Contact-displacement PD deposition for electroless copper application

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CONTACT-DISPLACEMENT PD DEPOSITION FOR ELECTROLESS COPPER APPLICATION

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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Abstract

Electroless (EL) Cu, a potential seed layer material for Cu interconnects used in nanoelectronics, is intimately dependent on the surface activation of catalytic Pd particles. A comprehensive understanding on the deposition mechanism of Pd particles is thus critically important. In this thesis, the contact-displacement method of depositing Pd onto TiN surface is investigated in depth using statistical methods to track the time evolution of distributions of particle size, range, and density. The three classical phenomena of nucleation, growth, and ripening occur concurrently in this open system, leading to interesting evolution of particle statistics not predicted by any of the classical theories. In particular, there exists a secondary nucleation stage before the onset of ripening, where particle density reaches a maximum. Using this window allows us to achieve EL Cu deposits with very low surface roughness which allows conformal high aspect ratio via fills with satisfactory results.

The existence of a nucleation barrier on the trigger point of secondary nucleation is shown to be linked to the formation of a hydrophilic surface associated with the removal of a native Ti oxide. Based on this new insight on surface chemistry, a new “double activation” method is demonstrated in this thesis wherein an etch step containing a hydrophilicity promoter is used. This new activation procedure increases the nucleation rate significantly, and yields more and smaller Pd particles. The larger EL Cu grain size that results yields films that are lower in resistivity by up to 50%. We believe this method is generally applicable to all electroless deposits which are kinetically limited by surface barriers.

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List of Publications

Journal and Conference:

1. Lau, P.P., C.C. Wong, L. Chan, A. See, and S.B. Law, *Classification of palladium nucleation processes based on nucleus size distribution*. Journal of the Electrochemical Society, 2004. 151(6): p. C436-C438.
2. Lau, P.P., C.C. Wong, and L. Chan, *Improving Electroless Cu Via Filling with Optimized Pd Activation*. Applied Surface Science, 2006. 253(5): p. 2357
3. Lau, P.P. and C.C. Wong, *Reduction of Pd catalytic particle size by a double activation process*. Thin Solid Films, 2009. 517(6): p. 1939-1943..
4. Lau, P.P. and C.C. Wong, *Surface Modification in Contact-Displacement Palladium Deposition Process*. Submitted to Journal of the Electrochemical Society.
5. Lau, P.P., C.C. Wong, K.T. Tan, L. Chan, A. See, and S.B. Law. *Catalytic Palladium Nucleation Stages and Its Effect on Film Roughness of Electroless Copper*. in *Symposium of Microelectronics*. 2003. Singapore.
6. Lau, P.P., O. Prabhakar, C.C. Wong, and L. Chan. *Statistical Study of Simultaneous Nucleation, Growth, and Ripening in an Open System*. in *The 3rd International Conference on Materials Processing for Properties and Performance (MP3)*. 2004. Singapore.

7. Lau, P.P., B. Seow, M. Rick, C.A. Bode, and J.E. Tristan. *Implementation of Photolithography RtR Control in 300 mm Foundry*. in *European Advanced Equipment Control/Advanced Process Control Conference*. 2006. Aix-en-Provence, France.
8. Lau, P.P., C.K. Wong, S.Y. Ling, J. Chaw, S. Kumar, and C.A. Bode. *Fab Wide Feed-Forward and Feedback Gate Length Advanced Process Control*. in *IFAC Workshop on Advanced Process Control for Semiconductor Manufacturing*. 2006. Singapore.
9. Lau, P.P., C.K. Wong, R. Shankar, S.Y. Ling, and C.P. Lim. *Electrical Gate Performance Improvement with Feed-Forward and Feedback Control*. in *Advanced Equipment Control/Advanced Process Control Symposium - Asia*. 2006. Taipei, Taiwan.

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CHAPTER 1 Introduction

In this chapter, the advantages and challenges of Cu metallization are discussed. The recent trends and developments of Cu interconnect process technology are reviewed. The advantages and challenges of the potential candidate process - electroless Cu deposition - for future Cu metallization are discussed. The importance of activation process on the properties of electroless Cu deposits forms the motivation of this study.

1.1. Copper Metallization

Interconnects in deep-submicron integrated circuits (ICs) comprise a multilevel structure of fine wiring located on the top of the transistor circuitry of logic and memory chips. To avoid significant degradation of circuit speed, on-chip interconnections should permit rapid signal transmission among the various parts of the circuitry. Ever since the development of the integrated-circuit in the early 1960's, the materials most widely used for the wiring structures have been aluminum (Al) as the conductor (or eventually an Al-Cu alloy for better reliability), and silicon dioxide as the insulator. As the device dimensions in Ultra Large Integrated Circuits (ULSI) are scaled down, the formation of high performance yet reliable interconnections with traditional metallization materials and processes is becoming very difficult. The delay time induced by the aluminum's resistance in the interconnects could potentially constitute an unavoidable bottleneck for the device performances and finally offset the benefits of dimensions scaling. In 1997, the transition to copper (Cu) as the conductor was initiated with the announcement by IBM that they had

developed a technology for forming Cu interconnect lines and vias for IC applications. This was one of the most important changes in materials that the semiconductor industry had experienced since its inception. Since that breakthrough, in March 2000, and ahead of its competitors, AMD reportedly applied Cu to its microprocessor circuits at the 0.18 μm technology node, enabling it to introduce the first GHz-rated microprocessor.

1.1.1. Advantages of Copper Metallization

Copper (Cu) has become a strong candidate to replace the current Al metallization in integrated circuits due to its lower resistivity and higher electromigration resistance [1-3]. Implementation of Cu and low-k materials allows scaling of the intermediate wiring levels and minimizes the impact on wiring delay. Furthermore, Cu films exhibit much better electromigration (EM) characteristics and stress-void resistance than Al films.

Most importantly, compared to using Al, lower manufacturing costs can be obtained by employing Cu. Cu metallization is usually implemented with a dual damascene architecture [4]. In damascene processing, interconnects are formed by first etching vias and trenches in a dielectric layer, and then filling them with Cu. Dual damascene requires 20~30% fewer steps than the traditional subtractive metal patterning or single damascene process [5, 6], leading to a potential cost reduction. Currently, Cu deposition is achieved by electrodeposition. Electrodeposition of Cu for IC fabrication for the production of interconnection lines down to 0.20 μm width has been successfully used since 1997. This method allows much lower deposition temperature than Al sputtering and enables the use of low-k dielectric materials

whose thermal stability is lower than that of SiO_2 . As a result, it represents a very attractive alternative to the conventional IC fabrication processes [7].

1.1.2. Challenges in Copper Metallization

In the dual damascene process, conventional physical vapor deposition (PVD) processes such as physical collimated and ionized sputtering process are used to deposit a thin copper seed layer for a subsequent electrodeposition process. However, the PVD processes provide limited bottom coverage and step coverage capabilities for deposition of the diffusion barrier and Cu seed layers in high-aspect-ratio via holes and metal line trenches. The problems in step coverage will cause Cu to pinch-off while carrying out electrodeposition and voids result inside the trench.

Since the PVD techniques yield marginal seed layer coverage on the next generation of dual damascene structures, other types of deposition techniques have to be sought after as a solution to the problem. Many metallization schemes are currently under development and novel materials such Ru alloys [8], Co [9], or MnOx [10] have been introduced to act as diffusion barriers or seed enhancement layers. However, the incorporation of such metals may affect the Cu fill ability, electrical properties and reliability, especially in sub- 30 nm interconnects. Hence, more extendible solution for the issue of seed conformality in high aspect ratio structures, electroless Cu seed, seedless electrodeposition, chemical vapor deposition (CVD) Cu seed, atomic layer deposition (ALD) seeds [11] and enhanced PVD seeds are being studied [12] has been sought to provide a possible solution for Cu seeding for 45 nm technology node.

1.1.3. Advantages of Electroless Copper Deposition

Electroless deposition is experiencing increased interest in microelectronics due to the need to replace expensive vacuum metallization methods with less expensive and selective deposition methods. The feasibility of using selective electroless metal deposition for integrated circuit (IC) fabrication has been demonstrated by Ting et al [13] and Shacham-Diamand [14]. Electroless Cu has been investigated for the application in very large scale integration (VLSI) as early as 1987 [15]. In principle, coatings of uniform thickness and composition are easier to obtain using the electroless process, since it does not have the current density uniformity problem of electrodeposition. Electroless Cu has the advantage of highly conformal coverage, low cost, high purity and good adhesion to barrier. Therefore, electroless Cu deposition is now being researched extensively for application in ultra large scale integration (ULSI) [16-21]. Although promising results have been shown [22], electroless Cu is still not a mature process for ULSI. As such, the electroless Cu process will be discussed in more detail in this study.

1.1.4. Challenges of Electroless Copper Deposition

The deposit purity of electroless Cu films is lower than that of electrodeposition films, due to the codeposition of traces of electroless bath components. Typical acid-Cu electroplating baths produce films of 99.9% purity, 8.92 g/cm³ density, and 1.72 $\mu\Omega\cdot\text{cm}$ volume resistivity (at 20 °C), whereas electroless Cu is 99.2% purity, 8.8 g/cm³ density, and 1.90 $\mu\Omega\cdot\text{cm}$ resistivity (at 20 °C) [23].

In the process of electroless Cu deposition, a suitable catalyzed surface is essential for the plating reaction to occur. The initial catalytically active region is normally a metal catalyst, often highly dispersed Pd, which is active for oxidation of most common electroless reducing agents. The nature and distribution of Pd nuclei formed during the activation process for electroless Cu deposition have proven to be very important to the deposition behavior and the deposit quality [18, 24]. The final surface concentration of Cu deposited is highly dependent on the initial amount of Pd nuclei present. Researchers have also reported that the roughness of electroless Cu could be lowered if the density of Pd nuclei increases and the agglomeration of Pd nuclei is reduced. The distribution of Pd on the barrier surface affects the surface roughness of electroless Cu [18]. Nevertheless, the role of the Pd nuclei in determining the particle size of the EL deposit is not well understood. Therefore, it is necessary to study the dependency of electroless Cu surface roughness on Pd nuclei properties.

1.2. Objectives

In the electroless Cu process, Cu nucleates from catalytic particles on the substrate. The initial Cu grain structure is largely determined by the properties of catalytic particles [25]. The main objective of the thesis is to develop a Pd activation process for smoother, better via filling, and lower resistivity electroless Cu to meet the requirements of future ULSI metallization as well as providing a plating base where resistivity is crucial. Several widely used Pd activation processes for electroless Cu are discussed. A contact-displacement Pd deposition process was chosen because no vacuum is required, it has good selectivity and good adhesion to

the substrate, and it is cost effective [18, 26]. To develop a better Pd activation process for achieving high quality electroless Cu, a fundamental understanding of the Pd deposition mechanism and its effect on electroless Cu deposition process is essential. The evolution of particle size and size distribution of Pd particles is investigated in detail in this thesis. Since surface condition of the substrate plays an important role in determining the deposition behavior of Pd particles [27, 28], chemical state analysis was carried out to understand surface modification during the Pd activation process. A new Pd activation method is then developed to achieve the desirable Pd properties for a lower resistivity electroless Cu film.

1.3. Major Contributions of Thesis

- Classified the Pd deposition process with size and size distribution evolution into growth, secondary nucleation and ripening stages. The existence of optimum activation time has been identified for ideal size and density of catalytic Pd particles.
- Presented the in-depth study of Pd deposition and identified surface modification as the triggering point of secondary nucleation stage.
- Demonstrated smoother and lower resistivity EL Cu deposit and improved EL Cu via filling capability with optimum Pd deposition
- Demonstrated the application of surface modification and presented a novel double Pd deposition process for Pd particles refinement

1.4. Thesis Organization

This thesis is organized into eight chapters, with the first two Chapters presenting the literature review. Chapter One presents a brief introduction on the background, objectives, and organization of the thesis. This is followed by a discussion of electroless Cu deposition in Chapter Two. Chapter Three shows the experimental details. Chapter Four presents the classification of Pd activation process through the change of particles size, density and size distribution. The analysis of the Pd deposition mechanism is shown in Chapter Five. The studies of the Pd activation effect on electroless Cu surface roughness and via filling are presented in Chapter Six. A new Pd activation process is introduced in Chapter Seven. Finally, conclusions and recommendations are outlined in Chapter Eight.

CHAPTER 2 Literature Review

This chapter provides the background for the work shown in this research work. Electroless Cu technology is reviewed in terms of the thermodynamics, bath composition, reaction mechanism, operation temperature, and deposition substrate requirements. The factors affecting the electroless Cu deposition are discussed. Secondly, various activation methods to overcome the energy barrier for electroless Cu deposition are listed and discussed. The advantages and disadvantages of the methods are considered. Lastly, the fundamentals of nucleation, growth and ripening mechanisms are introduced.

2.1 Electroless Cu

2.1.1 Thermodynamics

Electroless Cu deposition can be described as two reactions that occur simultaneously on a catalytic surface, namely, an oxidation reaction of a reducing agent and a reduction reaction of Cu ions. Electroless Cu deposition is a thermodynamically favorable process since the sum (E^0) of the standard redox potentials of the oxidation and reduction reactions is positive (i.e. the standard Gibbs free energy of reaction is negative, $\Delta G^0 = -nFE^0$) [14].

Although electroless Cu deposition is thermodynamically favorable, spontaneous solution decomposition does not occur because the electroless Cu plating process is kinetically inhibited. The activation energy for this process has been estimated to be $\sim 0.63\text{eV}$ [14], which is much more than what room temperature

can provide. The Gibbs free energy diagram in Fig. 2.1 illustrates the potential barrier (E_a) which prevents spontaneous solution decomposition. This potential barrier can be reduced by the formation of reactive intermediate species on a catalytic surface having a lower activation energy (E^*). The methods to reduce the potential barrier for electroless Cu deposition will be discussed in *section 2.2*.

Figure 2.1: Schematic Gibbs free energy diagram

2.1.2 Bath Composition

The basic electroless bath consists of an oxidizing agent (which also provides the cupric ions), reduction agent, and a complexing agent in alkaline medium. Cu deposition is thermodynamically more favorable in an alkaline solutions. While most commercial formulations are for PCB-based fabrication and utilize KOH or NaOH to achieve alkalinity, to date there has been no commercial electroless Cu bath for VLSI or ULSI manufacturing.

A number of common reducing agents have been suggested for use in electroless Cu baths, such as formaldehyde, dimethylamine borane, borohydride, hypophosphite, hydrazine, and dithionite [28]. In practice, however, virtually all

commercial electroless Cu solutions have used formaldehyde as reducing agent. This is due to the combination of cost, effectiveness and ease of control of formaldehyde systems.

The standard potential of formaldehyde (HCHO) depends on the pH of the solution. The equation of the chemical reaction is written as:

$$E^0 = +0.056$$

$$E^0 = -1.070$$

The standard potential shown in the equations above indicates the ease of oxidation for the reducing agent, formaldehyde in the electroless Cu solution. For stronger reducing effect, the larger negative value of the potential is preferred. By comparing the two reducing potentials, we can conclude that formaldehyde is easier oxidized at a higher pH level. Thus, electroless Cu solutions using formaldehyde as a reducing agent employ a high pH, above pH 12 [28].

Because simple Cu salts are insoluble at pH above 4, the use of an alkaline plating media necessitates the use of a complexing, or chelating component. Tartrate salts, alkanol amines, ethylenediaminetetra-acetic acid (EDTA) have been used as complexing agents for electroless Cu baths [28].

Besides Cu salt, reducing agent, complexing agent, and a source of alkalinity, additives such as stabilizers, rate promoters, accelerators, and surfactants [28] are present in commercial electroless Cu solutions. These components are important and

control parameters such as initiation, plating rate, stability, deposit stress, color, ductility, and so on.

The most common and well-studied electroless Cu bath composition is Copper Sulfate-Formaldehyde (CuSO₄-HCHO) using EDTA as the complexing agent. Cu precipitates at elevated pH values, and to prevent this from happening, a complexant is added to the electroless Cu bath. In the absence of complexant, Cu would react with formaldehyde immediately (uncontrollable) or form a precipitate with hydroxide. The complexant inactivates the Cu ions by forming a ring around the Cu ions, which reduce their chemical activity with formaldehyde. The alkaline condition is necessary to cause the electroless Cu deposition to be autocatalytic (spontaneous) [14, 28].

2.1.3 Basic Chemistry and Mechanism

The oxidation reaction of formaldehyde (HCOH) in alkaline condition (pH~13) is:

The associated reduction reaction of Cu under alkaline condition (pH~13) is:

The overall chemical reaction can then be summarized as:

The sum of their potential ($-0.216V + 1.07V = +0.854V$) is a positive term, indicating that electroless Cu deposition process is thermodynamically favorable. Spontaneous deposition does not occur as it is kinetically inhibited. The activation energy for the process is $\sim 0.63\text{eV}$, which is much more than what room temperature can provide [14]. The potential barrier can be overcome by the presence of a catalytic surface (such as Cu, Au, Ag, Pt, Pd, etc), which needs lower activation energy for reaction.

2.1.4 Operating Temperature

Besides chemistry, operating temperature is the most critical operating parameter. The temperature at which the plating reaction occurs is the principal variable that determines the rate of the reaction. Too low a temperature will shut the plating off, whereas too high may cause excessive plating and instability [28]. The operating temperature of electroless Cu solution using formaldehyde as the reducing agent has been reported to be between $20\text{ }^{\circ}\text{C} \sim 80\text{ }^{\circ}\text{C}$ [26, 28-30]. It was found that, increasing the operating temperature would enhance the deposition rate; however, the high bath temperature would cause the Cu surface to be rough and may even decompose the bath.

