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INVESTIGATION OF ADDITIVES FOR USE IN ELECTROLESS PLATING SOLUTIONS FOR FABRICATION OF NANOWIRES

by

Elliott J. Bird

A thesis submitted to the faculty of
Brigham Young University
in partial fulfillment of the requirements of

Master of Science

Department of Chemical Engineering
Brigham Young University
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BRIGHAM YOUNG UNIVERSITY

GRADUATE COMMITTEE APPROVAL

of a thesis submitted by

Elliott J. Bird

This dissertation/thesis has been read by each member of the following graduate committee and by majority vote has been found to be satisfactory.

Date	Dean R. Wheeler, Chair
Date	William G. Pitt, Member
Date	Thomas H. Fletcher, Member

BRIGHAM YOUNG UNIVERSITY

As chair of the candidate's graduate committee, I have read the thesis of Elliott J. Bird in its final form and have found that (1) its format, citations, and bibliographical style are consistent and acceptable and fulfill university and department style requirements; (2) its illustrative materials including figures, tables, and charts are in place; and (3) the final manuscript is satisfactory to the graduate committee and is ready for submission to the university library.

Date

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ABSTRACT

INVESTIGATION OF ADDITIVES FOR USE IN ELECTROLESS PLATING SOLUTIONS FOR FABRICATION OF NANOWIRES

Elliott J. Bird
Department of Chemical Engineering
Master of Science

This study focused on improvement of electroless plating methods by use of particular bath additives. The techniques developed here can enable us to plate very thin layers selectively on a nonconductive substrate and thus create metallized features on a nanoscale. Through the development of such bottom-up techniques this work contributes a key technology to achieving self-assembled nanocircuits.

The use of additives in an electroless plating environment can modify the barriers to nucleation (or seeding) and growth. Two additives, namely 3-mercapto-1-propanesulfonic Acid (MPS) and 1,3-propanedisulfonic acid (PDS), notably increased the selectivity of electroless metallization on chemically modified surfaces, which can be

used to create patterned structures. More specifically, the additives increased the growth rate of metal on an aminosilane-coated surface relative to an uncoated surface.

This work includes an examination of metal layer thickness and conductivity in addition to selectivity. The layer thickness was determined through the use of atomic force microscopy on surfaces that exhibited conductivity. The conductivity of the surface metal was determined through a measurement on a four-point probe measurement.

In this series of experiments, the disulfonate-containing additive PDS provided the highest nucleation density, highest conductivity and the best selectivity ratio. The palladium metal deposit on the PDS-treated surface was nearly uniform in height and its conductivity approached the bulk conductivity of palladium with a metal height of less than 30 nm. MPS-treated surfaces also provided increased nucleation density when used during the seeding step, but the resulting conductivity was less than that of the PDS-treated samples. We recommend the use of PDS as an effective electroless plating additive for use in palladium electroless plating processes.

ACKNOWLEDGMENTS

I wish to thank Dr. Wheeler, Dr. Harb and other professors in the ASCENT group who provided constructive feedback and help with this project. I would also like to thank Dr. Pitt and Dr. Fletcher for being very easy to work with in getting this done very quickly.

I also would like to thank the Chemical Engineering Department. During my time at BYU I have had contact with every professor in the department and many of them worked hard to help me succeed. Also, some of them had to learn more military lingo than they may have cared to know.

Lastly, I wish to thank my wife and kids. Without my wife’s continual support of our military lifestyle none of this would have been possible.

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1.1 Problem Statement

The electronics and semiconductor industries depend on advancement in electrochemical technology to further develop smaller electronic devices, which depend on creating nanoscale metallic connections. Current methods of metallization achieve linewidths on a scale of 60 nm to 80 nm [1] and are projected to achieve only modest decreases from current values [2]. In order to metallize devices on a smaller scale, research into alternative methods of metallization is necessary. Such methods must be able to achieve the smaller scale with little or no loss to the conductivity of the deposit [1, 3].

1.2 Metallization Techniques

There are a few different industrial methods used to deposit metal on surfaces. These processes can be classified into two major categories: *top-down* and *bottom-up*. Top-down methods require the use of an external control mechanism to create patterned metallization [1, 4]. The two major top-down methods are chemical vapor deposition and electroplating. Bottom-up methods, in contrast, are primarily controlled by local interactions on the surface [5]. Electroless plating is a bottom-up technique that is currently used industrially to apply metal coatings to surfaces [6]. Each of these three major techniques is discussed in the following paragraphs.

Chemical vapor deposition (CVD) is used as a means of depositing small amounts of metal. CVD uses concentration and temperature gradients as the main driving force causing transfer of metal to the surface [7]. In this process, a source of metal is heated to promote vaporization. The vaporized atoms are transported to a surface and deposited on the surface where metallization is desired. The vapor deposition method will coat metal on a great variety of materials, but it does not provide the selectivity needed for our purposes. This method is commonly used to seed substrates with metal for use in electroplating techniques [7]. A related deposition technique is atomic layer deposition, sometimes called atomic layer epitaxy [8].

Electroplating is a well-studied method and is the most common metallization technique in use today. A vitally important electrochemical process used by the semiconductor industry was pioneered by IBM researchers and is known as the *damascene* process [9]. This process relies on the use of photolithography and electrochemical methods to coat surfaces with copper. First, the substrate is coated with a thin layer of metal through vapor deposition. Additional metal is then deposited by placing the substrate in an electrolytic plating bath and an electrical current is applied to reduce metal ions on the substrate and create a thicker layer of metal [10, 11]. This deposition processes has been studied to understand and improve the technique [10, 12]. The patterning process requires a large amount of external control and limits the ability of the overall method to achieve metallization on much smaller scales. The required photolithography method is limited in the scale of the lines it can create. The metallization steps also require a carefully controlled planarization step to remove excess metal. Due to these considerations, it is difficult to achieve the nanoscale level of control needed for our purposes. Particularly, the use of a non-conductive substrate is less well suited to selective or patterned electroplating [9].

The main bottom-up method used for metallization is electroless plating. This method relies on chemical interactions on the surface instead of an external electrical field [13]. In the electroless plating method, metal ions are contained in a plating solution and they are reduced by the addition of a reducing agent into the bath. The reducing agent provides electrons to the metal ions that will reduce onto the metal seeds on the substrate. This method has the potential to achieve the feature size required for nanocircuits. There are many studies on the development of such techniques to better control metallization [14-17]. Electroless plating is a bottom-up approach because the metallized features are placed on the surface through manipulation of chemical reactions instead of using an external forcing mechanism [9].

This work focuses on improvement of electroless plating methods for use in nanotechnology. The refinement of these techniques will better enable us to plate very thin layers selectively on a nonconductive substrate and thus create metallized features on a nanoscale. Through the development of this bottom-up technique we will contribute a key component to achieving self-assembled nanocircuits [13].

To further develop combined top-down and bottom-up nanocircuit fabrication methods an interdisciplinary group from the BYU Departments of Chemistry, Physics and Chemical Engineering was formed. This group is called the ASCENT (ASsembled nanoCircuit Elements by Nucleic acid Templating) group and it has a goal to develop a circuit that is smaller than is currently achieved by photolithographic methods [9]. The ASCENT group researches methods for molecular circuit assembly through use of DNA templating, chemical patterning, and chemically-directed surface assembly. To accomplish this we need better methods to metallize the nanocircuit [18]. Creating metal deposits with high selectivity and quality on nanoscale templates is one of the primary technologies needed by the group [9]. The ASCENT group recently published a paper showing the potential for the plating of metal on a chemically patterned surface [4], while Adam Woolley, a faculty member in the ASCENT group, stated in his previous research that two major obstacles must be overcome in the metallization tasks: selectivity and conductivity [19].

