to a temperature. The temperature also has an effect on growth process of the average particle with a P-value of 0.278 but not as important as the sample thicknesses. This is an indicator that there is an energy associated with the thickness that drives the overall performance of the average particle size distribution along with time exposure.

When observing the effects plots of the factors over average diameter is seen in figure 4.16 that the bigger critical particles are caused by the maximum range of each factor. The bigger the factor the bigger the critical particle will be. There is a difference among samples also; higher temperature proves a good environment for particles to coarsen. Also for sample film thickness it seen a big slope between 5 to 8 nm which is an indication the process of growth of the particles is rapidly and that it can occur in a short amount of time.

The interaction plot in figure 4.17 shows that each parameter affects individually the critical particle diameter. There is a slight interaction among two factors that could affect the overall performance of the population. As expected the time and film thickness slightly interact at the beginning of the ripening process for thicknesses below 5.25nm. After the process has ended the nucleation stage the interaction decrease until each factor affect individually the average diameter of the particle. This explains why it is so difficult to control the ripening process in the samples because each factor is responsible of the performance of the population. This test demonstrates that a controlled film thickness can produce a pattern in the PSD and it has a big

impact on the overall performance of the system because it is the main factor responsible of the growth particles throughout the system.

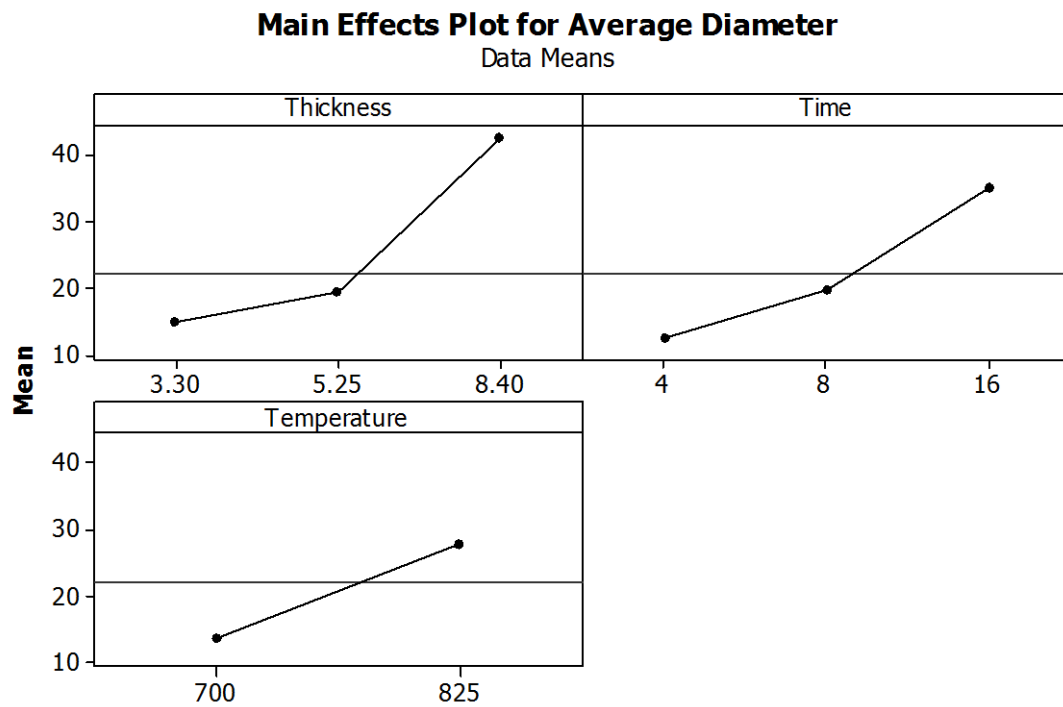


Figure 4.17: Main effect plot in terms of the critical average diameter

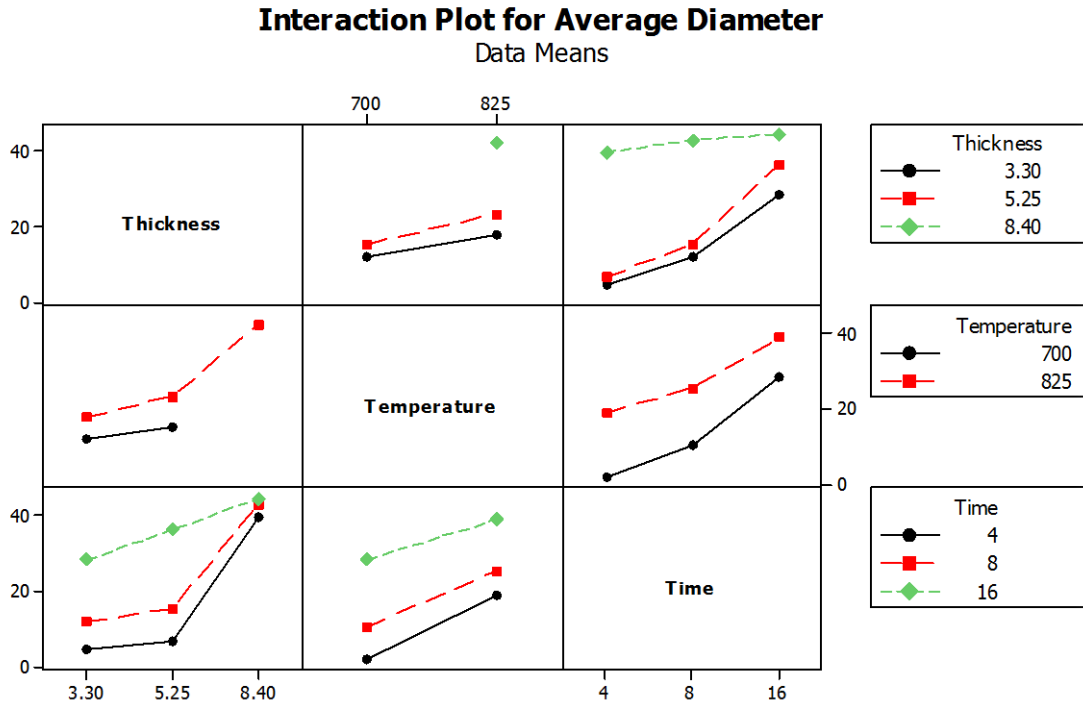


Figure 4.17:Interaction plot in terms of the critical average diameter

4.5 Surface Coverage

In this study OR phenomenon can be monitored using two dimension system to determine the surface coverage or volume fraction of the samples using the following equation;

$$t_{req.} = \frac{\pi d}{6\sqrt{3}}$$

$$Surface\ Coverage = \frac{t_{req.}}{t_{dep.}}$$

In which the thickness required ($t_{req.}$) is calculated using the diameter of the average particle and so the percentage of the surface coverage is represented by the thickness required over the thickness deposited into the substrate. Figure 4.18 represents the surface coverage of the average

particle. The surface coverage between 0 and 1 shows the volume fraction in each sample in which one layer of particles is exhibit. While for percentages greater than 1 it means that particles piled up and there is more than one layer of particles in the sample as seen for small thickness. The lower temperature shows stacking of the particles and as time passes the interaction among causes them to evolve into bigger particles while the volume fraction diminishes as established in Ostwald ripening theory.