2.1.5 Catalytic Surface and Activation for Electroless Cu Deposition

In the process of electroless Cu plating, it is necessary to activate the surface of the specimen. The kinetic barrier to electroless Cu deposition can be overcome by the use of a catalytic film, such as Cu, Au, Ag, Pt, Pd, Ni or Co, when using formaldehyde as the reductant. Ohno et al. have determined that Cu is most catalytically active for formaldehyde oxidation as compared to other common reductants [31]. The electrocatalytic activity of various metals for formaldehyde oxidation has been evaluated by a number of workers. Bindra et al. determined that palladium and platinum were among the best catalysts in alkaline media [32]. Results were expressed in terms of a volcano plot (Fig. 2.2), which compares the normalized peak current for formaldehyde oxidation to the enthalpy of formation of the metal formate. The metal formate is a proposed intermediate in the formaldehyde oxidation pathway.

Figure 2.2: Plot of HCHO oxidation currents in 1M NaOH vs. enthalpy of formation of metal formate

The mechanism for formaldehyde oxidation is dependent on the nature of the catalytic substrate. In some cases (e.g., group VIII metals – Ni, Pd, Co, Pt, etc), the reaction is not accompanied by hydrogen generation and proceeds as follows [32]:

However, for group 1B metals (e.g., Cu, Ag, Au, etc), the reaction is accompanied by hydrogen production as shown in the following chemical reaction:

Since the electroless process occurs through the transfer of electrons during redox process, the surface must be electrically conductive for electron transfer to take place. Most barriers (TiN, Ta, TaN, Ti, etc) are conductive but the formation of a surface oxide layer on exposure to atmosphere renders them insulative and thus not suitable for electroless growth. In such a case, a wet (electrochemical) activation process using a mixture of palladium salts (PdCl₂, Pd acetate, etc) and hydrofluoric acid (HF) will be necessary. The HF etches away the oxide [28] and allows the Pd to be deposited in-situ. The discontinuous Pd nuclei are catalytic for electroless Cu growth (Fig. 2.3).

Figure 2.3: Reactions occurring during electroless Cu deposition, showing oxidation of HCHO on Pd nucleus and subsequent reduction and deposition of Cu around Pd nucleus (initial stage)

Once a layer of electroless Cu film has formed, subsequent growth will be spontaneous as Cu itself is autocatalytic to further electroless Cu growth. This means that the formaldehyde can continually be adsorbed and oxidized on the depositing surface and Cu complex being continually reduced, thereby indefinitely sustaining the reaction until either of the reactants is exhausted.

Further review of the state-of-the-art Pd activation methods for electroless metal deposition is included in *section 2.2*. The advantages and disadvantages of various methods are discussed. The reasons for a contact-displacement method to be chosen as the study of this project are justified.

2.1.6 Factors Affecting Electroless Cu Film Properties

2.1.6.1 Effect of Catalyzed Surface

Electroless Cu deposition is initiated on the randomly distributed catalyst particles on the substrate and the initial Cu grain structure is largely determined by the surface morphology. J. Shu et al reported that the nature and distribution of Pd nucleus formed during the process are very important to the deposition behavior and the quality of the deposit [25]. It has also been reported that the distribution of Pd on the barrier surface affects the surface roughness of electroless Cu [27]. Large Pd nuclei lead to rapid localized electroless Cu growth on these Pd nuclei, causing uneven growth over the substrate [28]. The roughness of electroless Cu can be lowered if the density of Pd nuclei increases and agglomeration of Pd nuclei is reduced [27]. A rough Cu seed is not desirable as the electric field (during electrodeposition of Cu) tends to be high at the sharp edges (peaks) of the rough film, leading to rapid plating at those regions.

It can be concluded that the catalyzed surface condition is a fundamental determinant of the properties of electroless Cu and consequently, that of electroplated Cu. This project will focus on the study of Pd nuclei deposition behavior on the substrate for subsequent electroless Cu deposition.

2.1.6.2 Effect of Bath Composition on Deposition Rate and Resistivity of Film

Dubin et al. [26] provided some correlation of bath parameters to deposition rate and resistivity, as shown in Table 2.1. Both CuSO_4 and EDTA concentration have no effect on resistivity, while higher HCHO concentration leads to an increase in deposition rate and resistivity.

Table 2.1: Correlations of bath parameters to deposition rate and resistivity [26]

Solution parameter	Effect on deposition rate	Effect on resistivity
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ concentration increase	Increase	No effect
HCHO concentration increase	Increase	Increase
EDTA concentration increase	No effect	No effect

2.1.6.3 Effect of pH and Temperature on Deposition Rate

The deposition rate as a function of temperature and pH has been characterized by some researchers. There is a large drop in potential at about 40-60°C, which corresponds to the beginning of significant Cu deposition [33] (Fig. 2.4a). No deposition is observed for pH < 11. So, a pH > 12 is required to achieve stable deposition [33, 34] (Fig. 2.4b).

(a)

(b)

Figure 2.4: Effect of (a) temperature and (b) pH on deposition rate [26,21]

The overall rate law for electroless Cu deposition can be presented as:

$$R = K \frac{[C_{Cu^{2+}}]^a [C_{HCHO}]^b}{[C_{OH^-}]^c [C_{EDTA^{4-}}]^d}$$

where K is the observed rate constant at a *given temperature*, and a , b , c , d are the observed reaction orders for the reactants. This accounts for the role of reactant concentration and temperature in affecting the rate of deposition.

2.1.6.4 Effect of Temperature on Resistivity

As reported by Dubin et al., temperature has the strongest effect on resistivity [26] (Fig. 2.5). The drop in film resistivity is due to the enhanced nucleation at higher temperature, leading to a more compact film, thereby causing the resistivity to decrease subsequently.

Figure 2.5: Effect of temperature on resistivity and deposition rate [26]

2.2 Electroless Cu Activation Methods

Good catalyzation is the key to the entire electroless Cu process. In this section, several of the most commonly used catalyzation methods are introduced. The advantages and disadvantages of the methods are discussed briefly.

2.2.1 Binary precious metal salt catalyzation

Acidic solutions of simple precious metal salts, including PdCl_2 , PtCl_2 , etc may be used as catalysts for electroless plating in some instances [35]. Because these salts are not tightly bound to the substrate surface, they may be removed by excessive rinsing. These solutions generally promote plating only on the most active surfaces, thus providing a good method of selectivity in certain applications.

2.2.2 Sequential two-step Sn-Pd catalyzation

This two step catalyst system was reported in 1955 [36] and has proven to be reliable and effective in metallizing nonconductive surfaces. In this method, an acidic Sn (II) solution, typically SnCl_2 dissolved in dilute hydrochloric acid, is first used to provide a uniform film of Sn^{2+} ions over the entire substrate surface. Because Sn (II) is inherently a strongly adherent material, the resultant film would be retained during rinsing. Then immersion in a dilute hydrochloric acid solution of PdCl_2 causes the more noble Pd ion to be reduced onto the substrate at the expense of the adsorbed Sn (II), which would be oxidized to Sn (IV). This is a well established method that extensive research has already reported [24]. The major disadvantage of this process is the lack of selectivity, which means that all the exposed surfaces are heavily

catalyzed. With the incorporation of Sn evaporation in the first step of catalyzation, the selectivity of this method has been improved [37].

2.2.3 Pd colloidal catalyzation

This type of catalyst system is by far the most prevalent type in commercial use [38, 39]. Pd/Sn colloid has been commercially used as the activator for electroless Cu deposition for over 30 years and its structure [40-42], and electrochemical kinetics [43-48] have been extensively studied. The colloid is about 1 to 5 nm in size, consisting of a Pd-rich inner core and bearing hydrous Sn (IV) chlorides in the outer sphere. The overall colloid is negatively charged. Excess Sn (II) plays a key role in the stabilization of the catalyst solution. A high salt content is also present in modern versions of the colloidal catalyst. This system is more stable, more active per unit of Pd, and it allows good selectivity. However, its sensitivity to air and its high cost leave room for improvement and for a substitution. Pd nanocolloids protected with sodium alkyl sulfate have been developed as possible new activators for electroless Cu deposition [49].

2.2.4 Contact-displacement catalyzation

The contact-displacement method was first suggested by Dubin et al for electroless metal deposition on TiN [26] and Si [18]. The advantages of this method include good selectivity, good adhesion to the substrate, non vacuum environment, and cost effectiveness. From the investigation by Patterson et al, in comparison with sequential Sn-Pd and Sn/Pd colloidal catalyzation, optimum plating was achieved

when using this method [28, 50]. Due to the advantages mentioned, this method has been popular in electroless metal deposition research [26, 29, 40, 51, 52]. In order to improve the uniformity and adhesion of Pd on the substrate, modifications of the solution have also been reported [27, 53, 54]. Joseph et al [55] indicated that the Pd concentration in the seed layer was approximately 1%, which was low enough to avoid wafer contamination and its undesirable consequent resistivity increase in the subsequently electroplated Cu layer.

2.2.5 Other catalyzations

Selective Cu plating has been performed using Pd/Si plasma immersion ion implantation or Pd₂Si deposition [56, 57]. Experimentally, it was observed that the metal silicides support the electroless Cu reactions similar to their metal counterparts. Good deposition is obtained on Pd₂Si and PtSi [58]. The gradual transition from a Pd-rich surface to a Pd-deficient substrate improves the adhesion of the plated Cu film [56]. Photochemical catalyzation methods using an atmospheric pressure excimer lamp-assisted photoselective activation process [59, 60], excimer lamp selective decomposition of activation precursors [61] and laser-assisted deposition of metals from salts and organometallics [62] have been used to selectively activate the specimen surface.

Each of these catalyzation techniques results in an incorporation of a high density of disjointed catalytic sites on the surface to be metallized, thereby creating nucleation centers that will enable initiation in subsequent electroless deposition.

A contact-displacement method is used in this project because of the advantages mentioned in *section 2.2.4*.

2.3 Fundamental deposition phenomena

In this section, a brief review is given for three individual classical phenomena – nucleation, growth, and ripening. The intention is not to give a full treatment of all aspects of the three phenomena, but to provide a basis for the comparison with the situation where all three phenomena occur concurrently, which will be shown later in *Chapter 4*.

2.3.1 Nucleation

Gibbs, Volmer, Becker, and Döering, and others developed the theory of formation of new phases since 1928 [63]. This theory is known as the classical theory of nucleation. As will be shown next, the classical theory is valid at small or moderate supersaturations where the nuclei consist of a very small number of building units of the order of unity.

In a homogeneous molecular system (liquid or vapor) there are always small fluctuations of the density in the sense of small molecular aggregates, which are compatible with the given state of aggregation. Such density fluctuations can be called “homophase” fluctuations. On the other hand, there might be the so-called “heterophase” fluctuations, which could lead to a visible transition to another state of aggregation [63].

The occurrence of heterophase fluctuations in a metastable system is in close analogy to a polymerization or polycondensation process: to an existing fluctuation of $(l-1)$ atoms, an addition of 1 atom produces a cluster of l atoms. The dissolution of just one atom from this cluster reduces it to the original $(l-1)$ cluster. The number density of clusters with a given size depends on time and cluster size [64]. The whole chain of clusters that could exist in a supersaturated or supercooled system is schematically depicted in Figure 2.6. The reactions shown in Figure 2.6 can be considered as standard chemical reactions [65].

Figure 2.6: If a single phase system is thermodynamically in a metastable state, such that in equilibrium it would be in a two-phase state, there can exist heterophase fluctuations of different size or number of atoms l in it [65].

In equilibrium, both reaction paths, i.e., $(x) + (1) \rightleftharpoons (x+1)$ have equal probability. Their concentrations can be described by the law of mass action:

$$\frac{[x+1]}{[x][1]} = \exp(-\Delta G_x / k_B T)$$

where the brackets denote concentrations and $\Delta G_x = \varepsilon(x+1) - \varepsilon(x)$ is the difference of the free enthalpy of clusters ε of size $x+1$ and x (here, size means exactly the number of atoms in a cluster). In a non-equilibrium situation, the rate of formation of a cluster $(x) + (1) \Rightarrow (x+1)$ is different from the rate of decomposition $(x+1) \Rightarrow (x) + (1)$ [65].

The nucleation begins as just a few molecules are connected. Once a nucleus has formed, there is a tendency for them to be reabsorbed because these newly formed nuclei are very small and have a large surface area with respect to volume. This means that a large percentage of the atoms in the nuclei are on the surface with unsatisfied chemical bonds. In order for a nucleus to survive and not be reabsorbed, it must undergo rapid growth beyond its critical size. The critical size is the point when the nuclei will no longer spontaneously be reabsorbed into the solution.

Nucleation theory is based upon thermodynamic models that link the nucleation rate to supersaturation. These models, so-called “homogeneous” nucleation, cannot describe all systems. In most cases “heterogeneous” nucleation occurs.

2.3.1.1 Homogeneous Nucleation (HON)

Homogeneous nucleation (HON) occurs when the clusters of the new phase are in contact only with the old phase and with no other phases and/or molecular species. Nucleation of droplets in the bulk of ideally pure supersaturated vapors is a classical example of HON [66]. Since the nucleation nature of Pd on TiN is heterogeneous, HON is not discussed in detail here.

2.3.1.2 Heterogeneous Nucleation (HEN)

Heterogeneous nucleation (HEN) takes place when the old phase contacts and/or contains other phases and/or molecular species. HEN is more widespread in both nature and technology than is HON, because the old phase always has in itself foreign molecules, microscopic particles, bubbles, and so on or is in contact with other phases which limit it spatially. The surfaces of these phases and of the various particles may be places on which the formation of the clusters of a new phase is preferred [67]. Pd deposition on TiN in this project is considered as HEN.

Figure 2.7 depicts schematically the old phase in the initial and final states 1 and 2, respectively, before and after the formation of a cluster of n molecules on the surface of another phase called the substrate [67].

Figure 2.7: Old phase of M molecules before (*state 1*) and after (*state 2*) heterogeneous formation of a cluster of n molecules on the surface of a substrate.

2.3.2 Growth

Growth is generally caused by imposed supercooling and supersaturation. The particle size density distribution, $f(R,t)dR$, obeys a continuity equation in the size space, where

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial R} \left(\frac{dR}{dt} f \right) = 0$$

and $\frac{dR}{dt}$ could be viewed as the velocity with which a particle moves in radius space.

$f(R,t)$ is a number density per radius interval.

$$\text{flux density} = \frac{dR}{dt} \cdot f(R,t)$$

If no sources for the particle exist, then there is only a motion from one radius class $R, R + dR$ to another. Therefore, a continuity equation holds, i.e. the divergence of the flux density equals the time derivative of the density in the interval under consideration. The interval here is the radius class, and the divergence the partial derivative of the flux density with respect to radius. Time evolution of a dispersion of particles changes their size due to different growth laws [65]. All the growth laws can be written as:

$$\frac{dR}{dt} = \frac{1}{R^m}$$

where m is the exponent in the differential growth law (either $-\frac{1}{2}$, 0 or 1).

It was reported that, in the case of growth laws for interface kinetics without curvature in constant growth rate ($m = 0$), the given size distribution in radius space simply shifts to larger values. Its spread and standard deviation remain unchanged, only the average radius increases linearly with time and the volume or solid fraction increases in proportion to the third power of time [68], but, the particle density remains constant. A schematic for the growth law with $m = 0$, is shown in Figure 2.8.

Figure 2.8: Size distribution as a function of time with $m = 0$. The simple shift shown is observed for growth due to interface reactions of first or second order. R_0 denotes an arbitrary radius to normalize the radius coordinate, e.g., it could be the initial mean radius.

For the growth law, when droplets are moving in a fluid with Stokes settling velocity $\left(m = -\frac{1}{2}\right)$, bigger particles grow faster than smaller ones. As a result, the standard deviation of the distribution increases with time (Figure 2.9). However, for the growth controlled by either diffusion of heat or mass ($m = 1$), the evolution of the size distribution shows the opposite result [64] (Figure 2.10).

Figure 2.9: Evolution of an initial distribution with time if dispersed droplets move in the gravity field with Stokes settling velocity ($m = -1/2$). R_0 is again an arbitrary normalization constant, e.g., the initial mean radius.

Figure 2.10: Size distribution as a function of time with $m = 1$.

2.3.3 Ripening

In this project, a very important phenomenon has been observed. It is the *Ostwald ripening* of Pd particles during the activation process. The physical chemist, Wilhelm Ostwald first described the ripening process in 1896 [69-72]. Alternatively, this process is commonly known as *coarsening*. This process is characterized by a decrease in the interfacial area. Accordingly, there is a reduction of particles, and the large particles grow at the expense of the smaller ones [70]. The driving force of this process is derived from the reduction in interfacial energy [72]. This well-known curvature dependence of the chemical potential, which assumes an isotropic surface energy, is shown by this equation:

$$\mu = \mu_0 + V_m \gamma \kappa$$

where κ is the mean interfacial curvature and μ_0 is the chemical potential of an atom at a flat interface, V_m is the molar volume and γ is the surface energy. From this equation, it is clear that atoms will flow from regions of high to low curvature. This results in the disappearance of surfaces possessing high curvature and an increase in the size scale of a dispersed second phase, which is consistent with the necessary decrease in total energy of the two-phase system [71].

In systems consisting of dispersed particles of varying sizes, the solubility of the particles in the medium was found to be affected by the particle size [72]. The well-known Thomson-Freundlich equation, relates the solubility to particle size as:

$$\ln \frac{S_a}{S} = \frac{2M\sigma}{RT\rho a}$$

where S is the true solubility, S_a is the solubility in contact with a particle of radius a , ρ is the density of the solid of molecular weight M , σ is the interfacial tension between solid and liquid, R is the gas constant and T is the temperature. It can be seen from the equation that with a decrease in particle size, the solubility will increase. The smaller particles tend to dissolve and precipitate onto larger particles; in the final state the system tends to form a single particle [72].

In ripening, the classical Lifshitz-Slezov-Wagner (LSW) theory assumes that it occurs in a closed system. In such a system, the volume fraction of the phase undergoing ripening remains constant. The driving force of LSW ripening is the reduction of surface energy of the phase. Thus, the total surface area of the phase decreases during ripening [73]. This is a conservative process, in which the total volume or mass in the system is preserved. Ripening for the open system was studied previously by Beenakker et al [74]. Gusak et al reported on the non-conservative flux-driven ripening showing simultaneous growth and ripening of an intermetallic compound phase in the open system [75].