1.3 Desirable Qualities for Deposition

In order for electroless plating to be considered a viable solution to achieving nanoscale features there are a number of desirable qualities that the metal deposit must meet. Figure 1-1 summarizes these characteristics. The methods must be able to produce patterned features on a nanoscale that are selective and conductive. User-controlled patterns require that the deposition reaction be selective, or that the metal will bind to the substrate only in the desired location. In order to achieve conductive nanoscale structures the method must produce uniform metallization with high nucleation density. Uniformity means that the metal crystallites are of similar size and distributed evenly in the desired location on the substrate. This project attempts to increase uniformity and nucleation density by adjusting process steps, particularly the seeding and plating steps in an electroless plating method.

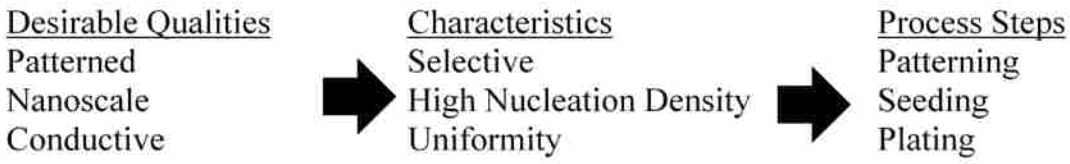


Figure 1-1: Desirable deposit and related process steps

Figure 1-2 illustrates the importance of nucleation density for electroless plating. In part (a) the nucleation density is low, and the metal clusters are spread apart. As the metal clusters grow in this diagram they become large until they reach the point where the metal clusters are adjoined to allow for conductivity. The required line width required for conduction would be large. Part (b), in contrast, shows the consequence of greater nucleation density. The clusters grow together sooner and thereby require a smaller cluster size or line width to be conductive.

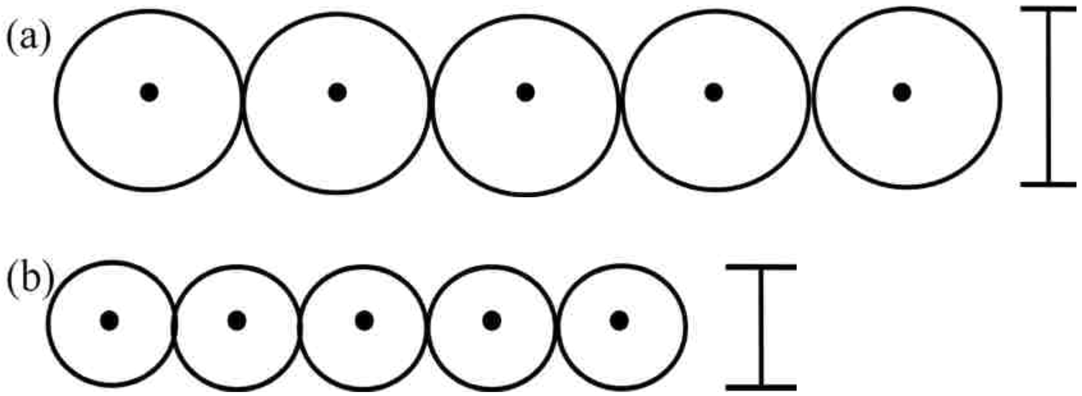


Figure 1-2: Nucleation Density comparison. Black dots indicate seed locations for (a) low-density and (b) high density uniform placement. Bars indicate minimum line width for conductive lines.

1.4 Issues to Overcome for Electroless Plating

There are a variety of factors that could possibly influence nucleation, selectivity and quality of the deposit. Electroless plating solutions are metastable [16], meaning that the metal ions in the solution are ready to plate onto a site as soon as the energy required to nucleate is overcome [3, 20]. Minor shifts in the chemistry of the solution have a great effect on the plating ability. Adjusting pH, temperature, time in solution and positioning of the substrate (a silicon wafer) in solution can have a great effect of the ability of the solution to properly plate on a surface.

A key element to help overcome the difficulties of plating on a nanoscale is the use of plating additives. Additives are surface-active molecules that are used in electrochemical processes to achieve a variety of effects for metallization [10, 21]. Additives are used to both accelerate and inhibit plating of metal on surfaces. They are widely used in the damascene process to allow for trench filling and also to control the uniformity of the deposit [12, 22].

Using additives in an electroless plating environment can modify the barriers to nucleation. Additives could increase selectivity of electroless metallization by enhancing metallization in templated locations, while also decreasing metallization in other areas. The use of additives could help control seeding and growth of the metal atoms at the nucleation sites on the surface of the desired substrate. Research into the effect of plating additives in an electroless plating system will lead to a better understanding of chemical interactions on the surface that can enhance the plating of metal.

1.5 Scope of Work

This project investigates the possible advantages of particular additives for nanoscale electroless deposition of metal. We find that additives can have a positive effect on the quality of the deposits by affecting two critical steps of the plating process: seeding and growth. To varying degrees the tested additives influenced the metal deposition by lowering the barriers to nucleation [12]. Our hypothesis is that the use of particular sulfur-containing additives will provide more uniform metallization, higher conductivity, and selectivity.

This study uses a number of analytical tools available here at Brigham Young University to study the effect of plating additives on the electroless plating. Scanning electron microscopy (SEM) was used to determine nucleation density on the surface. The conductivity of the plated samples was determined through the use of a four-point probe. Atomic force microscopy (AFM) was used to determine height of metallization of the samples to more accurately determine the conductivity of the samples. Through these techniques we obtained data on surface coverage, density and growth rate. These data provided the evidence of how the additives are affecting the deposition of metal on the surface.

The remainder of this thesis provides more information about the methodology and results. Chapter 2 provides the background information from pertinent literature and related experimental work. Chapter 3 contains the experimental methodology and design. Chapter 4 contains the experimental results and pertinent discussion. Finally, Chapter 5 contains the main conclusions and discusses areas for further research.

2 Background

2.1 Introduction

This chapter explains technologies related to this work, including a discussion of electroless plating methods, metal use, additive selection, conductivity and a brief introduction to the analytical tools used in this study. The first section will explain some basic concepts of electroless plating that includes basic concepts, DNA templating, seeding and bath stability. The next section will explain our decision as to which metal to use in our study. A discussion on additive uses and our methodology for determining which additives to test is contained next. Finally, this chapter describes prior work on plating conductive metal on a surface.

2.2 Electroless Plating

2.2.1 Concepts

While electroless metallization is a well-developed industrial field used within the chemical process industry [23], metallization on a nanoscale is still not fully developed or understood [23]. In most industrial applications, rapid metallization on a surface is the desired outcome. The plating baths used by industry for electroless plating are not well suited to our requirements to plate on a nanoscale due to this aggressive nature. Industrial baths may not plate evenly enough to achieve required uniformity of the metal on the surface. In the assembly of nanoscale electronic devices, the nucleation of metal on the surface needs to be controlled so that the metallization occurs only in the templated region, or has selectivity. To address these issues a number of groups are researching methods to adapt electroless plating methods to nanoscale problems [24-26].