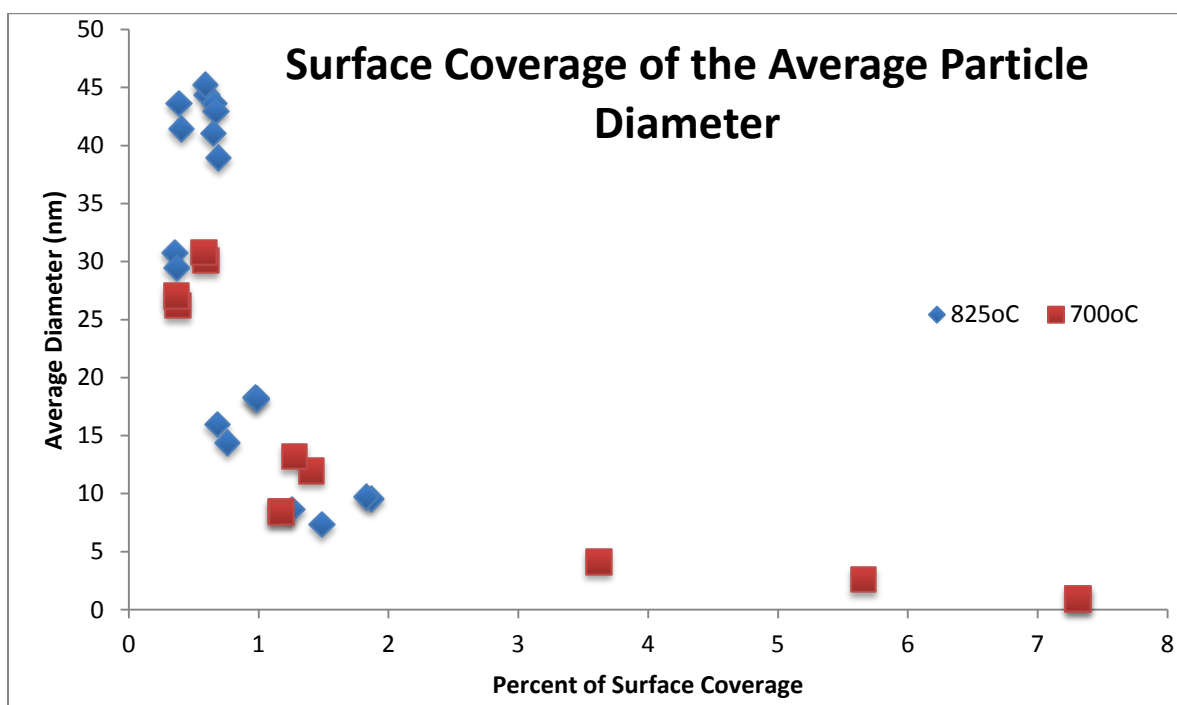


Figure 4.18: Surface coverage plot of the average particle size

4.6 Discussion

As seen in the above chapter, the particle size distribution is dependent upon the factors that surround the system. The film thickness has big impact on the performance of the population in terms of growth. Higher film thicknesses and higher temperatures can produced the bigger particles but the OR phenomenon cannot be properly observed in a period of 16 minutes because the process starts before the 825°C nominal temperature is reached. At that point it can only be seen the last stage of the ripening process which is equilibrium. To observe OR phenomenon the film thickness must be less than 5.4nm, for which it is possible to calculate coarsening rate and state a difference among them. There is evidence that particle size distribution can be controlled for film thicknesses of 2.1-5.4nm at the two temperatures. In the nucleation stage it can be seen that particles can double size but as time passes it became one time bigger per time interval.

The data was supported with the statistical test to confirm the effect of the factors over the critical average diameter. It is seeing that the main factor that affects the PSD is the film thickness; particles will grow bigger as the film thickness increases. The temperature also will have an effect on the PSD but it will mostly affect the maximum diameter that a particle can reach. The amount of energy applied to the system determines how fast the particles will coarsen. It is also clear that each factor contributes individually to the PSD making it difficult to predict an exact particle size distribution for a film thickness.

The population can show a pattern for the particle size distribution for thicknesses below 5.4nm. A desire average particle can be obtained and figures 4.6 to 4.7 provide the required data to produce a particle of an approximate size. It is demonstrated with this experiment that particles will respond according to the environment that surrounds them specially the surface in which they will grow.

CHAPTER 5

CONCLUSIONS

The presence of Ostwald ripening phenomenon is present among the samples studied. Particles are consuming neighboring atoms and growing at expense of smaller particles. As time passes the critical particle grows and the number of particle diminishes. The following conclusions drawn based on the obtained results:

1. Samples containing the bigger thicknesses at the maximum temperature provide the bigger particles encountered in the experiment but the process occurs so fast that it was impossible to follow the coarsening process
2. For bigger thicknesses than 5.4nm and higher temperatures, the large diameter obtained points out towards a lack of nucleation. The OR process seems to have started before the nominal temperature is reached. When monitoring particles it can only be seen constant growth because particles are in the equilibrium phase.
3. For smaller thicknesses than 5.4 nm a trending in the PSD can be followed. Particles can double size in the first time interval and after that it only grows one time its original size per 4 minutes time interval.
4. The temperature has an important effect on the particle size in which it provides appropriate energy to maximize the size of the particles. The maximum temperature produces the biggest particles while the smaller one the smallest particles.
5. There is an energy associated with the film thickness that enhances nucleation and produces very fine particles that grow as time passes. This energy of activation is bigger than the one produced by the temperature because the critical particle diameter depends on it.

6. The pattern growth can be followed and repeated only over a surface of SiO_2 in a range of 2.1-5.4nm film thicknesses. To produce a desire approximation of a particle it important to apply the same factors or contributor to reach the desire particle size.
7. The interaction between the thickness and the time exposure to temperature only affects the nucleation of the particles. As the OR process evolve the factors interaction is less and each will affect the population individually.
8. In real systems LSW will only contribute to the determination of the existence of OR phenomenon on the samples but will not show the particle size distribution because of its volume constraints.
9. The higher coarsening rate can be observed for film thickness in the range of 4 to 5nm. Values below shown a decreasing coarsening rate equal to values bigger than 5.4 film thickness.
10. The system is mostly influenced by the thickness of the sample making it the main contributor for the particle size.
11. There is enough evidence to replicate the experiment and produced particles from a desire value at least for in the film thickness range of 4.5 to 5.4nm. This because system is ruled for the time exposure and the thickness of the sample.
12. It can be concluded that for the best production CNT over a SiO_2 substrate, the best surface must lie between 2-3nm film thicknesses.

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