Furthermore, a mean field assumption is adopted in LSW theory. This mean field theory assumes that the concentration of diffusing species in the matrix phase is uniform. Interparticle diffusional interactions are neglected, and this mean field theory is valid only in the limit of zero volume fraction of the ripening phase in an infinite matrix and it becomes increasingly inapplicable at higher volume fractions [76]. As a result, experimentally measured particle radii distributions rarely agree with LSW predictions [69]. Diffusion controlled ripening of the ripening phase at high volume fractions has been studied theoretically [77-83]. The mean field theory was challenged by Vedula et al [84], and DeHoff established a communicating

neighbor theory later on [85]. The communicating neighbor theory is used to account for the interactions of particles in a finite system.

CHAPTER 3 Experimental Techniques

In this experimental section, we introduce the substrates and chemical baths used. The steps involved in sample preparation are outlined in *section 3.3*. Various characterization techniques were used in this project, the details of those techniques are presented in *section 3.4*. The software which was used for micrograph analysis is also shown in this chapter.

3.1 Activation Bath

The activation solution used in this study has been proposed by Diamand et al in electroless Cu research [32]. The HF etches away the oxides [26], and allows the Pd to be deposited in-situ. The deposited Pd is catalytic for electroless Cu growth. The composition of the activation bath is as follows:

Table 3.1: PdCl₂ activation bath composition

PdCl₂ (59%)	100~500 mg/L
HCl	3 ml/L
HF	10~30 ml/L
Temperature	Room temperature
Time	1~5 min

3.2 Electroless Copper Bath

As mentioned earlier, there is no commercially available electroless Cu bath suitable for ULSI and VLSI manufacturing. Hence, there is a need to obtain a bath composition that is stable and suitable for volume manufacturing.

Formaldehyde, HCHO is rather volatile and its concentration can drop to <60% at high temperatures of deposition within a few hours [59], so a higher amount is preferred. However, excess HCHO could lead to higher resistivity electroless Cu deposit. Furthermore, HCHO vapor is also carcinogenic, hence a compromised amount of HCHO is used.

EDTA is used as a complexing agent to increase the stability of the electroless Cu bath. Insufficient EDTA led to bath instability since the uncomplexed Cu would lead to bath decomposition.

Triton-X (PEG mono[p-(1,3,3-tetramethylbutyl)phenyl]ether) is used as a surfactant and wetting agent. The surfactant is necessary to help hydrogen desorb from the Cu film as well as to enhance wetting of the sample surface during immersion. There could also be a mild stabilizing effect on the electroless Cu bath [14]. But, excessive surfactant will over-stabilize the bath, leading to no electroless Cu deposition.

It has been reported that the deposition rate at 40°C is ~4 nm/min [86]. This deposition rate is too slow for any practical use. As a result, other investigators recommended that high temperature deposition is desirable as it leads to lower resistivity. Thus, the investigation utilized a temperature of ~65°C [14]. The composition of the electroless Cu bath is summarized in Table 3.2.

Table 3.2: Composition of Electroless Cu Bath

Chemical	Concentration
CuSO₄·5H₂O	5 g/L
EDTA	12 g/L
Triton X-100	0.05 g/L
HCHO	5 ml/L
TMAH	Adjust pH

3.3 Sample Preparation

The sample preparation involves four steps: substrate preparation, substrate cleaning, activation process, and the electroless Cu deposition process. For each experiment shown in the thesis, each data point represents one sample which is prepared one after another. Each experiment was carried out two times to confirm the validity of the data achieved.

3.3.1. Substrate Preparation

Among the barriers that can be used for Cu metallizations, the first choice was TiN. This is due to its widespread use in the industry as a barrier in Al metallization. Consequently a TiN barrier film was used in this study. The TiN films were deposited by the chemical vapor deposition method (CVD). 250 Å of CVD TiN film was deposited on 5000 Å PECVD SiO₂/Si(100) substrate. The specimen was fabricated by Chartered Semiconductor Manufacturing, Inc, Singapore.

3.3.2. Substrate Cleaning

The removal of organic and inorganic contaminants was carried out with the RCA cleaning steps at room temperature. SC1 solution consists of $H_2O:H_2O_2:NH_4OH$ with the ratio of 5:1:1. The content of SC2 solution is $H_2O:HCl:H_2O_2$ with ratio of 6:1:1. The samples were then immersed in diluted HF to expose a clean surface for activation and electroless Cu process. After removal of sample from each cleaning bath, the samples were rinsed with DI water to remove remaining cleaning solution on the surface and prevent contamination of the next cleaning bath.

3.3.3. Activation Process

Blanket wafer samples were cut to dimension of $2\text{cm} \times 2\text{cm}$ using a diamond scriber. The samples were cleaned with DI water and immersed in the Pd activation bath with the composition shown in *section 3.1* for different activation time. After the completion of Pd activation, the samples were rinsed with DI water again.

3.3.4. Electroless Cu Deposition

The pH of the solution is adjusted by tetra-methyl-ammonium hydroxide (TMAH) to 12.8 and a deposition temperature of 60°C . The deposition time varies with thickness required.

3.4 Characterization Technique

Various characterization techniques were used. The details are presented in this section.

3.4.1. Field Emission Scanning Electron Microscope (FESEM)

The Pd particle distribution behavior and size were observed using a field emission scanning electron microscope (FESEM – JEOL JSM 6340F) with voltage of 5 keV and current of 8 μ A. A digital FESEM micrograph was subsequently analyzed with the software “*UTHSCSA ImageTool*”. The details and steps using the software will be shown in *section 3.5*.

3.4.2. Energy-Dispersive X-Ray Spectroscopy (EDS)

When the atoms in a material are ionized by a high-energy radiation they emit characteristic X-rays. EDS is an acronym describing a technique of X-ray spectroscopy that is based on the collection and energy dispersion of characteristic X-rays. The EDS spectrometer used in this project was integrated with the FESEM with the spot size around 1 μ m. The X-ray spectrum consisted of a series of peaks representative of the type and relative amount of each element in the sample. The number of counts in each peak could be further converted into elemental weight concentration either by comparison with standards or by standardless calculations.

3.4.3. X-Ray Diffractometer (XRD)

X-ray diffraction was used to monitor the texture and grain size evolution of the electroless Cu film. The texture of the copper film was measured using a Shimadzu X-Ray Diffractometer (XRD)-600. The intensity and wavelengths of X-rays (spectra) generated by Cu films were analyzed.

Table 3.3: Measurement conditions for X-ray Diffraction

X-ray tube	
Target	Cu
Voltage	50.0 (kV)
Current	20.0 (mA)
<i>Slits</i>	
Divergence slit	1.00000 (deg)
Scatter slit	1.00000 (deg)
Receiving slit	0.30000 (mm)
Scanning	
Drive axis	2 Theta (Theta=0.5000 deg)
Scan range	40.0000-76.0000 (deg)
Scan mode	Continuous scan
Scan speed	3.0000 (deg/min)
Sampling pitch	0.0500 (deg)
Preset time	0.75 (sec)

XRD provides a simple method for measuring the grain size in a polycrystalline film, based on the Scherrer's equation [87, 88].

$$L = 0.94\lambda / W_{eff} \cos \theta$$

where L is the structural coherence length (which is essentially equivalent to the average grain size), λ is the wavelength of the x-ray radiation (0.1542 nm), and W_{eff} is the effective full width at half maximum (FWHM) of the x-ray peak located at 2θ . This equation shows an inverse relationship between grain size and diffracted peak profile width: the wider the peak, the smaller the crystallites. It should be noted that besides grain size contribution, peak broadening could also be due to some other factors, such as instrumental broadening and microstrain. In order to determine the peak broadening due to instrumental parameters, which include beam size, sample-to-detector distance, and air scatter, a bare Si substrate, the same type as used for film deposition, was scanned using the same XRD setup. It was found that the measured FWHM (W_{system}) of the (111) Si peak ($2\theta = 28.5^\circ$) was 0.241° . The W_{eff} was calculated from the measured peak width (W_{meas}), using equation [89]:

$$W_{eff}^2 = W_{meas}^2 - W_{system}^2$$

A well-developed Cu (111) peak near 44.3° was the peak used in this study to estimate the grain size. A Gaussian line shape was fitted to the Cu (111) peak using standard software. The FWHM was then calculated by the software using this Gaussian line shape. From the uncertainty associated with a given fit, the software yielded an uncertainty for FWHM; this uncertainty was used to obtain the error associated with the measured grain size.

3.4.4. Atomic Force Microscopy (AFM)

The electroless copper surface roughness measurement was conducted with Digital Instruments NanoScopeTM Scanning Probe Microscopes.

The measurement was operated using TappingModeTM AFM. The TappingModeTM AFM operates by scanning a tip attached to the end of an oscillating cantilever across the sample. The tip “taps” slightly on the sample surface during scanning, contacting the surface at the bottom of its swing.

The advantages of TappingModeTM AFM:

- Higher lateral resolution on most samples (1nm to 5 nm)
- Lower forces and less damage to soft samples imaged in air
- Lateral forces are virtually eliminated, so there is no scaping

However, there is a disadvantage of TappingModeTM AFM:

- Slightly slower scan speed than contact mode AFM

The surface roughness measurement of the electroless copper film was conducted using TappingModeTM AFM, while height mode imaging was used for the measurement. The measurement in this project was the RMS (Root Mean Square) roughness measurement.

RMS is the standard deviation of the Z values within a given area as shown in the equation:

$$RMS = \sqrt{\frac{\sum_{i=1}^N (Z_i - Z_{ave})^2}{N}}$$

where Z_{ave} is the average Z value within the given area, Z_i is the current Z value, and N is the number of points within a given area.

3.4.5. Transmission Electron Microscopy (TEM)

In Transmission electron microscopy (TEM), a thin solid specimen (≤ 200 nm thick) was bombarded in a vacuum with a highly-focused, monoenergetic beam of electrons. The beam was of sufficient energy to propagate through the specimen. A series of electromagnetic lenses then magnifies this transmitted electron signal. In this study, the TEM was carried out with a JOEL JEM-2010.

3.4.6. Time-of-Flight Secondary Ion Mass Spectroscopy (SIMS)

SIMS is an analytical technique used for obtaining mass spectra of ions of samples under analysis. Besides just taking mass spectrums, SIMS can be used for depth profiling (real-time collection of mass spectra with respect to depth of sample), imaging (for location of defects), and line scan (real-time collection of mass spectra with respect to lateral distance – lateral profiling). In the case of semiconductor research, the two most commonly used techniques are depth profiling and imaging.

ToF-SIMS profiling was done at IMRE with a ION-TOF system, with a 25 kV, ~2.8 pA Ga beam for analysis and a 3 kV, ~60 nA Ar beam for sputtering. Oxygen flooding was used to enhance the intensity of the secondary ions with the chamber pressure at $\sim 5.0 \times 10^{-5}$ mbar. The flooding also helped to reduce roughness induced during sputtering. The flood gun was used for charge compensation due to the presence of a non-conducting layer. All data obtained were normalized with the Ga spectrum.

3.4.7. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) which is also known as Electron Spectroscopy for Chemical Analysis (ESCA) is a chemical analysis technique that makes use of photoelectrons generated by a chemical, when latter is irradiated upon by soft x-ray. The chemical states are identified by the photoelectron energy. The XPS spectrum is obtained by plotting the number of detected electrons per energy level against their kinetic or binding energy. The binding energy is related to kinetic energy by the following equation:

$$KE = h\nu - BE$$

where KE is the kinetic energy, $h\nu$ is the energy of the incident photon, and BE is the binding energy of the atomic orbital from which the electron originates. Each element has a unique set of binding energies. As such XPS can be used to identify and determine the concentration of the elements in the surface. Chemical

shifts arise when differences in chemical potential and polarisability of compounds occur. These chemical shifts can be used to identify analyzed materials.

The X-ray photoelectron spectroscopy (XPS) analyses were completed in Kratos AXIS spectrometer with the soft x-ray generated by a 1253.6 eV Mg K α source. The base vacuum in the XPS analysis chamber was about 10⁻⁹ Torr. Only the surface scan was conducted for the samples. For insulating samples, once the photoelectrons are emitted out of the sample surface, a positive charge zone will establish quickly in the sample surface. As a result, the sample acquires a positive potential (varying typically from several volts to tens of volts) and the kinetic energies of core electrons were reduced by the same amount, C :

$$BE = h\nu - (KE - C)$$

It is known that the surface charging results in the shift of the XPS peaks to higher binding energy. In this case, the binding energy was calibrated with an internal reference peak. The C 1s peak from the adventitious carbon based contaminant with the binding energy of 284.8 eV, was used as the reference for calibration.

3.5 Software for Micrograph Analysis

The analysis of the Pd particle size and coverage of Pd particle on barrier surface were performed using UTHSCSA *ImageTool* program (developed at the University of Texas Health Science Center at San Antonio, Texas and available from the Internet by anonymous FTP from maxrad6.uthscsa.edu). FESEM analysis at magnification of 10,000x was used for the quantitative study of the Pd particle size and size distribution. In order to capture the distribution and uniformity of Pd particle on the sample surface, three micrographs from different regions, that were 5,000 μm apart were chosen. Data points from time evolution study shown in the next few chapters is combined with data analysis from the three micrographs.

The steps of analysis of the FESEM micrograph are shown in Fig. 3.1. The image was first calibrated to the scale shown on the FESEM micrograph and the threshold of the image was adjusted to show only the Pd particles (bright dots). The number and area of each individual particle were counted and calculated with the software. The diameter of the Pd particles was calculated by assuming that Pd is of a perfect round shape. With 10,000x magnification, the estimated error of the calculated size is about 3.5 nm with the resolution of FESEM in secondary electron imaging that can be as low as 1.5 nm for an ideal sample.

Figure 3.1: Steps of software analysis for FESEM micrograph (a) calibration, (b) threshold adjustment, (c) particle identification, and (d) particle analysis

CHAPTER 4 Classification of Catalytic Palladium

Deposition Processes

As mentioned in *section 2.5*, the kinetic barrier of electroless Cu deposition can be overcome by use of a catalytic film. Bindra et al. determined that Pd and platinum (Pt) were among the best catalysts in alkaline media when using formaldehyde as the reductant [32]. Pd has been the universal choice as a catalyst for initiating electroless deposition due to its nobility, or resistance to dissolution in electroless solutions and to excessive oxidation [90]. Furthermore, formaldehyde oxidation on Pd and other group VIII metals is not accompanied by hydrogen generation. This explains why Pd is extensively used as the catalyst for electroless metal deposition. Surface catalyzation methods for electroless Cu deposition are reviewed in *section 2.2*. This forms the motivation for the study of catalytic Pd deposition and its effect on electroless Cu properties.

The Pd particle density and mean size changes with time. The experimental results and discussion of the detailed studies on Pd particle density and size change with activation time are presented in this section.

4.1. Contact-Displacement Deposited Pd

The Pd particle size, size distribution and particles density studies were completed by FESEM micrographs and analyzed using *ImageTool* software. The nucleation of Pd on TiN is considered as a heterogeneous nucleation (HEN), which

refers to the stages whereby atoms from solution are absorbed on the surface of a solid and combine together to form discrete clusters that grow with time. Figure 4.1 shows Pd particles on activated TiN surface. Pd particles are located sparsely on the activated TiN surface. The EDS spectrum (Figure 4.2) of the white dots in the FESEM micrograph clearly shows a Pd peak which confirms the white dots are Pd particles.

Figure 4.1: FESEM micrograph of TiN surface after being immersed in $5.64 \times 10^{-4} \text{ M PdCl}_2$ activation bath for 2 minutes.

Figure 4.2: EDS spectrum of Pd particles

Figure 4.3 shows the XRD spectrum of TiN surface with Pd activation was prepared at a very slow scanning rate. The scanning rate was set at 0.04 degree/min to obtain an acceptable noise-to-signal ratio. The TiN/SiO₂/Si substrate was activated in the Pd solution for 10 minutes. The XRD scanning was carried out from 38° to 70° to capture the Pd (111), (200), and (220) peaks at 40.114°, 46.661°, and 68.083° respectively. From the powder diffraction ICDD card files [91] of FCC Pd, the Pd (111)/(200) and (111)/(220) ratios were 2.38 and 4 respectively. From Figure 4.3, the (111)/(200) and (111)/(220) ratios were 3.03 and 6.67 respectively. Hence, we can conclude that the Pd particles deposited on TiN surface are polycrystalline. It is reported that each Pd particle deposited by contact displacement was indeed constructed by clusters of small Pd nanocrystallites of only about 5 nm [92]. They exhibit a preferred orientation despite the fact that Pd was deposited on amorphous CVD TiN surface. As a general rule, the surface free energy decreases with increasing atomic layer spacing, i.e., increasing number of nearest neighbors of the surface atoms [93]. For FCC crystals, (111) orientation is preferred because it has lowest free energy. The surface energy for FCC crystal obeys the order: $\sigma_{(111)} < \sigma_{(100)} < \sigma_{(110)}$ [94].

Figure 4.3: XRD spectrum of TiN surface with 10 mins of Pd activation. Slow XRD scan rate (0.04 degree/min) was used to obtain acceptable signal-to-noise ratio.

Figure 4.4 shows the TEM micrograph of Pd particles on TiN. Due to the dispersed nature and low coverage of Pd particles, only very few Pd particles can be seen in one TEM micrograph. In this micrograph, the sizes of Pd are in the range of nanometer scale. As a result, the TEM method was found to be impractical and inefficient to be used for the study of the statistical behavior of Pd nucleation phenomena. Hence, FESEM was then exclusively used to study Pd particle size and number density throughout this project.

Figure 4.4: Plan view TEM micrograph showing the location of Pd particle

In order to have a more quantitative statistical study of Pd nucleation, FESEM analysis at magnification of 10,000 times was used. A comparison of the Pd particles micrographs taken at 10,000x and 30,000x magnification are shown in Figure 4.5.