In this work the desired characteristics from the plating are selectivity, uniformity and a conductive deposit. To achieve selectivity you need to deposit in a specific area as seen in Figure 2-1 (a) and (b). This is accomplished through an evenly dispersed seed layer in the desired templated region. The interactions with different chemical functionalities on the surface of the substrate can produce selectivity, allowing us to plate metal on activated surfaces and better control metallization. Uniformity in deposit thickness and density is accomplished by increasing the nucleation density on the surface in the specific area as seen in Figure 2-1 (c). Uniformity requires a well-controlled growth rate at the nucleation points so that the metal-metal junctions grow together and evenly cover the surface of the templated region. Finally, the best conductivity is achieved when the metal-metal junctions between crystallites are large and contain a minimum of impurities or other defects as shown in Figure 2-1 (d). A uniform deposit will provide less resistance to electrical current, or have high conductivity.

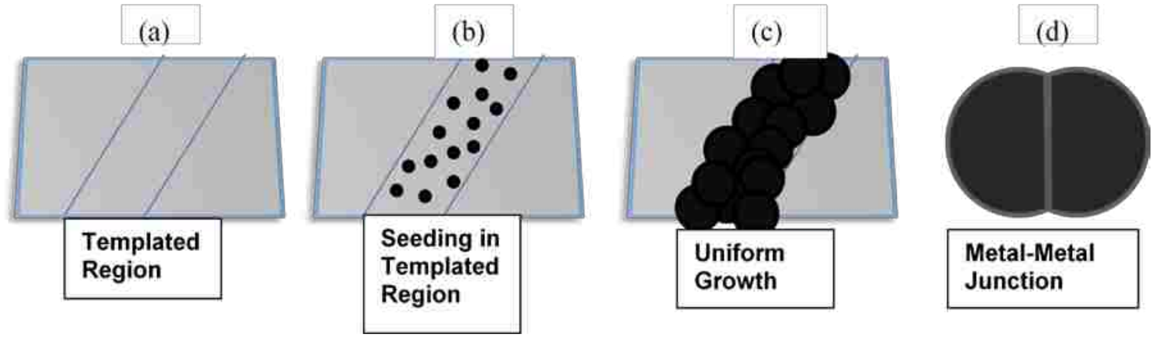


Figure 2-1: Explanation of desired characteristics (a) templated regions treated with substrate for metallization; (b) Seeding layer in the templated region; (c) Growth of the nucleation sites; (d) illustration of a metal-metal junction with no impurities or defects.

2.2.2 DNA Templating

DNA has been considered an attractive means of templating or controlling metal deposits on a surface due to its ability to form complex structures upon hybridization. In this method DNA is placed on a surface as a template or scaffold (Figure 2-1 (a)) and attracts metal due to its inherent negative charge. Work done here at BYU showed the potential for using DNA to create templates for metallization [4, 27]. Contemporary work at Duke University also involved plating silver onto DNA to produce conductive wires. They did this by functionalizing the DNA with a reducing agent in order to metallize silver metal onto the DNA [28].

A major problem with much of the electroless plating work to date is the selectivity to the treated DNA is not as high as desired. One observes the presence of background or nonselective metal particles on the surface [19]. The nonselective particles could be due to nonselective surface plating or particles falling out of solution. These particles produce “noise” making it difficult to distinguish wire conductivity from background conductivity For the purposes of developing conductive continuous wires we need to identify a methodology and mechanism to increase selectivity. The research at Duke [28] seems to overcome this problem, but their proposed mechanism works only for silver. Previous studies have used this similar procedure to limited success [29, 30]. Working to duplicate the Duke work may be of benefit; however, we chose to investigate metallization using a more oxidation-resistant metal such as palladium.

2.2.3 Seeding

Researchers in the nano-templating area have looked at the use of catalysts, in the form of seed layers, to assist the plating of the metal [31]. Researchers in Japan claim that in order to accomplish metallization in the case of DNA templating, a catalyst must be bound to the DNA [32]. This catalyst referred to in their research as well as in research at the Naval Research Laboratory (NRL) [23] is what is considered the seed layer (or seeding) in the present work. Dressick and coworkers at the NRL researched electroless plating baths and their reaction mechanisms extensively [31]. Their research showed the need for developing a seed layer to facilitate nucleation sites favorable to metallization [23].

Seed layers are necessary building blocks to form metallized surfaces for a variety of applications. In the damascene process, CVD is used to place a seed layer on the surface to initiate and enable electrodeposition [7]. Additionally, a seed layer can be attached to the surface through the use of a spin coating of metal on the surface [33]. For electroless plating, seeding is accomplished by exposing the substrate to low-concentration metal ions in solution and then rinsing the substrate in a reducing solution to reduce the metal ions bound to the surface [1]. Most commonly Pd(II) and Sn(IV) are used. Alternatively, colloidal forms of metal have been used [31]. These seeds then form a layer on the surface that allows for further metallization of the substrate [13].

This work builds on the prior work toward the development of consistent plating methods, particularly with respect to additive effects in seeding solutions. This project additionally address the problems of selectivity and nucleation of the metallization sites needed for work in the ASCENT group [4, 34].

2.2.4 Bath Stability

Electroless plating baths are metastable in that they are prepared to plate once the barriers to nucleation are overcome. Recent work has shown the variety of factors that contribute to the stability of a plating solution [35]. The stability of the bath will contribute directly to the ability to selectively plate on a desired surface. The baths need to be maintained such that they do not nucleate in solution and thereby form metal particles or precipitated complexes. The use of a seed layer provides nucleation sites for the metal ions in the bath to attach and bind to, but if the bath is not stable enough the precipitates in the solution will instead fall out of solution and attach to the substrate. These precipitates will not bind to the desired seeds on the surface and therefore not be selective.

The stability of the bath can be controlled through the use of additives and by adjusting pH, temperature and concentrations of the reducing agents [35]. When the solution is exposed to the surface after the addition of the reducing agent the metallization reaction takes place in a batchwise process. As this changes reactant concentration, the exposure time will also affect the stability of the solution as well as its ability to preferentially plate to the desired nucleation sites. The bath recipe used here [6] appears to have sufficient stability for our plating procedures.

2.3 Metal Use

Currently, copper is the metal of choice for industrial use in circuits and microprocessors because of its high conductivity. However, copper oxidizes easily on any exposed surfaces and as the scale of the wires becomes smaller a larger fraction of the copper will be converted to an oxide layer that does not conduct electricity as well. To overcome this problem we decided to use a more noble metal that less readily forms an oxide on the surface, but is also reasonably conductive. Palladium was chosen as a good candidate to achieve the desired results. At 25° C, the conductivity of palladium is $9.48 \cdot 10^6$ S/m [36], compared to $5.96 \cdot 10^7$ S/m [37] for copper. Palladium does not oxidize as easily as copper; also its Fermi level is nearly identical to that of the carbon nanotubes being used in the project for semiconductors. The similar Fermi level means the metal-carbon interface presents less of an energy barrier for the electrons. Furthermore, palladium is widely used as a seeding material for many electroless plating methods [33], meaning in this case it can be both seed and main deposit. In summary, palladium meets the requirements to interface well with the nanotubes, not oxidize, and be a conductive medium for the wires.

2.4 Additives

Additives are used throughout the electrochemical industry for use in electroplating systems [12]. Specifically, sulfur- and sulfonate-containing additives provide the functionalities usually desired to accelerate plating in a trench-filling method (e.g., damascene process) for use in fabricating microprocessors [38]. The sulfonate functionality of the additives is shown to provide acceleration in electroplating methods for copper [10, 12, 24, 25]. This is accomplished because the additives appear to decrease the energy barrier to reduce the metal ions.