Figure 4.5: FESEM micrographs of Pd particles on TiN (a) 10,000x magnification and (b) 30,000x magnification

The statistical results of the Pd particle size distribution are shown in Figure 4.6. With magnification of 10,000x, more Pd particles were captured in the micrograph than that captured at 30,000x magnification.

Figure 4.6: Comparisons of Pd particle size distribution at two magnifications.

To compare the difference of the size distribution curve, the y-axis was normalized to percentage and shown in Figure 4.7. The curves were found to have a similar trend. However, the sizes of the particles were 10 nm larger when the micrographs were taken at lower magnification. This is consistent with the difference in the sizes of the specimen pixel at the two magnifications. The specimen pixel is 10 nm and 3.3 nm at 10,000x and 30,000x magnification, respectively. Since the distributions are similar except for a constant shift, this would not affect the time evolution study of Pd particle size distribution. It could be concluded that, the statistical studies of Pd nucleation could be done using FESEM at a magnification of 10,000x because the results are as reliable as those obtained at higher magnification.

Figure 4.7: Pd particle size distributions analyzed from FESEM micrographs taken at different magnifications.

To ensure the uniformity of Pd particles, a TiN/SiO₂/Si substrate was cleaned with diluted HF and RCA cleaning steps presented in section 3.3.2 to remove the organic and inorganic contaminants on the TiN surface. The FESEM micrographs in Figure 4.8 show the Pd particle distribution for different regions of TiN surface deposited with same deposition condition. The Pd particle size distributions of the micrographs are shown in Figure 4.9. The size distribution curves for each individual micrograph and summation of the three are considered identical with standard deviation of the average size and density of 1.33 nm and 0.07 μm^{-2} respectively while the average Pd particle size is at 114.2 nm and density is 1.19 μm^{-2} . This confirms the uniformity of Pd particle size and distribution on TiN. In *section 3.5*, we have shown that the estimated error is 3.5 nm for particle size measurement, the estimated error of the calibrated measurement is about 3% of the size of Pd particle. This shows that the error of measurement is small compared to the Pd particle size.

Figure 4.8: FESEM micrographs of Pd particles at different regions of TiN demonstrate the uniformity of Pd particle distribution.

Figure 4.9: Pd particle size distributions analyzed from FESEM micrographs taken at different regions of TiN.

4.2. Pd Particle Size Distribution on TiN

The Pd particle size distribution on TiN with different Pd activation time is shown in Figure 4.10. For clarity, the distribution curve is separated into two graphs. The distribution curve for 3 minutes activation is included in both the curves for ease of comparison. All the curves exhibited unimodal distribution. The range of Pd particles size distribution increases during the growth stage, narrows before ripening starts, and increases again when ripening starts. The change of distribution range will be discussed in detail later.

(a)

(b)

Figure 4.10: Pd particle size distribution on TiN with different activation times (a) 1, 2, 2.5, and 3 minutes, (b) 3, 3.5, 4, and 5 minutes

Figure 4.11 shows the changes of Pd particle size distribution range and semi-interquartile range with time. Measurement of distribution range is the simplest for showing the spread of particle size in a population. The use of semi-interquartile

range is seldom reported; however, it is included in our analysis of distribution range due to the fact that semi-interquartile range is little affected by extreme values, it was used as a supplement for distribution range as a measure of the spread. As seen in Figure 4.11 (a), an increase in the distribution range from 1 minute to 2 minutes of activation time was observed. After which, a slight drop in the range was noticed until the time reaches 3 minutes. The range increased eventually when the activation time became longer. The semi-interquartile range curve in Figure 4.11 (b) shows a slight variation with the distribution range. The decreasing trend was extended to 3.5 minutes of activation time. The observation of increasing trend in range but not semi-interquartile range from 3 minutes to 3.5 minutes indicates the formation of large Pd particles in small quantity while the peak in the size distribution is narrower.

According to the statistics of growth [64], in interface controlled growth, a given size distribution shifts in radius space simply to larger values provided the growth rate is constant. Its spread will remain unchanged and only the average radius will increase linearly with time and the volume or solid fraction increases proportional to the third power of time. The changes in the distribution ranges in Figure 4.11 indicate that Pd deposition on TiN is not purely a constant growth phenomenon. Instead, it comprises all three phenomena of nucleation, growth, and ripening.

(a)

(b)

Figure 4.11: Pd particle size distribution ranges change with activation time (a) particle size distribution range, (b) semi-interquartile range

The Pd nucleation on TiN by contact-displacement method takes place in an open system because the source of accessible Pd (in solution) can be considered infinite compared to the amount deposited. During the growth of nucleated Pd

particles, new particles continue to nucleate on the surface, and even during the ripening stage, both nucleation of new particles and normal growth of existing particles are occurring simultaneously. The increment of distribution range from 1 minute to 2 minutes of activation implies the growth of nucleated Pd particles and nucleation of new particles – increasing the maximum and decreasing or maintaining the minimum at the same time. The disappearance of large particles was observed when the activation time reached 2.5 minutes and 3 minutes. This resulted in a decrease in the distribution range during the transition of growth stage to the secondary nucleation stage. The reason for the large particles disappearing at this transition point could be attributed to the removal of TiN substrate underneath the Pd particles. With the in-situ removal of Ti-oxide during a Pd activation process, more fresh TiN surface was exposed. We can deduce that secondary nucleation occurred with the complete Ti-oxide removal. The occurrence of the secondary nucleation in the XPS analyses of TiN surface during Pd activation will be shown in *chapter 5*. After three minutes, there was an increase in the distribution range, but a further decrease in the semi-interquartile range was observed. At the point where ripening began, large particles grew at the expense of small particles. An increasing trend in the distribution range was found in our study. This is difference from the classical approach of the ripening process whereby the size distribution range in the second phase, i.e., Pd particles in this case, would shrink due to the decrease in the total count of the second phase. The reason for the difference between our finding and classical ripening process is that our system is an open system and the continuous formation of new particles causes the population of the smallest particles to remain on the surface through out the deposition process. As the measurement of semi-interquartile range disregards the extreme numbers, a decrement in the value resulted. For a long time after ripening began, the distribution ranges increased.

4.3. Pd Particles density and Average Particle Size Evolution with Time

The changes in Pd particles density and mean particle size with activation time are shown in Figure 4.12. The number of Pd particles increases tremendously at one point followed by a rapid decrease. Based on the analysis from the change of distribution ranges, three kinetic processes can be identified, namely, growth, secondary nucleation, and ripening. However, these processes are not distinct, but in fact overlap with each other during the whole activation process [95]. From this experimental result, we can hypothesize that nucleation, growth and ripening processes occur at the same time.

Figure 4.12: Pd particle density and mean particle size on TiN with different activation time in $10^{-3} M$ PdCl_2 activation solution

Pd particles begin to grow once the nucleation on TiN occurs. According to McCoy B.J. [95, 96], a metastable supersaturated phase will not only generate particles according to the classical theory of nucleation, but will also cause

deposition on the particles and consequent growth of the clusters. By this interpretation, nucleation without accompanying growth is impossible. In the Pd nucleation process, nucleation and growth of Pd particles occur concurrently. In the growth stage shown in Figure 4.12, the Pd particle number density decreases slightly. This small fluctuation also indicates that the rate of particle increase by nucleation is equal to the rate of particle decrease due to ripening. The increase in Pd particle size also noticed in the growth stage is a result of the growth and ripening process.

In the secondary nucleation stage, a sudden increase in particles density was observed at 2.5 minutes of activation time. This occurred at the end of the growth stage and the beginning of the secondary nucleation stage. Besides the sudden increase in new particles, both the size distribution range and semi-interquartile range decreased (Figure 4.11). As shown in Figure 4.12, the peak of the particle size distributions at 2, 2.5, and 3 minutes activation shifts to a smaller value with higher count when the activation time increases. This shows that, upon the transition of the nucleation process to the secondary nucleation stage, large particles disappear and causes the decrease in distribution ranges. This phenomenon has not been reported in any classical nucleation studies.

4.4. Simultaneous Nucleation, Growth, and Ripening Process

Concurrent secondary nucleation and ripening was reported during the activation processes of Pd deposition in *section 4.3*. However, the three stages are not totally distinct from each other. Concurrent nucleation, growth, and ripening were found in this ‘open’ heterogeneous nucleation system. In order to have better

control of Pd particle density and size, one should understand the change of Pd particle density and size with deposition time. In this section, we propose the cases of deposition event that's causing the change of total number Pd particles with time and associate them to the classified stages of Pd deposition process.

4.4.1. Change of total number of particles with time

Only nucleation and ripening events contribute to the change of total particle number, $\frac{\partial N_T}{\partial t}$.

$$\frac{\partial N_T}{\partial t} = \frac{\partial N_N}{\partial t} + \frac{\partial N_R}{\partial t} \quad \text{----- (4.1)}$$

In the following sections, three possible variations of the particle size distribution change with time are discussed.

Case 1: Nucleation-Dominated

The nucleation rate is much faster than the ripening rate, in which $\frac{\partial N_N}{\partial t} \gg \frac{\partial N_R}{\partial t}$. As a result, the particle change due to ripening is comparatively negligible. This applies to the very early stage of deposition when the surface coverage of particle is very low. Due to the low surface coverage, the concentration gradient among the particles is very small. Hence, the ripening rate is considered negligible. The total number of particle increases with time in this case.

Case 2: Ripening-Dominated

When the ripening rate is very fast, the new particle nucleation process becomes comparatively negligible. This applies to the stage where the surface coverage is high. The ripening rate increases significantly when the surface coverage is high. The total number of particles decrease due to ripening is faster than the total number increase due to nucleation ($\frac{\partial N_R}{\partial t} \gg \frac{\partial N_N}{\partial t}$). Total number of particle decreases with time.

Case 3: Balanced Nucleation and Ripening

In the third case, the increase of particle numbers by nucleation is equal to the decrease of particle numbers by ripening. The total number of particles remains constant. All three phenomena play significant parts in changing the particle size distribution.

Figure 4.13 illustrates the change of the total particle number with time for the above three cases. In the nucleation-dominated case (Case 1), the total particle number increases with time; in the ripening-dominated case (Case 2), the total particle number decreases with time; and, the total particle number remains constant for the balanced nucleation and ripening case (Case 3).

Figure 4.13: Change of total number of particles with time for three different cases.

4.4.2. Experimental Analysis

Pd particle size distributions deposited with different times are shown in Figure 4.14. The particle size distribution for the growth stage is shown in Figure 4.14 (a), the range of the distribution increased from 70 nm to 110 nm when deposition time increases from 1 minute to 2 minutes. The range of distribution narrowed down by 10 nm when the deposition time is 30 s longer. This change is so

small that it could be due to natural fluctuation. The change of Pd particle density is small during the growth stage in Figure 4.15.

During the secondary nucleation stage, the nucleation rate increases tremendously and overshadows the ripening phenomenon. The increase in Pd particle density may indicate the nucleation-dominated case (Case 1). When the ratio of nucleation rate over growth rate and ripening rate is high, the distribution peak may shift to smaller size because of an overwhelming new population of freshly nucleated small particles.

As deposition time increases, Pd coverage on the surface increases, and ripening dominates because of the decrease in mean particle spacing on a densely populated surface. The range of the size distribution and average particle size increase rapidly, while the particle density decreases tremendously. Thus, it resembles the ripening-dominated case (Case 2) of the simultaneous nucleation, growth, and ripening model. Figure 4.16 illustrates the changes of Pd particles on the substrate through the stages of Pd deposition.

(a)

(b)

(c)

Figure 4.14: Pd particle size distribution on TiN at different deposition stages (a) growth, (b) secondary nucleation, and (c) ripening.

Figure 4.15: Change of Pd particle density with time.

Nucleation

Case 3: Growth (Balanced Nucleation and Ripening)

Case 1: Secondary Nucleation (Nucleation Dominated)

Case 2: Ripening (Ripening-Dominated)

Figure 4.16: Changes of Pd Particles during Simultaneous Nucleation, Growth and Ripening

By adopting the concept of the Thomson-Freundlich equation which relates the solubility to particle size (*section 2.3.3*), we are introducing here a factor called the “Ripening Tendency” to estimate the probability of ripening during the stage of concurrent nucleation and ripening. When there are more than two particles in a system, the computation of the concentration difference becomes more difficult. The rate of growth or solution of a particle is mainly influenced by its nearest neighbors, and the overall growth rate of the system is consequently dependent on the distribution of particle sizes throughout the volume [72]. We make use of the statistical measure for a particle size distribution and the average interparticle distance and define the Ripening Tendency, R_T as the ratio of standard deviation of the particle size distribution and average interparticle distance:

$$R_T = \frac{\text{standard deviation}}{\text{average interparticle distance}} = \frac{s}{d} \quad \text{-----} \quad (4.2)$$

From the experimental analysis, we observed a secondary nucleation stage whereby the nucleation rate increases significantly after a certain nucleation barrier has been overcome. We believe that the crossing of this boundary is triggered by a unique chemical event specific to the surface electrochemistry of this material system. Secondary nucleation creates more particles and increases the particle density, thus decreasing the inter-particle distance. Due to the shorter inter-particle distance, the surface tension differences between particles are higher. This in turn increases the ripening tendency. Once the ripening tendency is greater than a threshold value, ripening will dominate over nucleation. The ripening tendency of the Pd deposition process is shown in Figure 4.17.

Figure 4.17: Ripening Tendency, R_T during a simultaneous nucleation, growth and ripening deposition.

In Figure 4.17, we observe that ripening tendency drops when the deposition time is at 5 minutes. To further quantify this simultaneous nucleation, growth, and ripening deposition process, the ripening tendency was analyzed with prolonged Pd deposition time. Figure 4.18 shows the change of ripening tendency with particle deposition time. At short deposition time (less than 3 minutes), a slow increase in the ripening tendency was observed. The ripening tendency was low, which means that nucleation dominates the deposition process.

Figure 4.18: Ripening tendency with longer Pd deposition time.

The ripening tendency was also found to exhibit significant fluctuation during 3.5 to 7 minutes of deposition time. We hypothesized that within this window of concurrent nucleation, growth, and ripening, secondary nucleation and ripening are competing with each other. In agreement with the observation in Figure 4.17, the secondary nucleation decreases the inter-particle distance and causes the ripening domination over nucleation. On the other hand, the ripening process diminishes the small secondary particles. When the secondary particles are shrunk to sub-critical dimensions, they vanish from the pool, causing a discontinuous increase in the inter-particle distance. This will cause an abrupt drop in the ripening tendency, and a renewed dominance of nucleation over ripening. When the nucleation process again introduces secondary particles in the system, the change of inter-particle distance decreases and the ripening dominates over nucleation. This results in the high fluctuation of ripening tendency and the self-regulating cycle of the secondary nucleation and ripening process.

A steady increase in ripening tendency after 7 minutes denotes a persistent dominance of ripening over nucleation. At this stage, the surviving particles were getting bigger and more numerous. Size differences between new secondary particles and surviving particles are larger and the concentration gradients are greater. The ripening tendency is higher and newly arrived particles get absorbed by the surviving particles immediately, making this almost indistinguishable from growth. Furthermore, the sizes of surviving particles are large enough such that ripening no longer causes extinction so easily. The change of inter-particle distance is no longer discrete. This ends the self-regulating cycle of the secondary nucleation and ripening process. With the continuous change of the average inter-particle distance, the ripening tendency stops fluctuating and increases monotonically with time. The ripening tendency is now primarily affected by the standard deviation of particle size distribution rather than inter-particle spacing.

4.5. Summary

During the contact-displacement deposition of Pd on TiN surface, nucleation, growth, and ripening occur simultaneously. Three stages of deposition can be distinguished through the Pd particle size distribution range and semi-interquartile range. The three stages are named according to the more dominant phenomenon as growth, secondary nucleation, and ripening. Secondary nucleation increases the total number of particles in the system while ripening reduces it. In addition to that, we also demonstrate the existence of a nucleation barrier, the removal of which serves as a trigger point for secondary nucleation. This trigger event determines the relative dominance of nucleation or ripening during this concurrent phenomena deposition process.

We have identified a cyclical ripening tendency fluctuation during Pd deposition through this contact-displacement method. The phenomenon is triggered by a unique chemical event specific to the surface electrochemistry of this material system which results in a substantial increase in the nucleation rate. The self-regulating cycle of nucleation and ripening process arises after the nucleation rate reaches a maximum. The discreteness in the change of average inter-particle distance is due to the extinction of small particles by ripening. The ripening tendency fluctuates due to the discrete change of average inter-particle distance. When the ripening rate becomes higher, the newly deposited particles are absorbed by the surviving particles immediately. The average inter-particle distance changes continuously and the particle density no longer fluctuates. A change of standard deviation of the particle size distribution also plays a greater part in determining the ripening tendency.

CHAPTER 5 Chemical Transitions in Contact-

Displacement Palladium Deposition

The Pd deposition process through the contact displacement method has been used to pretreat TiN surface prior to electroless Cu deposition [28, 50, 54]. Pd particles deposited on TiN surfaces is a key element affecting the properties of deposited Cu thin film. The density and size of the Pd particles were found to affect the resistivity of the Cu film [97]. In *Chapter 6*, we will show that high Pd particle densities with small sizes not only produce lower resistivity but also a better via filling capability electroless Cu film [98]. Changing the chemistry, solution concentration and deposition time can modify Pd particle densities and sizes.

In *Chapter 4*, we demonstrated the existence of nucleation barrier on the trigger point of secondary nucleation and dominance of nucleation or ripening during this concurrent phenomena deposition process. We believe that the crossing of this boundary is triggered by a unique chemical event specific to the surface electrochemistry of this material system. Therefore, XPS analysis of TiN surface chemical states during different stages of deposition was carried out to understand the chemical transitions within the Pd deposition process. The confirmation of the surface chemical analysis will be shown in *section 5.2* through Ti oxide removal experiments.

5.1. Chemical State Analysis

TiN has a high affinity for oxygen, the reaction of TiN with oxygen is thermodynamically favorable ($\Delta G = -139$ kcal/mol) [99, 100], and forms oxide readily upon exposure to the air [29]. The immediate regrowth of oxide not only causes poor adhesion to the deposited Cu, it also affects the deposition behavior of Pd through the contact-displacement process. A two-step Ti oxide removal and Pd activation process was first used by Patterson et al [28]. A Pd/HF solution, which removes oxide on the TiN while depositing Pd particle was then, proposed [29]. There are several studies showing the mechanisms of the displacement reactions between Pd ions and TiN layer [29, 101]. In general, the contact displacement method was achieved through oxidizing TiN to TiF_6^{2-} while released electrons reduced the Pd^{2+} to a metallic Pd on the substrate [29, 101].

Contact-displacement deposition is a process involving redox reaction [29, 50, 101]. Wu et al [101] proposed the chemical reaction for the contact displacement Pd deposition as follows:

From the chemical reaction, we expected the change of Ti 2p and O 1s spectrum because of the change in the oxidation states of titanium. Figure 5.1 shows the Ti 2p XPS spectra of TiN surface after cleaning and before Pd deposition. The peaks at Ti 2p at binding energies of 463 ($2p_{1/2}$) and 456.9 eV ($2p_{3/2}$) come from TiN. Peak positions at 464.5 ($2p_{1/2}$) and 458.8 eV ($2p_{3/2}$) indicate - multilayer TiO_2 where the Ti atoms are connected via Ti-O-Ti linkages [102]. For TiO_x , the Ti $2p_{1/2}$ and $2p_{3/2}$ is at 461.5 and 455.4 eV respectively.

Figure 5.1: Ti 2p XPS spectra of TiN surface after cleaning and before Pd deposition. TiN, TiO_2 and TiO_x were identified.

In Figure 5.2, we compare the shift of Ti 2p binding energy peaks of two samples, one representing the growth stage (1 minute activation) and the other representing the ripening stage (3.5 minute activation) with the sample before Pd deposition. The Ti-N peak is found to remain at 456.9 eV and 463 eV, indicating no change in the TiN composition during Pd deposition. The reduction of Ti-O at 458.8 and 464.5 eV suggests the effective Ti oxide removal of the multilayer Ti oxide (Figure 5.2 (b) and (c)). The peak at 458 eV is found to be first layer Ti oxide where

Ti atoms bind to the substrate [102]. The Ti peak position at 456.4, 462.4 and 463.4 eV suggests formation of complex Ti compounds during the Pd activation process.

Figure 5.2: Comparison of Ti 2p binding energies shift during Pd deposition. (a) before Pd deposition. (b) 1 mins. Pd deposition representing growth stage, and (c) 3.5 mins. Pd deposition representing ripening stage.

The O 1s XPS spectrum for the TiN surface before Pd deposition is shown in Figure 5.3. A significant Ti-O signal (530.4 eV) at the TiN substrate before the activation process indicates the existence of Ti oxide. The other binding energy peak at 532.1 eV is associated with the SiO₂ layer underneath TiN. As the XPS technique is surface sensitive, the photons have penetrating power in a solid in the order of 1~10 μm [103]. The Si-O signal came from the silicon dioxide film underneath the TiN film.

Figure 5.3: O 1s XPS spectra of TiN surface after cleaning and before Pd deposition. Si-O and Ti-O were identified.

For a treated sample, reduction of the Ti-O signal for activated samples indicates the effective Ti oxide removal during the activation process (Figure 5.4). This result confirms the reduction of the Ti-O peak in Ti 2p spectra shown in Figure 5.2. At both activated samples, the BE peak at 532.5 eV corresponds to Si-O in SiO₂. 529.7 eV at 1 min represents the Pd-O bond. A shift of + 0.2 eV for the 3.5 min samples suggest the incorporation of an hydroxyl group on Pd oxide. The peak position at 531.8 eV is attributed to the presence of an hydroxyl group on the surface [104-106].

Figure 5.4: Comparison of O 1s binding energies shift during Pd deposition. (a) before Pd deposition. (b) 1 mins. Pd deposition representing growth stage, and (c) 3.5 mins. Pd deposition representing ripening stage.

The presence of an hydroxyl group indicates the surface is hydrophilic, which is favorable to film deposition [107]. In heterogeneous nucleation, the free energy needed for heterogeneous nucleation is equal to the product of homogeneous nucleation and a function of the contact angle:

$$\Delta G_{het}^* = \Delta G_{hom}^* \phi(\theta) \quad \text{-----} \quad (6.4)$$

where

$$\phi(\theta) = \frac{1}{4}(1 - \cos \theta)^2(\cos \theta) \text{ ----- (6.5)}$$

this is a function of the wetting angle and accounts for the catalytic potency of the substrate with respect to nucleus formation [63]. The graphic representation of $\phi(\theta)$ is shown in Figure 5.5. The wetting angle determines the ease of nucleation by reducing the energy needed. When the surface becomes hydrophilic with adsorption of hydroxyl groups, the wetting angle becomes smaller. As a result, the free energy needed for nucleus formation is lower.

Figure 5.5: Plot of the wetting function, $\phi(\theta)$ vs the wetting angle, θ . It varies from zero to unity when θ varies from 0 (complete wetting) to π (complete nonwetting).

The nucleation rate is dependent on the critical free energy needed for nucleus formation:

$$I = N \exp\left(\frac{-\Delta G^*}{k_B T}\right) \text{ ----- (6.6)}$$

ΔG^* is the critical free energy needed, N is the number of potential nucleation sites per unit volume, and k_B is the Boltzmann constant.

From equation (6.6), the nucleation rate is found to increase with the reduction of critical free energy required which is a result of contact angle reduction. This explains our finding of the abrupt increase in the nucleation rate at the secondary nucleation stage when a hydrophilic surface is formed. In the next section, we will show that the onset of secondary nucleation occurs at the point where total removal of Ti oxide occurs.

5.2. Ti Oxide Removal

The deposition of Pd in contact-displacement deposition showed a strong dependence on HF concentration. Nagahara *et al.* investigated the influence of HF concentration on the initial stages of Pd deposition on Si and found the rate of Pd deposition correspondingly increased as the HF concentration in the activation solution increased [108]. The composition of the activation solution was modified to achieve deposition on a Ta/TaN surface. Hsu *et al.* showed that the surface morphologies and distribution of Pd on a Ta layer were strongly dependent on the ratio of buffered oxide etch and nitric acid during deposition [27].

From the studies shown earlier, we hypothesize that the secondary nucleation phenomenon is triggered by the adsorption of an hydroxyl group and formation of hydrophilic surface, which results in a substantial decrease of contact angle and increase in the nucleation rate. Kim *et al.* verified that the hydrophilicity of TiN surface was improved by a Ti oxide cleaning process through contact angle measurement [54]. HF addition to the Pd activation solution is to promote the removal of Ti oxide during the Pd deposition process. Hence, a study with different concentrations of HF in the Pd activation solution was carried out to confirm this hypothesis.

Figure 5.6 shows the evolution of Pd particle density with different concentrations of HF in the activation solution. In general, higher Pd particle density is observed with more HF in the solution. This is expected because increasing the HF concentration, the in situ Ti oxide removal rate is increased. Hence, more nucleation sites are created for Pd deposition. At the same time, the magnitude of the Pd particle density fluctuation is found to increase with HF concentration. Previous studies have shown that Pd particle density and size are affected by the dominance of nucleation, growth, and ripening processes during deposition. The fluctuation of the Pd particle density is mainly due to the competition between nucleation and ripening processes. The sudden increase in the Pd particle density denotes the beginning of secondary nucleation. We can observe that as HF concentration is higher, the secondary nucleation stage begins earlier because of a higher Ti oxide removal rate. This confirms our claim shown earlier that secondary nucleation starts when Ti oxide on a TiN surface is totally removed.

Figure 5.6: Pd particle density change with time and HF concentration. Higher HF content results in higher Pd particle density. The magnitude of particle density fluctuation is higher for solution with more HF.

Changing the concentration of HF does not make a significant change in the average Pd particle size. In Figure 5.7, the average Pd particle sizes are similar for samples deposited with low to moderate HF concentration. Additionally, it increases steadily with time. This shows that the growth rate of Pd particles is not affected by the HF concentration. However, this is not the case when HF concentration is high. The reduction in the average Pd particles could be due to the high nucleation rate with the presence of high HF concentration. The presence of a large amount of new particles will bring down the average particle size. Furthermore, HF does not only remove the Ti oxide, it also removes the TiN substrate. When the TiN is attacked by HF, a fresh layer of TiN is exposed and more nucleation sites are then created. Because of this, it is also possible that the HF removes the TiN underneath the deposited Pd particles and results in the removal of Pd from the TiN surface. This explains the small average Pd particles size when the HF concentration is high.

Figure 5.7: Average Pd particle size with different HF concentration in activation solution. The average Pd particle size for samples deposited with high HF concentration is different from that in medium and low concentration indicating excessive HF removal of Ti oxide and TiN.

The ripening tendency for the samples were calculated with Equation 4.4. In Figure 5.8, fluctuations of ripening tendency were observed for samples deposited with different HF concentrations. The ripening tendency for samples deposited with high HF content is much higher due to the high nucleation rate and shorter inter-particle distance caused by excessive Ti oxide and TiN removal. It is observed in Figure 5.6 that the Pd nuclei density is more than two-fold that for medium HF content compared with low HF content. In contrast to that, the ripening tendencies for the two sets of samples are comparable. But when the deposition time gets longer, the ripening tendency for samples deposited in low HF content solution is higher. When the nucleation rate is high, there is a sizeable difference between new secondary nuclei and surviving particles, which in turn results in a greater concentration gradient. Hence the ripening tendency increases accordingly.

Figure 5.8: Ripening tendency comparison for samples deposited in Pd activation solution with different HF concentrations.

5.3. Summary

XPS study on substrate surface before and after an activation process shows effective Ti oxide removal during Pd activation. Presence of an hydroxyl group on 3.5 min activated surface indicates the formation of a hydrophilic surface. Formation of the hydrophilic surface is found to promote the nucleation rate due to the improved wetting of substrate and reduction of contact angle. Total removal of Ti oxide causes the formation of an hydrophilic surface, which in turn results in a secondary nucleation stage. A study with different concentrations of HF in the Pd activation solution confirmed that secondary nucleation starts with total Ti oxide removal from the TiN surface. HF concentration in the activation solution affects the Ti oxide removal rate which in turn creates more Pd nucleation sites when the HF content is higher. At the same time, the magnitude of the Pd particle density fluctuation is found to increase with HF concentration. The fluctuation of the Pd particle density is mainly due to the competition between nucleation and ripening processes. As HF concentration is higher, the secondary nucleation stage begins earlier because of higher Ti oxide removal rate. The growth rate of Pd particles is not affected by the HF concentration. However, high HF concentration reduces average Pd particles by increasing the nucleation rate and probably removing the TiN underneath the deposited Pd particles which resulted in the removal of Pd from the TiN surface. The ripening tendency for samples deposited with high HF content is much higher due to the high nucleation rate and shorter inter-particle distance caused by excessive Ti oxide and TiN removal.

CHAPTER 6 Improving Electroless Cu Properties with Optimized Pd Activation

Cu has been widely used as an interconnect material for Ultra Large Scale Integration (ULSI) technology due to its low resistivity and high electromigration resistance [2, 3]. Cu metallization is implemented at a lower cost dual damascene architecture with the integration of physical vapor deposition (PVD) and electrochemical deposition (ECD) processes [4]. However, conventional PVD processes give limited bottom coverage and step coverage capabilities for deposition of the diffusion barrier and Cu seed layers in high aspect-ratio (AR) via holes and metal line trenches [5]. The problems in step coverage will cause Cu to pinch-off during ECD and voids will form inside the trench [109-111]. Webb et al combined thin PVD films with thin conformal electroless Cu films to form a composite seed layer of low overall thickness and good continuity [111]. Considering the requirements of further decreasing interconnect linewidth in ultra large scale integration (ULSI), size effect in the structures is one of the biggest challenges for technology node beyond 45 nm [112]. If the lateral dimensions of the Cu are scaled to values that are < 100 nm, the resistivity increases significantly. For a 50 nm narrow wire, the resistivity is roughly a factor of 2 higher than the bulk value [113]. For a Cu seed < 100 nm, the voltage drop across a 12" wafer will be too big, reaching the limit of the current two-step PVD Cu seed and ECP Cu bulk fill process. Surface and sidewall scattering further deteriorates the resistivity of Cu. In view of the current deficiencies of conventional physical vapor deposition (PVD) processes in step coverage, electroless Cu is a viable candidate for the next generation ULSI Cu seed process for via and trench fill [26, 112, 114, 115]. However, the conformal

nature of known electroless deposition processes limits its use as a process to completely fill IC features without void formation [111]. Several researchers have reported some improvements of electroless Cu fill capability through means of modifying the electroless bath chemistry and activation processes [116-118].

Since the importance of Cu seed roughness has been explained in *section 2.1.6.1*, the Pd particle effect on electroless Cu is focused on the film roughness. The effect of Pd particles density on electroless Cu roughness will be discussed here. Electroless Cu deposited on TiN surface with different Pd particle density shows large variations in roughness values. The variations in Pd particle size distribution, density and mean size affects the texture, grain size and roughness of electroless Cu deposited thereafter. Further investigation and confirmation of Pd particle effect on electroless Cu are illustrated in *section 6.1* and the filling capability of electroless Cu film in vias is demonstrated in *section 6.2*.

6.1. RMS Roughness

At the initial stage of the electroless Cu process, Pd particles serve as the anodic sites at which the reductant can be adsorbed and oxidized. The electrons released on oxidation travel through the Pd and allow Cu reduction and deposition. Due to the conducting nature of TiN, electrons also travel through it and Cu can also be deposited at areas around Pd [119, 120]. The resistivity of TiN is higher than Cu but lower than non-conducting materials. As a result, the Pd number density plays a part in determining the electroless Cu deposition behavior as well as the resultant electroless Cu film property. In this section, the effect of Pd particles density on

electroless Cu RMS roughness is shown. Figure 6.1 shows a more detailed investigation on the changes of Pd particles density and electroless Cu roughness with activation time. No electroless Cu was observed on the sample after activation for 1 minute. The roughness of the surface was the same as the roughness of TiN after activation. Thus, the RMS value of the surface with 1 minute of Pd activation was excluded in Figure 6.1. Electroless Cu film is smoothest when Pd nucleation reaches the stage when the ripening process begins.

Figure 6.1: The change of Pd particles density with time and roughness of the resulted Electroless Cu film

The electroless Cu roughness reaches a minimum at the starting point of the ripening stage. In comparison with the roughness at 2 minutes of activation time the electroless Cu film roughness dropped 44%. The reduction in roughness is found to be the formation of more textured films at 3.5 minutes activation time as shown in Figure 6.2 and Table 6.1. The correlation between the roughness and texture can be explained by the structure evolution during the deposition of polycrystalline films. If more Cu grains have (111) texture, more Cu atoms will be deposited with the same growth rate parallel to the surface. Thus, a smoother surface will be shown. Zhang *et al.* reported the same observation on an Al polycrystalline film deposition process [121].

Figure 6.2: XRD spectrum of electroless Cu film deposited with 2 mins. and 3.5 mins. Pd activation time

Table 6.1: XRD data of electroless Cu film texture ratio as a function of Pd activation time

	Powder specimen [122, 123]	2 mins. Activation	3.5 mins. Activation
Cu $_{111/200}$	2.86 x	4.08 x	4.91 x
Cu $_{111/220}$	5 x	5.92 x	6.72 x

At the ripening stage, electroless Cu deposition was fast, due to the high Pd uptake. It formed a film easily and thus a low roughness value resulted. But, Pd particles coarsened with prolonged activation time. The large Pd particles contributed to the rough electroless Cu film morphology after electroless Cu deposition. Figure 6.3 shows the tapping mode AFM height mode image of electroless Cu. The large islands indicate the location of Pd particles.

Figure 6.3: Tapping mode AFM height image of electroless Cu after 6 minutes of activation, big islands indicates the positions of big Pd particles

It is therefore concluded that the time for Pd activation should be carefully chosen such that a smooth electroless Cu can be achieved. According to the particles density, three stages of nucleation were identified during the nucleation process. They are growth stage, secondary nucleation stage, and ripening stage. The particles density and size affects nucleation of electroless Cu and roughness of electroless Cu film. Smoothest electroless Cu film can be achieved at the starting point of the ripening stage.

6.2. Via filling capability

It is important to note that the electroless Cu deposition process in our study is to deposit a seed layer for an electroplating process. The step coverage of this seed layer deposited inside the via hole has a significant effect on the via filling by electroplating. Hence, the electroless Cu via filling capability study shown in this section is used to assess the step coverage of electroless Cu on patterned structure. The better via filling capability denotes better step coverage and the more conformal the electroless Cu film deposition in the via holes the more suitable is the film as a seed for electroplating process.

The cross-section SEM micrographs on a patterned structure wafer in Figure 6.4 show the electroless Cu via filling capability with different Pd activation time. Vias with a width of 300 nm and aspect ratio of 1:4 were used for this study. To study the effect of Pd activation time on the conformality of electroless Cu via fill, the electroless Cu deposition condition was fixed. We observed from the

micrographs that the electroless Cu fill was not very conformal and voids were found in the via holes. This could be because the electroless Cu bath used in this study was a homemade solution which did not contain additives that could improve via filling capability. However, the via filling capability could be correlated to our electroless Cu roughness study with different Pd activation time in *section 6.1*.

In *section 6.1*, we achieved optimized smoothness electroless Cu film at 3.5 mins. Pd activation time, in which secondary nucleation occurred and reached the ripening stage. When Pd activation is longer, Pd particles are large, hence the electroless Cu roughness increases. We also pointed out that the filling capability would be better with a smoother electroless Cu film. From Figure 6.4, we confirmed the effect of electroless Cu smoothness on the via filling capability. At the optimized smoothness electroless Cu film point (Figure 6.4 (e)), the voids inside the vias were smallest compared with other Pd activation times. With 1 ~ 3 mins. Pd activation time, long and narrow voids were found, showing a degraded fill capability. At 4 ~5 mins. Pd activation time, the electroless Cu film deposited in the via was very rough and large voids were found. Also, large Pd particles were observed. This confirms again the need for smaller and more Pd particles to achieve a more conformal electroless Cu deposition. Figure 6.5 shows the via filling capability of electroless Cu with each corresponding step as presented in *section 6.1*.