A list of additives to test for a possible positive effect on plating was generated. Each of the additives was used in some form for plating of metal and a few were tested in prior electroless plating solutions. Preliminary tests were conducted here at BYU (described below) on the additives listed in Table 2-1. Figure 2-2 shows the structures of these molecules. Most of the additives have either thiol or a sulfonate functionality that is commonly associated with electroplating additives. Four of the additives showed a positive contribution to plating palladium, compared to samples that were not treated, and became the subsequent focus of our work. All the tested additives are described in more detail in the following subsections.

Table 2-1: List of Additives tested [12, 25, 38-40]

Full Name	Abb	Further Study
3-Mercapto-1-propanesulfonic Acid	MPS	Y
1,3-Propanedisulfonic Acid	PDS	Y
3-N,N-dimethylaminodithiocarbamoyl-1-propanesulfonic Acid	DPS	Y
Propanedithiol	PDT	N
8-hydroxy-7-iodo-5-quinoline sulfonic Acid	HIQSA	N
Dimethylamine Borane	DMAB	N
Sulfanilic Acid	SA	Y

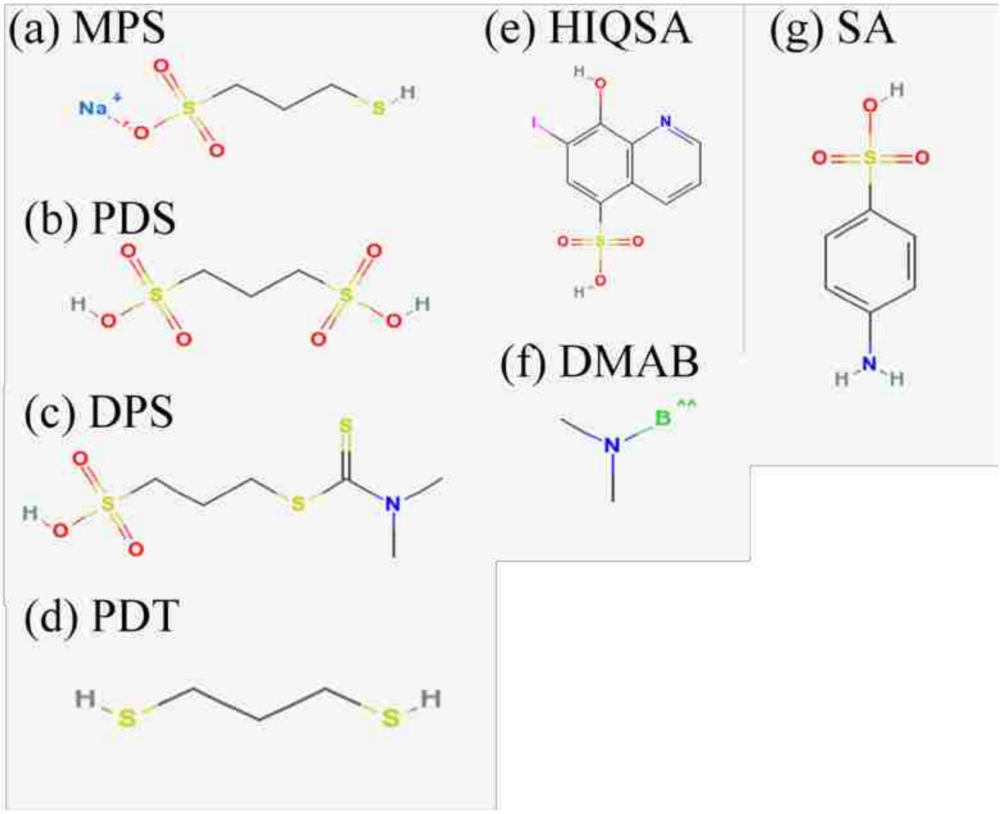


Figure 2-2: Structures of Plating Additives [41]

2.4.1 3-Mercapto-1-propanesulfonic Acid (MPS)

MPS is an additive associated with copper electroplating [12] for trench filling in the building of circuits. The mechanism by which MPS accelerates deposition of copper was studied and modeled by Guymon [42]. The conclusion was that it binds to the metal on the surface and attracts further metal ions to the surface, thus accelerating plating.

2.4.2 1,3-Propanedisulfonic Acid (PDS)

PDS is an additive also studied by Guymon [42], due to its similar chemical functionality to one end of the MPS molecule, which is associated with copper electroplating [12]. It is believed to act similarly to MPS, but it does not bind to the surface metal due to a sulfonate functionality on each end. Overall, in an electroplating environment it provides an acceleration in the plating of copper for the purpose of trench-filling in the damascene process [42].

2.4.3 3-N,N-dimethylaminodithiocarbamoyl-1-propanesulfonic Acid (DPS)

DPS is an electroplating additive for copper, but it was also used in electroless copper plating research by a group at Seoul National University in Korea. Their research showed that it provided greater metallization in an electroless copper plating process [24, 25]. They additionally tested the concentration effect of the additive on achieving higher quality deposition. They found that DPS acted as both an accelerating and suppressing agent at higher concentrations [25]. DPS was selected for this experiment to determine its effectiveness in electroless plating of palladium.

2.4.4 Sulfanilic Acid (SA)

A research group here in the US developed a plating method using SA for electroplating [40]. They are currently looking to patent the use of SA in the electroplating of palladium metal. SA was also selected for further research in this study.

2.4.5 Other Additives

Other researchers have tested HIQSA (See Table 1) for copper electroless plating [38] as well as DMAB (See Table 2-1) for gold electroless plating [39]. PDT is a thiol-terminated additive that has similar functionality as additives associated with copper electroplating [12]. The references cited above provide background on the possible effectiveness obtained by using these additives for electroless plating techniques.

2.4.6 Preliminary Additive Tests

For our preliminary screening tests we used the above additives to see if they exhibited any quantifiable effects on the plating of palladium on a silicon oxide wafer. The preliminary tests focused only on the plating process, but subsequent tests (Chapter 3) included a study of the additive effects on the seeding step as well. In these tests, each sample was treated with an aminosilane, seeded for five minutes, treated with a reducing solution and then plated for 15 minutes. These processing steps are the same as in subsequent experiments and are explained in more detail in Chapter 3.

After plating, each sample was tested on the XPS instrument to detect the presence of a characteristic palladium peak at an energy around 335 eV. Figure 2-3 through Figure 2-6 show some sample XPS spectrum from these initial tests. Figure 2-3 shows a sample that was not treated with any additive, which was seeded and plated as described above. There is not a readily distinguishable peak around 335 eV, showing that the surface scan did not detect palladium bound to the surface. Figure 2-4 shows a sample that was treated with PDS and there is a noticeable characteristic palladium double peak on the spectrum. Figure 2-5 shows a high resolution scan of an MPS-treated sample in the vicinity of the characteristic palladium peak, showing a detectable amount of palladium bound to the surface of the substrate. The final sample image in Figure 2-6, is a sample treated with PDT and it has little or no detectable palladium peak on the spectrum.

Through a series of such tests we examined each additive for its effectiveness toward increasing palladium metallization on the surface of the substrate. The four additives that generated a significant presence of palladium metallization through the presence of the characteristic palladium peak on the XPS spectrum were then selected for further study.