Figure 6.4: Cross-section SEM micrographs of patterned structure wafer showing electroless Cu filling capability with different Pd activation times, (a) 1 min, (b) 2 mins, (c) 2.5 mins, (d) 3 mins, (e) 3.5 mins, (f) 4 mins, and (g) 5 mins.

Figure 6.5: Via filling capability of electroless Cu at different Pd activation time. Pd particle density change with activation time. The resultant electroless Cu is found to be the smoothest and has the most conformal fill at 3.5 mins. Pd activation.

6.3. Summary

We have investigated the effect of Pd activation of TiN/SiO₂/Si on the electroless Cu surface roughness and fill capability. From the study of change in Pd particles size and density with activation time, the activation process could be classified into growth, secondary nucleation, and ripening stages. The smoothest electroless Cu film could be obtained with a Pd particles distribution that corresponds to the start of the ripening stage. The smoother electroless Cu film is attributed to the higher textured film deposited at this stage. This Pd nucleation

condition also yielded the most conformal electroless Cu via fill. This study suggests that further improvement in electroless Cu via fill may be possible with activation processes that yield higher density and smaller activation sites.

CHAPTER 7 Refinement of Pd Particles with A Novel Palladium Deposition Process

As shown in *Chapter 6*, high Pd particles density and small Pd particles were found to reduce the roughness of electroless Cu film as well as improving the step coverage of the film in the via holes. In *Chapter 5*, we identified that hydrophilic surface formation is the chemical event that triggers the increase of Pd nucleation rate in the secondary nucleation stage. We introduce here a novel method of surface activation that involves a hydrophilicity promoter that transforms the sample surface to a hydrophilic surface in order to achieve smaller and higher number density of Pd catalyst particles. This chapter outlines the impact of this novel activation process on Pd particles size and density. Through chemical state analysis, we confirm our hypothesis shown in *Chapter 5* that steps which encourage hydrophilic surface formation will increase the Pd particle density and in turn reduce the average Pd particle size. The impacts of the refined Pd particles on electroless Cu film properties are also presented here.

7.1 Experimental Details

In our novel Pd activation process, namely, double activation process, we used Pd etchant [124] as a chemical etchant to modify the TiN surface. The composition of the Pd etchant is shown in Table 7.1. The advantage of this Pd etchant is that it contains acetic acid, which is known as a hydrophilicity promoter [54] while the nitric acid and hydrochloric acid are able to remove the Pd deposited on the surface. This etchant also promotes the removal of native Ti oxide on the surface. Surface oxide formed in strong oxidant like nitric acid consists of hydroxyl groups that is weak acidic in nature [125]. Hence, the presence of strong acids in the etchant itself as well as in the activation solution should not affect the effectiveness of the hydrophilic surface formation by acetic acid.

Table 7.1: Composition of Pd Etchant

HCl	32 ml/L
HNO ₃	320 ml/L
CH ₃ COOH	320 ml/L

The steps for the double activation of the specimen surface are very similar to the single activation process described in *Chapter 3* with an additional Pd etching step followed by a second activation step. The steps for the double activation process and comparison with single activation are shown in Figure 7.1.

Figure 7.1: Steps of double activation process and comparison with single activation.

7.2 Pd Particle Density and Size

The comparison of Pd particles density and average size deposited by four activation steps is shown in Figure 7.2 and 7.3 to illustrate the significance of each step on the Pd deposition process. The details of the steps are shown in Table 7.2.

Table 7.2: Composition of Pd Deposition Steps

	Pre-Cleaning	1 mins. Pd Activation	30 s Etch	3.5 mins. Pd Activation
1	√			√
2	√	√		√
3	√		√	√
4	√	√	√	√

The increase in Pd particle density for samples which underwent etch processes compared to non-etch processes is more than 14 fold, as shown in Figure 7.2 (a). There is a 3 to 6 times reduction of average particles size observed for etch processes (Figure 7.2 (b)). This shows that the etch step with hydrophilic promoter (acetic acid) can effectively increase the nucleation rate of Pd particles on TiN surface. Comparing samples 3 and 4 that both underwent an etch step, there is a further increase of Pd particles density of 36% when the first activation step was introduced before an etch. The average particle size is also halved for sample 4. However, there is no particle density increase for sample 2 when the 2 steps of activation was carried out back-to-back without an etch step in between. The Pd particles for sample 2 are found to be bigger than sample 1. This shows that a two-step activation process will only be effective to increase the number of Pd particles on the surface and refine the Pd particles when there is an etch step included between

the two activation steps. It can be concluded that etching of TiN with a chemical containing a hydrophilicity promoter plays a crucial role in increasing the Pd particle density and the refinement of Pd particles. The first activation step is found to further increase the Pd particle density as well as reduce the average particle size.

Figure 7.2: Pd (a) particles density and (b) average particle size for the four samples prepared according to the condition shown in Table 7.2.

Figure 7.3 shows the transition of XPS O 1s spectra of TiN surface before the second activation steps during the double activation process. In Figure 7.3 (a), the Ti-O signal indicates that the Ti oxide has not been removed after the pre-cleaning step. BE peak at 532.5 eV corresponds to Si-O and it is found in Figure 7.3 (b) and (c) representing the SiO_2 underneath the TiN. After 1 minute of Pd deposition, the Pd-O bond at 529.7 eV represents the existence of Pd particles. No hydroxyl group formation was found on the surface after pre-cleaning and 1 minute activation. If the formation of hydroxyl group on the surface is the key for higher nucleation rate, the low Pd particle density at sample 1 and 2 is due to the absence of hydroxyl groups.

Figure 7.3: XPS O 1s spectra of TiN surface during double activation process: (a) RCA Cleaning, (b) 1 min 1st Pd activation, and (c) 1 min 1st Pd activation + 30 s Pd etch.

Interestingly, Pd-O bond is still observed after the etch step (Figure 7.3 (b)). This indicates that Pd particles are not totally removed during the etch step. We confirm the presence of Pd on the surface even after the etch step with a SIMS study presented in Figure 7.5 (b). The presence of an hydroxyl group with peak position at 531.8 eV is found on the etched surface. With the observation of high Pd particles density after this step, we confirm our hypothesis that formation of hydroxyl groups

and creating a hydrophilic surface is the key to increase the nucleation rate for this contact-displacement deposition process.

FESEM micrographs in Figure 7.4 show how the Pd particles are distributed on a TiN surface during the double activation method. Figure 7.4 (a) is the sample after the first 1-minute Pd activation. The number of Pd particles is small. After a 30 s Pd etching step, the TiN surface appears to be free of Pd particles in Figure 7.4 (b).

Figure 7.4: FESEM micrographs of TiN surface (a) after 1 min of Pd activation and (b) after 1 min. Pd activation and 30 s Pd etch.

In order to confirm if all the Pd particles were etched away, SIMS depth profiling was carried out to investigate the change of Pd quantity on the TiN surface during the Pd activation process. Due to the low coverage of Pd on the TiN surface, oxygen flooding was used to enhance the intensity of the secondary ions. First of all, we need to check if there is any Pd on the TiN surface after the Pd etching step. From Figure 7.4 (b), we do not observe any Pd on the TiN with FESEM. However, we can clearly see the signal of Pd from Figure 7.5 (b), which means that small amounts of Pd still exist at a very small size scale, which is beyond the resolution limit of the FESEM. In comparing the Pd intensity count of the etched sample (Figure 7.5 (b)) with 1-minute single Pd activated sample (Figure 7.5 (a)), the Pd signal in the etched

sample is found to be weaker. This means that the Pd etch step reduced the Pd amount on TiN surface (could reduce the Pd particle size or Pd number) but did not totally remove it.

(a)

(b)

Figure 7.5: SIMS profile of Pd activated surface with different treatment methods, (a) 1 min. single Pd activation, (b) 1 min. Pd activation and 30 s Pd etchant etched.

By comparing the FESEM micrographs of Pd particles deposited on the TiN surface by single and double activation methods in Figure 7.6 (a) and (b), more and smaller Pd particles are deposited with the double activation method. But, the substrate surface appears to have more etch pits for the double activation case. This is due to the strong Pd etchant used.

Figure 7.6: FESEM micrograph of Pd particles on TiN surface by (a) 3.5 min. Single Activation and (b) 3.5 min. Double Activation.

In Figure 7.7 (a) and (b), the SIMS profile of single and double 1 min. Pd activated samples are compared. The Pd signals were at a similar intensity count. However, from this SIMS depth profile, we observed that the thickness of TiN was reduced for the double activated sample. This shows that during the etching of Pd, Pd etchant not only etches Pd, it also etches the TiN film.

(a)

(b)

Figure 7.7: SIMS profile of Pd activated surface with different treatment methods, (a) 1 min. single Pd activation, and (b) 1 min. double Pd activation (1 min. Pd activation + 30 s Pd etchant etched + 1 min. Pd activation).

Figure 7.8 shows the evolution of Pd particle size distribution by double activation method. From 1-minute to 3.5-minutes of second activation time, only partial normal distribution is apparent in the size distribution curves. As activation time gets longer, the full curve of a normal distribution shows up. This is due to the limitation of the resolution of FESEM shown in the schematics in Figure 7.8.

From the Pd size distribution curves in Figure 7.8, the Pd size distribution peaks increase slowly from 1-minute to 3-minutes of second activation time. After 3 minutes, the Pd size distribution collapses and the peak slowly shifts towards a larger size range. This evolution of the size distribution is similar to that of the single activation case reported in Figure 4.10. This indicates that deposition of Pd on the TiN surface is always a concurrent nucleation, growth, and ripening process.

Figure 7.8: Pd particle size distributions on TiN deposited by double activation method. Double activation time ranges from 1 min to 5 mins.

Figure 7.9: Schematics showing the reason that only a portion of the normal size distribution curve can be seen at shorter activation time.

Figure 7.10 compares the Pd size distribution deposited with single and double activation methods at 3-minutes activation time. Although only part of the size distribution curve of the double activation case is shown, the number of Pd particles deposited using this method is much more compared to those of the single activation method. Furthermore, the size of the Pd particles is much smaller than that of the single activation method.

Figure 7.10: Pd particle size distribution on TiN comparison by single and double activation methods.

Figure 7.11 compares the Pd particle density deposited on a TiN surface by the single and double activation methods respectively. The reduction in particle density in the single activation process after 3 minutes is due to ripening. In contrast, the double activation process shows a continuing increase in particle density, indicating that secondary nucleation events overshadow ripening processes. This implies that the Pd etching process in the double activation method largely increases the nucleation sites for Pd. The increase in the nucleation rate may be attributed to the earlier removal of Ti oxide and formation of hydrophilic surface with the extra first activation and etching step. Hence, Pd number density of double activated sample is much more compared to that of the single activated sample.

Figure 7.11: Comparison of Pd particles density on TiN surface deposited by single and double activation methods.

The comparison of average Pd particle size deposited by the two methods is shown in Figure 7.12. The average particle size in the double activation case is 5 times smaller compared to single activation process, which can be attributed to the continuing increase in its particle density shown in Figure 7.8. This shows that the double activation process is effective in refining the Pd particle size.

Figure 7.12: Comparison of Average Pd particle size deposited by single and double activation methods.

Since the Pd etch step does not totally remove Pd, one might assume that the amount of Pd will be higher for a double activated sample. However, it is shown in Figure 7.13 (a) and (b) that, the intensity count of Pd on a 3.5-minutes double activated sample were lower than that of the case for single activated sample. We can then conclude that double activation process refines and increases the number of Pd particles, but does not increase the amount of Pd deposited on the TiN surface. This is beneficial for Pd to act as the activator for the electroless Cu process. A smaller and higher density of Pd particles on the surface is preferred for a better electroless Cu deposition process. In order to not increase the resistivity of resultant electroless

Cu, the amount of higher resistivity Pd should not be increased. Although researchers have shown that the Pd presence beneath electroless Cu film does not adversely affect the resistivity of electroless Cu, due to low Pd coverage on the surface, the preference is to keep the Pd coverage on TiN surface to a minimum.

(a)

(b)

Figure 7.13: SIMS profile of Pd activated surface with different treatment methods, (a) 3.5 mins single Pd activation, and (b) 3.5 mins double Pd activation (1 min. Pd activation + 30 s Pd etchant etched + 3.5 mins. Pd activation).

7.1 Double Pd Activation Effect on Electroless Cu Properties

7.4.1 Deposition Rate

The cross-sectional TEM micrographs in Figure 7.14 compare the electroless Cu film deposited on TiN for 5-minutes with 3.5-minutes single and double activation method respectively. From the TEM micrographs, the electroless Cu film deposited by the double activation method was thicker. The electroless Cu film with single activation was 76.67 nm, and that with double activation was 91.83 nm. This translates into 15.33 nm/min and 18.37 nm/min for the single and the double activation methods respectively. A 20% increase in the deposition rate is achieved with double activation method. From SIMS analysis, there was little difference in the Pd concentration on the TiN surface for both single and double activations. This means that the electroless Cu deposition rate is determined not only by the Pd amount deposited but is also determined by the Pd number density. For electroless Cu deposition, Pd acts as an electron carrier that supports the transfer of electrons from the reducing agent to the metal ions. With more Pd particles as nucleation sites for electroless Cu deposition reaction, there will be earlier formation of a continuous electroless Cu film. Once a layer of Cu is formed, growth will be spontaneous as Cu itself is autocatalytic to further electroless Cu growth. This explains the reason for a higher deposition rate for the double activation case when the Pd particles density is higher.

Figure 7.14: Cross-section TEM micrographs of electroless Cu deposited on TiN with (a) 3.5 mins. single activation (b) 3.5 mins. double activation

7.4.2 Electroless Cu Grain Size and Resistivity

XRD spectra were used to calculate the electroless Cu grain size using Scherrer's equation as mentioned in *section 3.3.3*. Figure 7.15 shows the XRD spectra of electroless Cu film deposited on TiN with 3.5-minutes single and double Pd activation methods. From the XRD spectra, we observe that Cu (111) is the preferred orientation in electroless Cu film deposition. As shown in Table 7.3, electroless Cu film deposited with the single activation method, the Cu (111)/(200) and (111)/(220) ratio were 4.17 and 8.33. For double activation case, the Cu (111)/(200) ratio and (111)/(220) ratio were 4.73 and 10.10, respectively. This shows that electroless Cu deposited by double activation is more textured than that by single activation .

(a)

(b)

Figure 7.15: XRD spectra of electroless Cu film deposited on TiN surface with (a) 3.5 mins. single activation method and (b) 3.5 mins. double activation method.

Table 7.3: XRD data of electroless Cu film texture ratio comparison for single and double activation

	Powder specimen [122, 123]	Single Activation	Double Activation
Cu _{111/200}	2.86 x	4.17 x	4.73 x
Cu _{111/220}	5 x	8.33 x	10.10 x

In our study, we confirm that electroless Cu grain size is affected by the catalytic Pd number density and particle size. A comparison of average electroless Cu grain size deposited with single and double activation grain is shown in Figure 7.16. In general, double Pd activation produces larger electroless Cu grains. Plan view FESEM micrographs of electroless Cu film are shown in Figure 7.17. The grain size shown in this figure is in agreement with the EL grain size data calculated by XRD. The grain size of electroless Cu deposited with a single activation method is smaller than that with the double activation method.

Figure 7.16: Comparison of average electroless Cu grain size deposited with 3.5 mins. Single Pd Activation and 3.5 mins. Double Pd Activation.

(a)

(b)

Figure 7.17: Plan view FESEM micrographs of electroless Cu deposited on TiN with (a) 3.5 mins. Single Pd Activation and (b) 3.5 mins. Double Pd Activation.

Chang *et al.* reported that initial deposition of electroless Cu on displacement-activation Pd catalyst is found to grow by surrounding the catalytic Pd rather than on any other places of substrates without catalysis [126]. Electroless Cu nuclei were found to randomly distribute on the surface of catalyst particles before they connected to form a continuous film [127]. For a double activation method, the increase in the Pd anodic sites enables faster formation of a continuous electroless Cu film on TiN, and in turn will lead to a higher electroless Cu deposition rate as reported in the previous section. It is also noted that higher nuclei density will lead to a faster onset of grain growth [128], and will result in a larger grain size. The increase in the electroless Cu grain size with the increase in deposition rate was also reported by Tseng *et al* [129].

The resistivity of electroless Cu film with double activation method is lower than that of the one deposited with single activation method. The resistivity is a complex property that depends very strongly on the combination of the surface scattering, grain boundary scattering, roughness, defects and impurities as a

consequence of the film's growth conditions. Zhang *et al.* and Camacho *et al.* have shown that the grain boundary is the most dominant contribution to the higher resistivity values for Cu films with a thickness less than 100 nm range [130, 131]. The lower resistivity achieved by the double activation is attributed to the larger electroless Cu grains observed in Figure 7.18.

Figure 7.18: Comparison of average electroless Cu resistivity deposited with 3.5 mins. Single Pd Activation and 3.5 mins. Double Pd Activation.

7.5 Summary

A new activation method was proposed to meet the need for smaller and more Pd catalytic particles on a TiN surface. We have used a double activation method to refine the catalytic Pd nuclei commonly used as an activation layer for electroless Cu deposition. The method produces Pd nuclei with a size reduction by a factor of 3 and density increase of more than 14 times. The formation of hydroxyl groups and creating a hydrophilic surface is the key to increase the nucleation rate for this contact-displacement deposition process. It can be concluded that etching of TiN with a chemical containing a hydrophilic promoter (acetic acid) plays a crucial role

in increasing the Pd particle density and refinement of Pd particles. A two-step activation process will only be effective to increase the number of Pd particles on the surface and refine the Pd particles when there is an etch step included between the two activation steps. The first activation step is found to further enhance the Pd refinement as it has not totally been removed in the etch step. With more nucleation sites, nucleation events outrun ripening events throughout the deposition time range. SIMS data show that the double activation step does not increase the net amount of Pd deposited on the TiN surface; it merely changes its nuclei size and density. This is beneficial for Pd as the activator for an electroless Cu process to prevent any adverse effect on the resistivity of electroless Cu. For a double activation method, the increase in the Pd anodic sites enables faster formation of a continuous electroless Cu film on TiN, and in turn leads to a higher electroless Cu deposition rate and faster onset of grain growth. Lower resistivity achieved by double activation is attributed to the bigger electroless Cu grains.