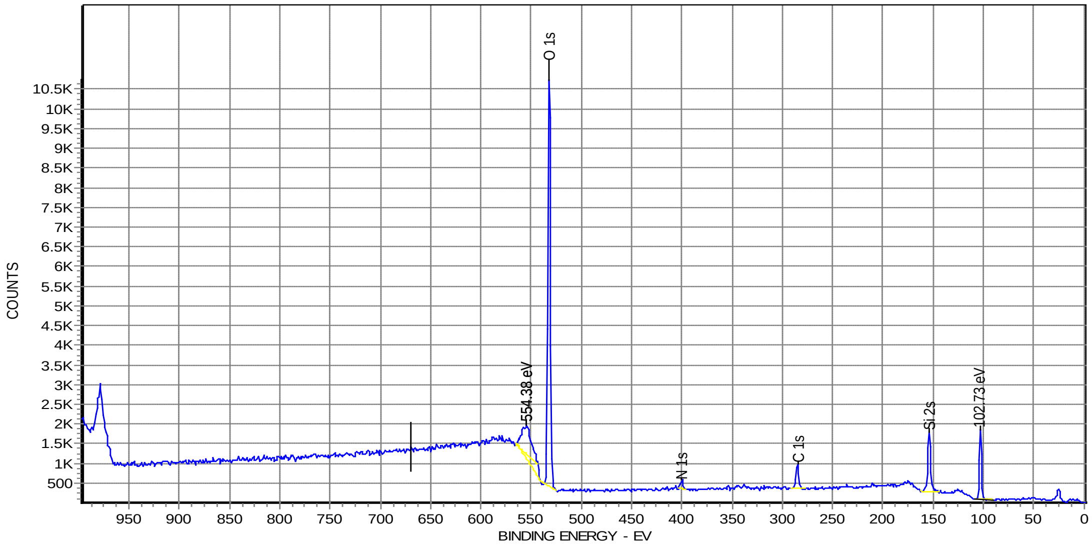


Figure 2-3: Untreated Sample XPS Spectrum. There is no appreciable peak at 335 eV, indicating no significant palladium presence on the surface.

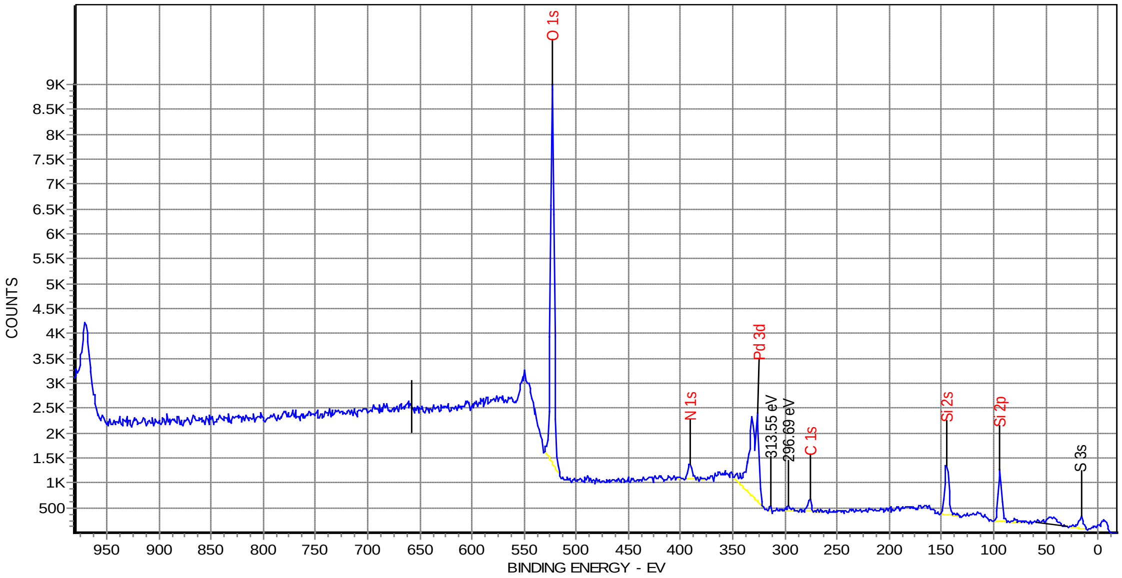


Figure 2-4: PDS treated preliminary XPS spectrum. Large peaks at 335 eV indicate palladium metal on the surface.

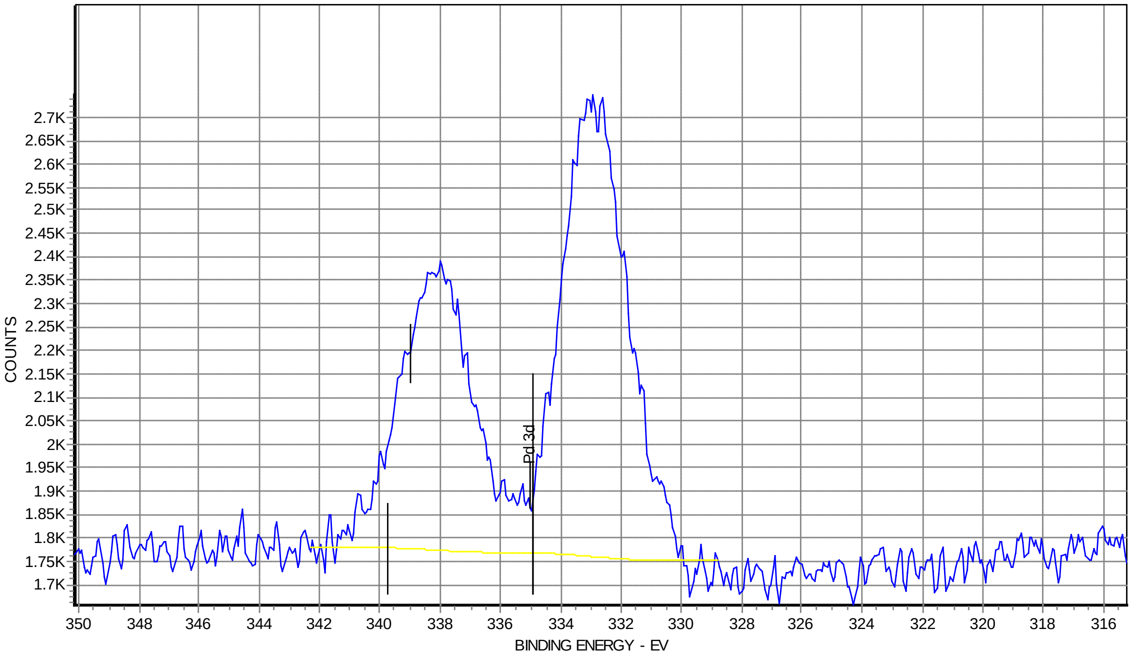


Figure 2-5: High Resolution XPS Scan on MPS treated sample. The large peaks at 335 eV indicate a strong presence of palladium on the surface.

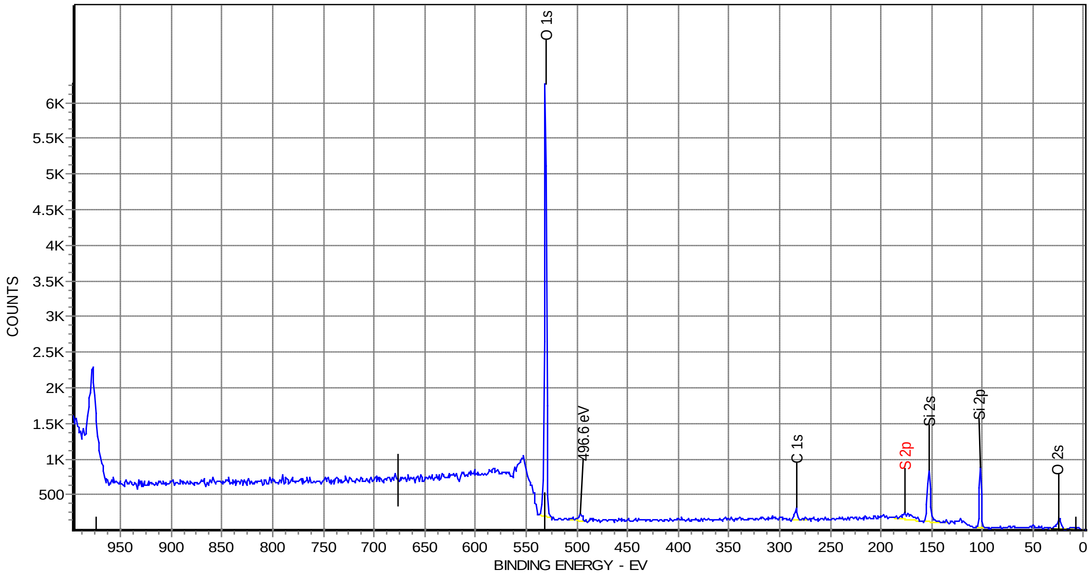


Figure 2-6: PDT treated sample. There are no peaks at 335 eV, indicating that this additive did not attract palladium metal to the surface.

2.5 Conductivity

As noted above, the plated metal deposit needs to be conductive. The stochastic nature of electroless plating makes it hard to achieve deposit uniformity and therefore good electronic conduction of the metal deposit. Jan Richter, from the University of British Columbia, modeled the limitations on conductivity of wires, predicting that 30 nm may be the smallest wires that are conductive [43, 44]. He followed up his work in a separate paper stating he tested the conductivity of 50 nm to 200 nm thick palladium wires and successfully measured an overall resistance of a single 50 nm-thick wire to be 734 Ω [45]. Taking the geometric information provided, we estimate that the wire's conductivity is $4.5 \cdot 10^6$ S/m (his calculation is $2 \cdot 10^6$ S/m), compared to a bulk palladium conductivity of $9.48 \cdot 10^6$ S/m [36]. The value is lower than the bulk conductivity, but this is expected when accounting for metal-metal junction resistances and the small geometry of the wire.

Other researchers have not been as successful at achieving good conductivity of nanowires. One such example is Keren from Technion-Israel Institute of Technology who admits that they were not able to measure good conductivity for the deposit, but attributed that to background noise (a selectivity problem) [3]. Also, Braun from the same university could not produce a conductivity measurement until he increased the voltage to 50 V across the wires [30]. Research by Hao Yan at Duke has shown ohmic behavior of lattices on the surface of silver for potential differences in the range of –0.2 V to 0.2 V with resistance of the grids being around 200 Ω [28, 46].

Research done here at BYU prior to the organizing of the ASCENT group showed the need to develop methods to measure and verify the conductivity of the plated metal [4]. One problem in determining conductivity of nanowires is that many researchers don’t publish results in units of conductivity since there has not been a standard way to report the conductive properties of nanoscale structures. Many researchers report either voltage, or resistance and then the reader is left to determine the conductivity. Through measuring the conductivity and reporting the results in easily comparable units it will show (Chapter 3) the effectiveness of the metal deposit through the use of a four-point-probe measurement.

2.6 Summary

There has been prior research on the use of electroless plating to achieve continuous metal deposition to form either wires or bulk surface deposits, but there currently is not a definitive solution to achieve nanoscale features through an electroless plating process. More research is needed into ways to better utilize electroless plating methods to achieve metallization on a nanoscale. The technical issues include bath stability, metal use, and additives. This study focuses on methods to improve electroless plating through the use of additives. Four additives were selected that showed an ability to increase deposition of palladium in initial tests. A series of tests were developed to assess deposit quality as described in the next chapter.

3 Experimental Techniques and Procedures

3.1 Introduction

This chapter explains the experimental techniques and design used in this thesis to determine the effect of select additives on metal deposit quality. The first part of this chapter explains the analytical tools that were used. Next, there is a discussion of the experimental design, including methods for each step of the plating process.

3.2 Analytical tools

A methodology that tests the effectiveness of the additives listed in Table 2-1 is needed. Each additive could have an effect on the seeding step, the plating step, or both. In order to test the effectiveness we used analytical techniques to determine the nucleation density, conductivity and selectivity when the substrates were treated with the additives, as well as for control experiments lacking additives.

There are many available techniques here at BYU that would meet the analytical requirements for this experimental design in order to determine how the additives influenced seeding and plating steps. In particular, the use of the scanning electron microscope (SEM), atomic force microscope (AFM), and four-point probe conductivity instrument.

After completing a series of process steps, each with different additives, the prepared sample was viewed under the scanning electron microscope (SEM) to show the nucleation density and rate of growth as a function of process step and plating time. Pictures from the SEM were taken at three separate magnifications at different locations on the sample. These pictures illustrate the effect of the seeding, additive, and plating time on the growth of palladium metal on the surface of the samples. Example images are shown in Figure 3-1.

Figure 3-1: Example SEM images with increasing magnification left to right

After analyzing the samples with the SEM, each sample was tested for conductivity to determine continuity and quality of the deposit. The samples were tested on a four-point probe (Figure 3-2) that allows for reasonably accurate measuring of surface-layer conductivity. The resistance values were combined with thickness measurements to determine the effective conductivity of plated metal on the surface for comparison with bulk conductivity. In order to determine thickness of plated metal on the surface, atomic force microscopy was used. The conversion to conductivity also requires a shape factor that depends on the geometry of the probe and the sample. The shape was determined using available literature on the four-point probe website [47].

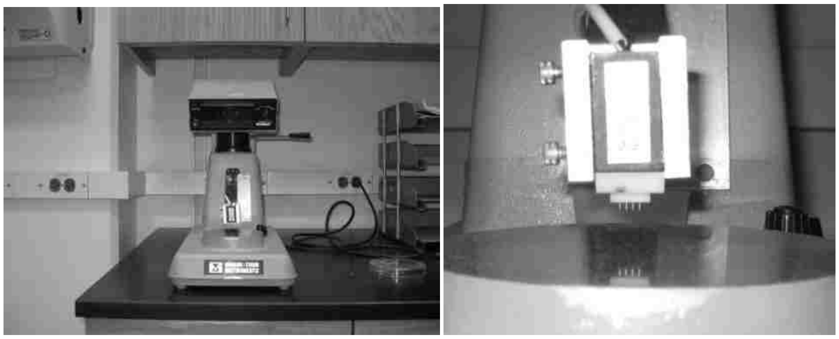


Figure 3-2: Pictures of four-point probe used in conductivity measurements

The AFM was used to determine the height of the plated metal. The AFM was used in tapping mode, where the tip is vibrating vertically with a characteristic frequency. The instrument measures changes in forces between the tip and the surface to determine local height of the sample. For each conductive sample, a series of AFM images were taken to determine the average height of the metallized surface.

3.3 Experimental Design

Our experimental design must answer the basic questions addressed in Chapter 1. Namely, we wish to investigate the possible advantages of the four additives for use in electroless deposition of metal. Through their surface activity, additives can have an effect on two of the critical steps of the metallization process: seeding and plating. The experimental design must test the additives for their effect on both of these steps in order to test the hypothesis that the four additives can provide more uniform metallization, higher conductivity, and better selectivity.

As mentioned in Chapter 2, there are various factors that can influence electroless metallization. Assessing the effect of each of these factors was beyond the scope of this work. For this reason, we held the seeding and plating bath compositions constant and focused on the effect of additive (pre)treatments between other steps. The overall experimental design flowchart is shown in Figure 3-3. The different pathways indicate variables or alternative processing steps that were examined. The reader may refer to this flowchart as we explain the methodology of the design below.