CHAPTER 8 Conclusion and Recommendations

8.1 Conclusion

The size effect in structures is one of the biggest challenges for technology nodes beyond 45 nm, including the requirements of further decreasing interconnect line widths in ultra large scale integration (ULSI). Cu resistivity increases significantly if the lateral dimensions of the Cu are scaled to values that are < 100 nm. Surface and sidewall scattering further deteriorates the resistivity of Cu. Electroless Cu is a viable candidate for a next generation ULSI Cu seed process for via and trench fill.

During the contact-displacement deposition of Pd on a TiN surface, nucleation, growth, and ripening occur simultaneously. Three stages of deposition can be distinguished through the Pd particle size distribution range and semi-interquartile range. The three stages are named according to the more dominant phenomenon as growth, secondary nucleation, and ripening. Secondary nucleation increases the total number of particles in the system while ripening reduces it. In addition to that, we also demonstrated the existence of a nucleation barrier which serves as the trigger point of secondary nucleation.

A factor called “Ripening Tendency” defined as the ratio of particle size standard deviation to the average inter-particle distance has been identified to analyze the relative dominance of nucleation or ripening process during a concurrent nucleation, growth and ripening deposition. Tracking the behavior of this ripening tendency, it can be shown that secondary nucleation will trigger a transient

oscillation of particle density because of the competition between nucleation and ripening. Secondary nucleation decreases the inter-particle distance and causes ripening to temporarily dominate over nucleation. At the early stage when particle sizes are small, ripening can cause a discontinuous change of average inter-particle distance as small particles are consumed and removed from the population. This results in an abrupt drop in the ripening tendency and brings about the next cycle of nucleation dominance. The cyclic behavior stops when growth can ensure that even the smallest new particles will not become extinct during the ripening phase. The average inter-particle distance changes continuously and this ends the fluctuation of the ripening tendency. Henceafter, newly deposited particles get absorbed by the surviving particles immediately, thus effectively merging ripening with growth. At this stage, a change of standard deviation of the particle size distribution plays a greater part in determining the ripening tendency.

We have investigated the effect of Pd activation of TiN/SiO₂/Si on the electroless Cu surface roughness and via fill capability to assess its step coverage and conformality in the via holes. The smoothest electroless Cu film could be obtained with a Pd particle distribution that corresponds to the start of the ripening stage. The smoother electroless Cu film is attributed to the more highly textured film deposited at this stage. This Pd nucleation condition also yields the most conformal electroless Cu films.

Chemical state analysis on a substrate surface shows that formation of an hydrophilic surface with total removal of Ti oxide is the key for an abrupt increase of nucleation rate. Formation of an hydrophilic surface is found to promote the nucleation rate due to the improved wetting of the substrate and the reduction of

contact angle. A study with different concentration of HF in the Pd activation solution confirmed that secondary nucleation starts with total Ti oxide removal from the TiN surface. As HF concentration is higher, the secondary nucleation stage begins earlier because of higher Ti oxide removal rate. The ripening tendency for samples deposited with high HF content is found to be much higher than for low HF content due to the high nucleation rate and shorter inter-particle distance caused by excessive Ti oxide and TiN removal.

The formation of hydroxyl groups and creating a hydrophilic surface is the key to increase the nucleation rate for contact-displacement deposition process. A new activation method – double activation has been proposed by introducing a chemical step that involves an hydrophilicity promoter for smaller and more Pd catalytic particles on the TiN surface. This method produces Pd nuclei with a size reduction by a factor of 3 and density increase of more than 14 times. SIMS data show that this new activation method does not increase the net amount of Pd deposited on the TiN surface. This is beneficial for Pd as the activator for the electroless Cu process to prevent any adverse effect on the resistivity of electroless Cu. The increase in the Pd anodic sites enables faster formation of a continuous electroless Cu film on TiN, and in turn leads to a higher electroless Cu deposition rate and faster onset of grain growth. Lower resistivity achieved by double activation is attributed to the larger electroless Cu grains.

In conclusion, the thesis has studied the deposition mechanism of contact-displacement Pd and the role of catalytic Pd particles density, size, and size distributions on electroless Cu film properties and via filling capability. The method of forming an hydrophilic surface for higher catalytic Pd particles density and lower

average size provides valuable guidelines in electroless chemistry for relevant industries and research

8.2 Recommendations

This work has demonstrated the need for small and uniform Pd catalyst particles to achieve better quality electroless Cu film. The control of the Pd catalyst size and size distribution is through the manipulation of deposition chemistry. To enable the full potential of the results explored here, further research is needed in the following areas:

8.2.1 Catalytic particles deposition study on non-conductive substrates

Electroless deposition is applicable to a wide range of metal substrate combinations, including metal-on-metal, metal-on-semiconductor and metal-on-insulator. This is particularly important with regard to metal deposition on electronically isolated substrate regions, such as those on a circuit board. The catalytic Pd deposition process presented here was deposited on conducting substrates. Electrons can travel through the substrate and reduce the metallic ions further for the anodic sites. It is expected that the size and size distribution of catalytic Pd is more important on non-conductive substrate determining the properties of the resultant electroless metallic film. The novel activation process introduced here could be used as an option to improve the electroless metallic film properties.

8.2.2 Surface wetting study in double zincation methods and other activation methods

In double zincation, zincate forms on the Al surface and is removed with nitric acid [132, 133]. Later on, a second zincation step is performed. Smaller and higher density zincate is deposited [134]; as a result, a more uniform EL Ni is achieved [135]. However, the mechanism on how the double zincation helps to refine the size of zincate and increases its number density has not been fully explored. It would be interesting to explore the relationship of surface wetting with catalyst size and density. Other chemical methods can be developed from the understanding of surface modification through steps of deposition.

References

1. J. R. Lloyd and J. J. Clement, *Electromigration in copper conductors*. Thin Solid Films, 1995. 262(1-2): p. 135-141.
2. G. Ritter, P. McHugh, G. Wilson, and T. Ritzdorf, *Two- and three-dimensional numerical modeling of copper electroplating for advanced ULSI metallization*. Solid-State Electronics, 2000. 44(5): p. 797-807.
3. J. A. Cunningham, *Using electrochemistry to improve copper interconnects*. Semiconductor International, 2000. 23(5): p. 97-8, 100, 102.
4. K. Rose and R. Mangaser. *Copper interconnect technology-new paradigms for BEOL manufacturing*. in *IEEE/SEMI. 1998 IEEE/SEMI Advanced Semiconductor Manufacturing Conference and Workshop*. 1998. Boston, MA, USA: IEEE. p. 347-353.
5. R. L. Jackson, E. Broadbent, T. Cacouris, A. Harrus, M. Biberger, E. Patton, and T. Walsh, *Processing and integration of copper interconnects*. Solid State Technology, 1998. 41(3): p. 49-50, 54, 56, 59.
6. G. Deltoro and N. Sharif, *Copper interconnect: Migration or bust*. Twenty Fourth IEEE/CPMT International Electronics Manufacturing Technology Symposium, 1999: p. 185-188.
7. Y. Shacham-Diamand, *Electrochemically Deposited Thin Films II*, ed. M. Paunovic. Vol. 94-31. 1995.
8. D. Jeong, H. Inoue, Y. Ohno, K. Namba, and H. Shinriki. *Novel PEALD-Ru formation technique using H_2 & H_2/N_2 plasma as a seed layer for direct CVD-Cu filling*. in *Proceedings of the IEEE 2009 International Interconnect Technology Conference*. 2009. Hokkaido, Japan: IEEE. p. 95-97.
9. N. Kumar, K. Moraes, M. Narasimhan, and P. Gopalraja, *Advanced Metallization Needs Integrate Copper Into Memory*. Semiconductor International, 2009. 30(5): p. 26.
10. L. Carbonell, H. Volders, N. Heylen, K. Kellens, R. Caluwaerts, K. Devriendt, E. A. Sanchez, J. Wouters, V. Gravey, K. Shah, Q. Luo, A. Sundarrajan, J. Lu, J. Aubuchon, P. Ma, M. Narasimhan, A. Cockburn, Z.

- Tokei, and G. P. Beyer. *Metallization of sub-30 nm interconnects: comparison of different liner/seed combinations*. in *Proceedings of the IEEE 2009 International Interconnect Technology Conference*. 2009. Hokkaido, Japan: IEEE. p. 200-202.
11. B. Han, K.-M. Park, K. Park, J.-W. Park, and W.-J. Lee. *Atomic Layer Deposition of Copper Thin Film using $\text{Cu}^{II}(\text{diketoiminate})_2$ and H_2* . in *Proceedings of the IEEE 2009 International Interconnect Technology Conference*. 2009. Hokkaido, Japan: IEEE. p. 173-174.
12. A. Roulea, M. Amuntenceib, E. Deronziera, P. H. Haumessera, S. D. Silvac, X. Avalec, O. Polletc, R. Baskaranc, and G. Passemard, *Seed layer enhancement by electrochemical deposition: The copper seed solution for beyond 45 nm*. *Microelectronic Engineering*, 2007. 84(11): p. 2610-2614.
13. P.-L. Pai and C. H. Ting, *Selective electroless copper for VLSI Interconnection*. *IEEE Electron Device Letters*, 1989. 10(9): p. 423-425.
14. Y. Shacham-Diamand, V. Dubin, and M. Angyal, *EL Cu deposition for ULSI*. *Thin Solid Films*, 1995. 262(1-2): p. 93-103.
15. C. H. Ting, M. Paunovic, and G. Chiu. in *The Electrochemical Society Extended Abstracts*. 1987. Philadelphia.
16. W. L. Goh, K. T. Tan, M. S. Tse, and K. Y. Liu, *The effects of HF/PdCl_2 activation on EL Cu film properties*. *International Journal of Modern Physics B*, 2002. 16(1-2): p. 197-204.
17. B. Johnson, R. Amster, and L. Vanasupa, *Grain nucleation and texture analysis of electroless copper deposition on a palladium seed layer*. *Journal of Electronic Materials*, 1998. 27(7): p. 923-927.
18. V. M. Dubin, *Electroless Ni-P deposition on silicon with Pd activation*. *Journal of The Electrochemical Society*, 1992. 139(5): p. 1289-1294.
19. K. T. T. M.S. Tse, W.L. Goh, K.Y. Liu, *Activation methods for EL Cu deposition of seeding layer for ULSI Cu interconnect metallization*. *ECS International Semiconductor Technology Conference (ISTC)*, 2001.

20. S. W. Hong, C.-H. Shin, and J.-W. Park, *Palladium activation on TaN_x barrier films for autocatalytic electroless copper deposition*. Journal of The Electrochemical Society, 2002. 149(1): p. G85-8.
21. T. Hara. *Review of advanced Cu interconnect process - Deposition of Low Resistance and Low Stress Copper Interconnection Layer*. in *VMIC Conference*. 2002. Singapore.
22. P. Singer, *Progress in copper: a look ahead*. Semiconductor International, 2002. 25(5).
23. P.L. Pai, M. Paunovic, A. T. Wu, G.Chiu, D.Carl, J.Cho, S.Kuo, and C. H. Ting, *Selective EL deposition for via filling*. IEEE VMIC, 1988.
24. J. Shu, B. P. A. Grandjean, E. Ghali, and S. Kaliaguine, *Autocatalytic effects in electroless deposition of palladium*. Journal of The Electrochemical Society, 1993. 140(11): p. 3175-3180.
25. S. Nakahara and Y. Okinaka, *Microstructure and mechanical properties of electroless copper deposits [for PCB]*. Annual review of materials science, 1991. 21: p. 93-129.
26. V. M. Dubin, Y. Shacham-Diamand, B. Zhao, P. K. Vasudev, and C. H. Ting, *Selective and blanket electroless copper deposition for ultralarge scale integration*. Journal of the Electrochemical Society, 1997. 144(3): p. 898-908.
27. H.-H. Hsu, C.-C. Hsieh, M.-H. Chen, S.-J. Lin, and J.-W. Yeh, *Displacement activation of tantalum diffusion barrier layer for electroless copper deposition*. Journal of the Electrochemical Society, 2001. 148(9): p. C590-598.
28. J. C. Patterson, C. Ni Dheasuna, J. Barrett, T. R. Spalding, M. O'Reilly, X. Jiang, and G. M. Crean, *Electroless copper metallisation of titanium nitride*. Applied Surface Science, 1995. 91(1-4): p. 124.
29. J. P. O'Kelly, K. F. Mongey, Y. Gobil, J. Torres, P. V. Kelly, and G. M. Crean, *Room temperature electroless plating copper seed layer process for damascene interlevel metal structures*. Microelectronic Engineering, 2000. 50(1-4): p. 473-479.

30. Y.-M. Lin and S.-C. Yen, *Effects of additives and chelating agents on EL Cu plating*. Applied Surface Science, 2001. 178(1-4): p. 116-126.
31. I. Ohno, O. Wakabayashi, and S. Haruyama, *Anodic oxidation of reductants in EL plating*. Journal of the Electrochemical Society, 1985. 132(10): p. 2323-2330.
32. P. Bindra and J. Roldan, *Mechanism of EL metal plating II. Formaldehyde Oxidation*. Journal of the Electrochemical Society, 1985. 132(11): p. 2581-2589.
33. J. S. H. Cho, H.-K. Kang, S. S. Wong, and Y. Shacham-Diamand, *Electroless Cu for VLSI*. MRS Bulletin, 1993. 18(6): p. 31-38.
34. S. S. Wong, J. S. Cho, H. K. Kang, and C. H. Ting. *Electroless copper deposition for multilevel metallization*. in *Electronic Packaging Materials Science V. Symposium*. 1991. Boston, MA, USA: Mater. Res. Soc.
35. Y. Lantsov, R. Palmans, and K. Maex, *New plating bath for electroless copper deposition on sputtered barrier layers*. Microelectronic Engineering, 2000. 50(1-4): p. 441-447.
36. F. E. Stone, *Electroless Plating: Fundamentals and Applications*. American Electroplaters Society, ed. G.O. Mallory and J.B. Hajdu. 1990. p. 317.
37. S. Dhingra, R. Sharma, and P. J. George, *Selective deposition of a thin copper film for metallization on silicon by the chemical bath process*. Solid-State Electronics, 1999. 43(12): p. 2231-2234.
38. F. Pearlstein, *Electroless nickel deposition*. Metal Finishing, 1955. 53(8): p. 59-61.
39. J. Charles R. Shipley and M. Newton, *Method of Electroless Deposition on an Substrate and Catalyst Solution Therefor*. 1961, Shipley Company, Inc. Wellesley, Mass: US. Patent #3,011,920, Dec 6, 1961
40. A. M. T. van der Putten, J.-W. G. de Bakker, and L. G. J. Fokkink, *Electrochemistry of colloidal palladium. An experimental study of sol formation and electrocatalysis*. Journal of the Electrochemical Society, 1992. 139(12): p. 3475-3480.

41. R. L. Cohen and K. W. West, *Characterization of tin-palladium sols*. Chemical Physics Letters, 1972. 16(1): p. 128-130.
42. M. H. Kiang, J. Tao, W. Namgoong, C. Hu, M. Lieberman, N. W. Cheung, H.-K. Kang, and S. S. Wong. *Planarized copper interconnects by selective electroless plating*. in *Advanced Metallization and Processing for Semiconductor Devices and Circuits - II. Symposium*. 1992. San Francisco, CA, USA: Mater. Res. Soc.
43. M. Froment, E. Queau, J. R. Martin, and G. Stremsdoerfer, *Structural and analytical characteristics of adsorbed Pd-Sn colloids*. Journal of the Electrochemical Society, 1995. 142(10): p. 3373-3377.
44. T. Osaka, H. Nagasaka, and F. Goto, *An electron diffraction study on mixed PdCl₂/SnCl₂ catalysts for electroless plating*. Journal of the Electrochemical Society, 1980. 127(11): p. 2343-2346.
45. J. Horkans, *Cyclic Voltammetric Study of Pd-Sn Colloidal Catalysts for Electroless Deposition*. Journal of the Electrochemical Society, 1983. 130(2): p. 311-317.
46. E. E. Kalu, *Electrochemical measurement of the activity of printable catalysts used for electroless metallization*. Plating and Surface Finishing, 2000. 87(10): p. 62-67.
47. T. M. Tam and R. Taylor, *The effect of additives on the deposition and dissolution of copper in pyrophosphate solution*. Journal of the Electrochemical Society, 1985. 133(6): p. 1101-1106.
48. E. J. M. O'Sullivan, J. Horkans, J. R. White, and J. M. Roldan, *Characterization of PdSn Catalysts for Electroless Metal Deposition*. IBM Journal of Research and Development, 1988. 32(5): p. 591-602.
49. C.-L. Lee, C.-C. Wan, and Y.-Y. Wang, *Pd nanoparticles as a new activator for electroless copper deposition*. Journal of the Electrochemical Society, 2003. 150(3): p. C125-30.
50. J. C. Patterson, M. O'Reilly, G. M. Crean, and J. Barrett, *Selective electroless copper metallization on a titanium nitride barrier layer*. Microelectronic Engineering, 1997. 33(1-4): p. 65-73.