The experimental design includes control samples. The control samples allow comparison to determine additive effects. In Figure 3-3, the control samples follow the bottom pathway that shows both no additive pretreatment and treatment in step B. There are two series of controls, ones that were treated with an aminosilane and ones that were not. Other than the use of additives, the blank samples were treated with the same seeding and plating process.

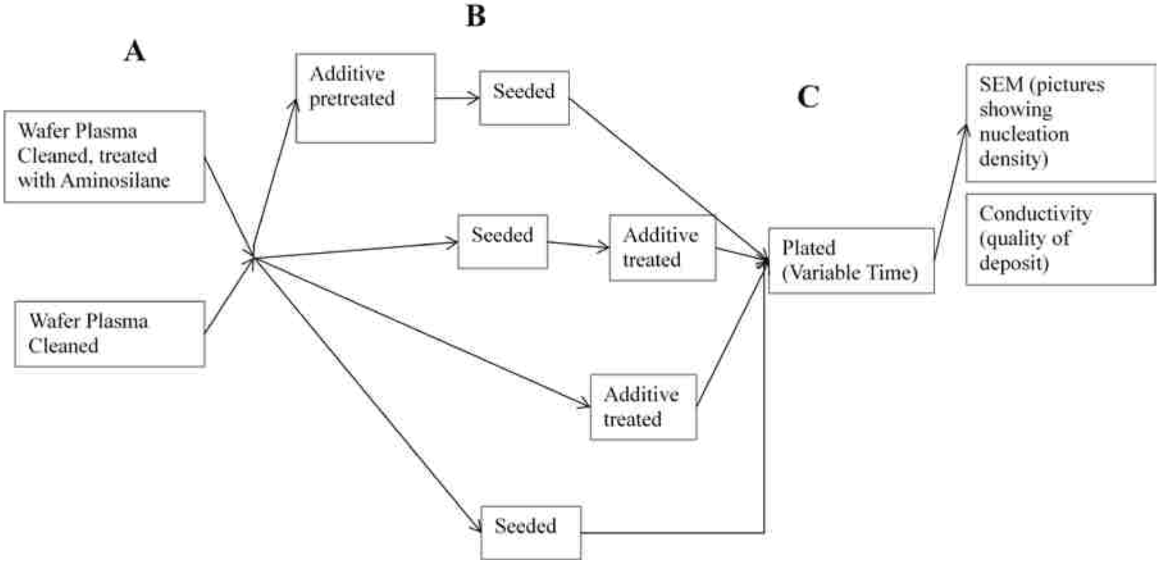


Figure 3-3: Experimental Design

For these experiments metal was plated on bulk surfaces rather than on templated surfaces. We used this bulk-plating methodology as a proxy for lines or other metallized regions that could be templated on the surface. The main reason for this simplification or idealization in the experiment is to increase throughput and focus our effort on the metallization steps. Chemomechanical or DNA templating is a time-consuming process that can lead to significant amount of variability and therefore to difficulty in getting statistically meaningful results [3, 19]. In contrast, on well-controlled substrates, we were able to generate reproducible results for a large number of samples.

Because our experiments were based on bulk plating, a way to quantify selectivity of the metallization process was needed. This was accomplished by comparing the metallization on two different substrates: one where plating should occur (aminosilane coated) and one where plating should not occur (non-coated). This is represented by step A in Figure 3-3. In addition, we measured the thickness of the metallized layers as a proxy for the minimum width of lines that could be generated. If the growth of the seeds proceeds isotropically or hemispherically, then the width of the lines will be about twice the thickness of the lines, or layer.

Prior experimental results did not address the rate of growth of the seeds or nuclei on the surface of the substrate. In our analysis we show the time resolution of the deposit growth by measuring the nucleation density and thickness versus time for different treatment procedures (step C in Figure 3-3).

3.3.1 Wafer Preparation

In the design we need to show the effects of differing substrates. This is signified as step A in Figure 3-3. The differing substrates serve to indicate the selectivity of the metallization. An aminosilane-treated substrate is commonly used to achieve metallization on the surface of silicon dioxide [4, 5, 32]. For these experiments we chose to use aminopropyltriethoxysilane (APTES) since it is commonly used for electroless plating and for other experiments within the ASCENT group. The APTES coating provides an exposed amine functional group on the surface and therefore should attract more metallization [4]. The amine group will exhibit a positive charge in the solution of pH of about 1.15 due to its pKa of 10.8 [48]. The palladium ions in solution will form negatively charged complexes with Cl^- that are then attracted to the surface amines [31]. In addition, the amine group also exhibits a chemical complexation effect with metal ions in solution. In contrast, the plasma-cleaned silicon oxide surface has an exposed oxide functional group that should not attract metal ions to bind to the surface due to its negative charge. In water it has a negative charge and so should repel the negatively charged metal complexes.

The samples used were prepared from a large thermal silicon oxide wafer, with oxide layer thickness of approximately 200 nm. The wafer was cut into approximately 1-cm-square sections. These sections were placed in a Yield Engineering System (YES) silane oven to vapor deposit APTES on each sample. Based upon prior calibration using this apparatus [49], the APTES coating appears to be a monolayer. Even if this is not exactly the case, the YES oven has the advantage of creating a reproducible uniform coating.

3.3.2 Seeding

As previously noted, the seeding step is a key component to achieving desired metallization on the surface. We reduced any additional variability by using the same ionic palladium seeding solution for every experiment. The seeding solution used in this experiment follows the seeding solution used by the Dressick group at NRL [31]. The seeding solution was 0.1 g $PdCl_2$, 0.2 g NaCl, and 1 mL 6 M HCl mixed with water to make 100 mL of solution. The pH was measured to be 1.15. The dilution water, as well as water used in all baths and rinsing steps in this work, was purified by a Millipore apparatus. The seeding solution loses its effectiveness about a week after mixing. NRL did not indicate what reducing solution was used in their work. The reducing solution used in this thesis was approximately 1.5 g to 2.3 g of sodium borohydride mixed with Millipore water to make 50 mL of solution.

The additives were used as a pretreatment in two of the experimental pathways shown as step B in Figure 3-3. These samples were pretreated with the additive prior to seeding and then plated. The additive pretreatment involved placing the samples in 0.1 M solutions of the additive for 20 minutes. From here the pretreated samples were immediately placed in the seeding bath. Between liquid treatments here, and in other steps of the experimental protocol, rinsing was not used unless explicitly indicated. However, samples were always “drip dried” between steps, meaning they were held vertically until no visible droplets remained on the surface.

The procedure for the seeding process was as follows. The samples were immersed in the seeding solution for five minutes and then immersed in a reducing solution for one minute. After removing the samples from the reducing solution, they were rinsed thoroughly with water prior to being immersed in either additive treatment or plating bath. In the experiment we desire to know if the additives influence the seeding step.

3.3.3 Plating

In this study we needed to determine if the additives have an effect on the plating step of our process. In order to reduce variability we used the same plating solution every time for these experiments. The plating solution used throughout this study was as follows: 1.01-1.05 g $PdCl_2$, 1.9 g NaEDTA, and 2.8 mL Ethylenediamine mixed in with Millipore water to make 100 mL of solution. The solution was allowed to sit at room temperature for 24-36 hours to chelate and completely dissolve the Pd salt, turning the solution clear. The pH of the plating bath was measured to be around 10.4. The plating bath without a reducing agent would remain usable for approximately two weeks. When ready to plate we would add 0.45-0.60 g of sodium hypophosphite reducing agent immediately prior to use of the plating bath. The addition of the reducing agent the slightly lowered the pH to around 10.2. Note that significant elevation of the bath above room temperature with this recipe causes it to become unstable and precipitate metal particles, making it unusable.