51. A. M. T. van der Putten and J.-W. G. de Bakker, *Anisotropic deposition of electroless nickel. Bevel plating*. Journal of the Electrochemical Society, 1993. 140(8): p. 2229-2235.
52. N. Feldstein, M. Schlesinger, N. E. Hedgecock, and S. L. Chow, *Electron microscope investigation of mixed stannous chloride/palladium chloride catalysts for plating dielectric substrates*. Journal of the Electrochemical Society, 1974. 121(6): p. 738-744.
53. S. Karmalkar and J. Banerjee, *A study of immersion processes of activating polished crystalline Si for autocatalytic EL deposition of Pd and other metals*. Journal of the Electrochemical Society, 1999. 146(2): p. 580-584.
54. J. J. Kim and S. H. Cha, *Optimized surface pre-treatments for Cu electroless plating in ULSI device interconnection*. Japan Journal of Applied Physics, 2001. 40(12): p. 7151-7155.
55. Y. Shacham-Diamand and S. Lopatin, *High aspect ratio quarter-micron electroless copper integrated technology*. Microelectronic Engineering, 1997. 37-38: p. 77-88.
56. R. L. Meek, *A Rutherford scattering study of catalyst systems for electroless Cu plating. II. SnCl₂ sensitization and PdCl₂ activation*. Journal of the Electrochemical Society, 1975. 122(11): p. 1478-1481.
57. J. H. Lin, Y. Y. Tsai, S. Y. Chiu, T. L. Lee, C. M. Tsai, P. H. Chen, C. C. Lin, M. S. Feng, C. S. Kou, and H. C. Shih, *Palladium seeding on the tantalum-insulated silicon oxide film by plasma immersion ion implantation for the growth of electroless copper*. Thin Solid Films, 2000. 377-378: p. 592-596.
58. C. Y. Mak, *Electroless copper deposition on metals and metal silicides*. MRS Bulletin, 1994. 19(8): p. 55-62.
59. D. J. Macauley, P. V. Kelly, K. F. Mongey, and G. M. Crean, *Atmospheric pressure excimer lamp-assisted photoselective activation process for electroless plating*. Applied Surface Science, 1999. 138(1-4): p. 622-626.
60. M.-H. Kiang, M. A. Lieberman, N. W. Cheung, and X. Y. Qian, *Pd/Si plasma immersion ion implantation for selective electroless copper plating on SiO₂*. Applied Physics Letters, 1992. 60(22): p. 2767-2769.

61. H. Esrom and U. Kogelschatz, *Modification of surfaces with new excimer UV sources*. Thin Solid Films, 1992. 218(1-2): p. 231-246.
62. G. J. Fisanick, J. B. Hopkins, M. E. Gross, M. D. Fennell, and K. J. Schnoes, *Laser-initiated microchemistry: dynamic probes of metallopolymer thin-film decomposition*. Applied Physics Letters, 1985. 46(12): p. 1184-1186.
63. I. V. Markov, *Crystal Growth for Beginners: Fundamentals of Nucleation, Crystal Growth and Epitaxy*: World Scientific Publishing Company (August 1995). 63-64.
64. Lorenz Ratke and P. W. Voorhees, *Growth and Coarsening: Ostwald Ripening in Materials Processing*. 1 ed. 2002: Springer. p. 250.
65. Lorenz Ratke and P. W. Voorhees, *Growth and Coarsening: Ostwald Ripening in Materials Processing*. 1 ed. 2002: Springer. p. 259-260.
66. D. Kashchiev, *Nucleation: Basic Theory with Applications*. 2000: Butterworth-Heinemann. p. 20.
67. D. Kashchiev, *Nucleation: Basic Theory with Applications*. 2000: Butterworth-Heinemann. p. 30-31.
68. Lorenz Ratke and P. W. Voorhees, *Growth and Coarsening: Ostwald Ripening in Materials Processing*. 1 ed. 2002: Springer. p. 99.
69. P. W. Voorhees, *Ostwald Ripening of Two-Phase Mixtures*. Annual Review of Materials Science, 1992. 22: p. 197-215.
70. N. D. Alikakos and G. Fusco, *The equations of Ostwald Ripening for dilute systems*. Journal of Statistical Physics, 1999. 95(5-6): p. 851-866.
71. P. W. Voorhees, *The theory of Ostwald Ripening*. Journal of Statistical Physics, 1985. 38(1-2): p. 232-252.
72. G. W. Greenwood, *Growth of dispersed precipitates in solutions*. Acta Metallurgica, 1956. 4(3): p. 243-248.
73. I. M. Lifshitz and V. V. Slyozov, *The kinetics of precipitation from super-saturated solid solutions*. Journal of the Physics and Chemistry of Solids, 1961. 19(1-2): p. 35-50.

74. M. J. Williamson, D. N. Dunn, R. Hull, S. Kodambaka, I. Petrov, and J. E. Greene, *Evolution of nanoscale texture in ultrathin TiN films*. Applied Physics Letters, 2001. 78(15): p. 2223-2225.
75. A. M. Gusak and K. N. Tu, *Kinetic theory of flux-driven ripening*. Physical Review B (Condensed Matter and Materials Physics), 2002. 66(11): p. 115403/1-14.
76. J. W. Bullard, *Numerical simulations of transient-stage Ostwald ripening and coalescence in two dimensions*. Materials Science & Engineering A (Structural Materials: Properties, Microstructure and Processing), 1997. 238(1): p. 129-139.
77. H. Fischmeister and G. Grimvall, *Sintering and Related Phenomena*, ed. G.C. Kuczynski. 1973, New York: Plenum. p. 119, 418-3.
78. B. J. McCoy, *Vapor nucleation and droplet growth: cluster distribution kinetics for open and closed systems*. Journal of Colloid and Interface Science, 2000. 228(1): p. 64-72.
79. R. W. Heckel and R. L. De Gregorio, *Growth and shrinkage rates of second-phase particles of various size distributions*. Metallurgical Society of American Institute of Mining, Metallurgical and Petroleum Engineers-Transactions, 1965. 233(11): p. 1994-2011.
80. A. J. Ardell, *The effect of volume fraction on particle coarsening: theoretical considerations*. Acta Metallurgica, 1972. 20(1): p. 61-71.
81. P. W. Voorhees and M. E. Glicksman, *Solution to the multi-particle diffusion problem with applications to Ostwald ripening. I. Theory*. Acta Metallurgica, 1984. 32(11): p. 2001-2011.
82. P. W. Voorhees and M. E. Glicksman, *Solution to the multi-particle diffusion problem with applications to Ostwald ripening. II. Computer simulations*. Acta Metallurgica, 1984. 32(11): p. 2013-2030.
83. J. A. Marqusee and J. Ross, *Theory of Ostwald ripening: competitive growth and its dependence on volume fraction*. Journal of Chemical Physics, 1992. 80(1): p. 536-543.

84. Z. Fang, B. R. Patterson, and M. E. Turner, *Influence of particle size distribution on coarsening*. Acta Metallurgica, 1992. 40(4): p. 713-722.
85. R. T. DeHoff, *A geometrically general theory of diffusion controlled coarsening*. Acta Metall. Mater., 1991. 39(10): p. 2349-2360.
86. M. J. DeSilva and Y. Shacham-Diamand, *Novel seed layer scheme to protect catalytic surfaces for electroless deposition*. Journal of The Electrochemical Society, 1996. 143(11): p. 3512-3516.
87. P. J. Goodhew, J. Humphreys, and B. Richard., *Electron Microscopy and Analysis*. 3rd ed. 2001, London: Taylor and Francis. p. 251.
88. Brücker, AXS GmbH: Karlsruhe, Germany. (website <http://www.brukeraxs.com/production/indexie.htm>)
89. H. P. Klug and L. E. Alexander, *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*. 2nd ed. 1974, New York: Wiley Interscience. p. 687-694.
90. H. Gerischer, *Advances in electrochemical science and engineering*, ed. H. Gerischer and C.W. Tobias. 1990, Weinheim, Federal Republic of Germany; New York, NY, USA: VCH. p. 232.
91. The International Center for Diffraction Data, *Powder Diffraction ICDD card files*.
92. Y.-C. S. Chia-Han Lai, Su-Jien Lin, Shou-Yi Chang, and Jien-Wei Yeh, *Atomic-Scale Observation on the Nucleation and Growth of Displacement-Activated Palladium Catalysts and Electroless Copper Plating*. Electrochemical and Solid-State Letters, 2005. 8(8).
93. M. Wuttig and X. Liu, *Ultrathin Metal Films: Magnetic and Structural Properties*. 1 ed. Vol. 206. 1905: Springer. p. 375.
94. X. Liu, *Functional Modification in Ultrathin Films: from Metastable Magnets to Molecular Materials*, in *Von der Fakultät für Mathematik, Informatik und Naturwissenschaften der Rheinisch-Westfälischen*. 2004, I. Physikalisches Institut der RWTH. p. 221.

95. G. Madras and B. J. McCoy, *Transition from nucleation and growth to Ostwald ripening*. Chemical Engineering Science, 2002. 57(18): p. 3809-3818.
96. B. J. McCoy, *A new population balance model for crystal size distributions: Reversible, size-dependent growth and dissolution*. Journal of Colloid and Interface Science, 2001. 240(1): p. 139-149.
97. C. H. Lee and J. J. Kim, *Self-annealing effect of electrolessly deposited copper thin films based on Co(II)-ethylenediamine as a reducing agent*. Journal of Vacuum Science and Technology B: Microelectronics and Nanometer Structures, 2004. 22(1): p. 180-184.
98. P. P. Lau, C. C. Wong, and L. Chan, *Improving Electroless Cu Via Filling with Optimized Pd Activation*. Applied Surface Science, 2006. 253(5): p. 2357.
99. J. Desmaison, P. Lefort, and M. Billy, *Oxidation of titanium nitride in oxygen: behavior of TiN_{0.83} and TiN_{0.79} plates*. Oxidation of Metals, 1979. 13(3): p. 203-222.
100. S. Logothetidis, E. I. Meletis, G. Stergioudis, and A. A. Adjaottor, *Room temperature oxidation behavior of TiN thin films*. Thin Solid Films, 1999. 338(1-2): p. 304-313.
101. Y. Wu, W. C. Chen, H. P. Fong, C. C. Wan, and Y. Y. Wang, *Displacement reactions between metal ions and nitride barrier layer/silicon substrate*. Journal of the Electrochemical Society, 2002. 149(5): p. G309-G317.
102. D. Kumar, M. S. Chen, and D. W. Goodman, *Characterization of ultra-thin TiO₂ films grown on Mo(112)*. Thin Solid Films, 2006. 515: p. 1475-1479.
103. J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, *Handbook of x-ray photoelectron spectroscopy : a reference book of standard spectra for identification and interpretation of XPS data*, ed. J. Chastain and R.C. King. 1995: Physical Electronics. p. 261.
104. L. Avalle, E. Santos, E. Leiva, and V. A. Macagno, *Characterization of TiO₂ films modified by platinum doping*. Thin Solid Films, 1992. 219(1-2): p. 7-17.

105. L.-J. Meng, C. P. M. d. Sa, and M. P. d. Santos, *Study of structural properties of ZnO thin films by X-ray photoelectron spectroscopy*. Applied Surface Science, 1994. 78(1): p. 57-61.
106. A. Toumrat, S. Achour, A. Harabi, N. Tabet, M. Boumaour, and M. Maallem, *Effect of nitrogen reactive gas on ZnO nanostructure development prepared by thermal oxidation of sputtered metallic zinc*. Nanotechnology, 2006. 17(3): p. 658-663.
107. S.-K. Rha, T. P. Chou, G. Cao, Y.-S. Lee, and W.-J. Lee, *Characteristics of silicon oxide thin films prepared by sol electrophoretic deposition method using tetraethylorthosilicate as precursor*. Current Applied Physics, 2009. 9: p. 551-555.
108. L. A. O. Nagahara, T.; Hashimoto, K.; Fujishima, A., *Effects of HF solution in the electroless deposition process on silicon surfaces*. Journal of Vacuum Science & Technology A (Vacuum, Surfaces, and Films), 1993. 11(4): p. 763-767.
109. C.-H. Lee, K.-H. Shen, T.-K. Ku, C.-H. Luo, C.-C. Tao, H.-W. Chou, and C. Hsia. *CVD Cu technology development for advanced Cu interconnect applications*. in *IEEE 2000 International Interconnect Technology Conference*. 2000. Burlingame, CA, USA: IEEE.
110. J. Wada, A. Sakata, H. Matsuyama, K. Watanabe, and T. Katata. *Cu dual damascene process for 0.13 um technology generation using self ion sputtering (SIS) with ion reflector*. in *IEEE 2000 International Interconnect Technology Conference*. 2000. Burlingame, CA, USA: IEEE.
111. E. Webb, C. Witt, T. Andryuschenko, and J. Reid, *Integration of thin EL Cu films in Cu interconnect metallization*. Journal of Applied Electrochemistry, 2004. 34(249).
112. S. I. Association, *The International Technology Roadmap for Semiconductors (ITRS)*. 2004.
113. W. Steinhoegl, G. Schindler, and M. Engelhardt, *Unraveling the mysteries behind size effects in metallization systems*. Semiconductor International, 2005. 28(5): p. 34-38.

114. Y. Shacham-Diamand and S. Lopatin, *Integrated electroless metallization for ULSI*. *Electrochimica Acta*, 1999. 44(21-22): p. 3639-3649.
115. H.-H. Hsu, K.-H. Lin, S.-J. Lin, and J.-W. Yeh, *Electroless copper deposition for ultralarge-scale integration*. *Journal of the Electrochemical Society*, 2001. 148(1): p. C47-C53.
116. S. Shingubara, Z. Wang, O. Yaegashi, R. Obata, H. Sakaue, and T. Takahagi, *Bottom-up fill of copper in deep submicrometer holes by electroless plating*. *Electrochemical and Solid-State Letters*, 2004. 7(6): p. C78-C80.
117. Z. Wang, O. Yaegashi, H. Sakaue, T. Takahagi, and S. Shingubara, *Bottom-Up fill for submicrometer copper via holes of ULSIs by electroless plating*. *Journal of the Electrochemical Society*, 2004. 151(12): p. C781-C785.
118. J.-H. Lin, W.-J. Hsieh, J.-W. Hsu, X.-W. Liu, U.-S. Chen, and H. C. Shih, *Gap-filling capability and adhesion strength of the electroless-plated copper for submicron interconnect metallization*. *Journal of Vacuum Science and Technology B: Microelectronics and Nanometer Structures*, 2002. 20(2): p. 561-565.
119. W. W. So, S. Choe, R. Chuang, and C. C. Lee, *Effective diffusion barrier metallization process on copper*. *Thin Solid Films*, 2000. 376(1-2): p. 164-169.
120. Q.-T. Jiang, R. Faust, H. Lam, and J. Mucha. *Investigation of Ta, TaN and TaSiN barriers for Copper interconnects*. in *Proceedings of the IEEE 1999 International Interconnect Technology Conference*. 1999. San Francisco, CA, USA: IEEE.
121. W. Zhang, L. Yi, J. Tu, P. Chang, D. Mao, and J. Wu, *Roughness and Texture Correlation of Al Films*. *Journal of Electronic Materials*, 2005. 34(10): p. 1307-1309.
122. *Electroplating Engineers of Japan, EEJA homepage*. (website: <http://www.eeja.com>)
123. *Steag Electronic Systems Homepage*. (website: <http://www.steag.com/2000/tecg.htm>)

124. W. Kern and C. A. Deckert, *Thin Film Processes*, ed. W. Kern and J.L. Vossen. Vol. 2. 1991: Academic Press. p. 888.
125. A. Malinauskas, *Encyclopedia of Surface and Colloid Science*, A.T. Hubbard, Editor. 2002, Marcel Dekker. p. 753.
126. S.-Y. Chang, C.-J. Hsu, R.-H. Fang, and S.-J. Lin, *Electrochemical Deposition of Nanoscaled Palladium Catalysts for 65 nm Copper Metallization*. Journal of The Electrochemical Society, 2003. 150(9): p. C603-C607.
127. R. Sard, *The Nucleation, Growth, and Structure of Electroless Copper Deposits*. Journal of The Electrochemical Society, 1970. 117(7): p. 864.
128. C. Eisenmenger-Sittner and A. Bergauer. *Correlations Between Island Nucleation and Grain Growth for Polycrystalline Films*. in *Mat Res Soc. Proc. Spring Meeting 2001*. 2001.
129. C.-H. L. Wei-Tsu Tseng, and Shih-Chin Lee, *Electroless Deposition of Cu Thin Films with CuCl₂-HNO₃ Based Chemistry: II. Kinetics and Microstructure*. J. Electrochem. Soc., 2001. 148(5): p. C333-C338.
130. W. Zhang, S. H. Brongersma, T. Clarysse, V. Terzieva, E. Rosseel, W. Vandervorst, and K. Maex, *Surface and grain boundary scattering studied in beveled polycrystalline thin copper films*. Journal of Vacuum Science & Technology B (Microelectronics and Nanometer Structures), 2004. 22(4): p. 1830.
131. J. M. Camacho and A. I. Oliva, *Surface and grain boundary contributions in the electrical resistivity of metallic nanofilms*. Thin Solid Films, 2006. 515: p. 1881-1885.
132. T.-M. Ko, W.-C. Ng, and W. T. Chen. *Zincation treatments for electroless nickel under-bump metallurgy in the flip-chip packaging*. in *Electrochemical Processing in ULSI Fabrication and Semiconductor/Metal Deposition II. Proceedings of the International Symposium*. 1999. Seattle, WA, USA: Electrochem. Soc.
133. K. L. Lin and S. Y. Chang, *Approaching a Uniform Bump Height of the Electroplated Solder Bumps on a Silicon Wafer*. IEEE Transactions on

Components, Packaging, and Manufacturing Technology, CPMT-B. 19(4): p. 747-751.

134. S. Jittinorasett, *UBM Formation on Single Die/Dice for Flip Chip Applications*, in *Faculty of Electrical Engineering*. 1999, Virginia Polytechnic Institute and State University: Blacksburg, Virginia.
135. D. A. Hutt, C. Liu, P. P. Conway, D. C. Whalley, and S. H. Mannan, *Electroless nickel bumping of aluminum bondpads. I. Surface pretreatment and activation*. IEEE Transactions on Components and Packaging Technologies, 2002. 25(1): p. 87-97.