Samples that were treated with an additive in two of the pathways were treated after the samples were removed from the reducing solution and thoroughly rinsed prior to being treated with the additive. The sample would be treated with a 0.1 M solution of the additive for twenty minutes before being placed in the plating bath.

Each sample was immersed in the plating solution for a variable amount of time (1-30 minutes). After removing the sample from the plating bath it was thoroughly rinsed with Millipore water and then dried under a nitrogen gas stream. After drying the samples were analyzed to determine nucleation density and other properties.

3.3.4 Sample Analysis

As noted in Section 3.2, each sample was imaged using an SEM. The images were used to determine nucleation density of the sample. This was done by manually counting the visible nucleation sites from the image and converting this value to a density based on the surface area. For example, in the image seen below in Figure 3-4 , the small white specks on the surface are assumed to be palladium metal bound to the surface. Based on earlier XPS results, selective EDAX results, and conductivity measurements this assumption is reasonable. The surface area is determined through the use of the scale bar seen on the bottom of each image. This methodology was used to create the graphs that follow in the next chapter.

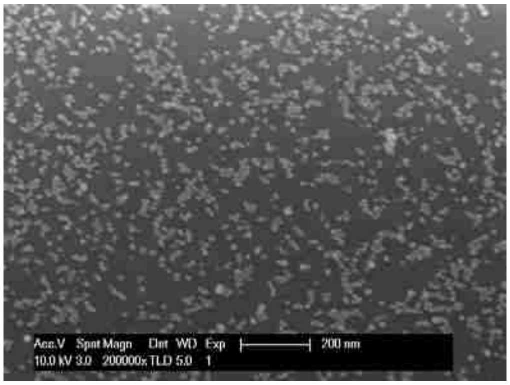
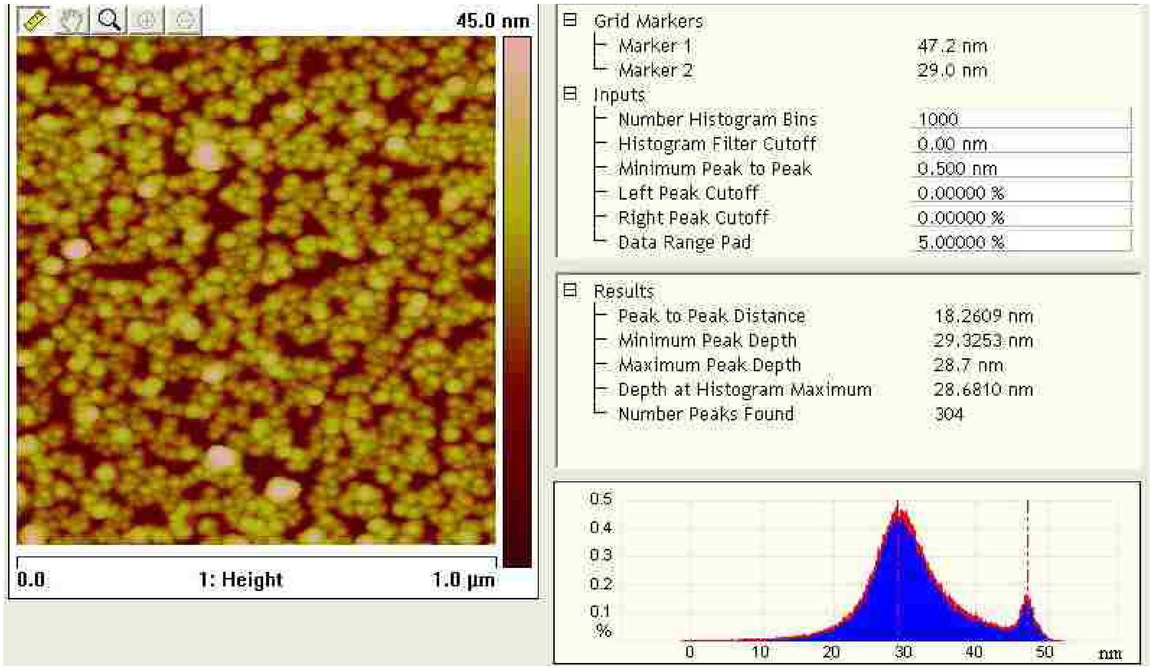


Figure 3-4: Sample image of metallization on the surface

The height of the samples was determined through the use of AFM. Below in Figure 3-5 is an example AFM image on a 1 μm^2 with accompanying height analysis. The histogram shown at bottom right is a depth measurement: the peak at the far right shows the baseline or substrate height for assumed unplated regions, while the higher peak shows an averaging of deposit height. The "Peak to Peak Distance" of 18.2606 nm would be the deposit thickness we report for this particular sample. Two independent 1 μm^2 regions were used for each sample to ensure reproducible results.

Every sample was measured for conductivity using the four-point probe instrument mentioned in Section 3.2. The probe reads out an apparent resistance, which is the ratio $I/\Delta V$, where I is the current between the outer two probe points and ΔV is the potential difference between the inner two probe points. The probe reads a maximum apparent resistance of 100 Ω. Many of the samples, such as all of the non-APTES-coated surfaces, exhibited resistances above this level, meaning they were effectively insulating. Using layer thickness determined by AFM, the apparent resistivity can be converted to a conductivity using the formula σ = π/ (*tR* ln2), where *t* is thickness and *R* is the resistance [47].



Grid Markers
- Marker 1: 47.2 nm
- Marker 2: 29.0 nm

Inputs
- Number Histogram Bins: 1000
- Histogram Filter Cutoff: 0.00 nm
- Minimum Peak to Peak: 0.500 nm
- Left Peak Cutoff: 0.00000 %
- Right Peak Cutoff: 0.00000 %
- Data Range Pad: 5.00000 %

Results
- Peak to Peak Distance: 18.2609 nm
- Minimum Peak Depth: 29.3253 nm
- Maximum Peak Depth: 28.7 nm
- Depth at Histogram Maximum: 28.6810 nm
- Number Peaks Found: 304

Figure 3-5: Sample AFM image showing height measurement

3.4 Conclusion

This chapter explained the techniques, procedures, and methodology used in this thesis. Each step was presented in sufficient detail to allow for the procedures to be repeated. The experimental design presented represents an effective methodology to answer the questions of how the additives affect the metallization of the wafer surface.

4 Experimental Results and Discussion

4.1 Introduction

The use of additives to accelerate plating is a well-known process commonly used in electroplating. The effects of additives on electroless plating are less well known; gaining this knowledge in the context of nano-templated metallization is the main research objective of this work. This chapter discusses results for a series of experiments that we used to determine and compare the effect of four additives on the quality of palladium deposits. The additives tested were MPS, PDS, DPS and SA whose structures are shown in Table 2-1 in Chapter 2.

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4.2 Comparative Experimental Results

The overall goals of this study are to show that plating additives can increase conductivity, increase selectivity, and metallize uniformly on the selective substrates. Through these experiments we found that all the additives increase the nucleation density of the metallization, when compared with untreated samples. Overall, MPS-pretreated and PDS-treated samples exhibited good conductivity and uniformity of metallization, while the PDS-treated samples had the greatest selectivity. In this section we discuss and summarize the main conclusions from this study concerning the additive effects on conductivity, selectivity and deposit thickness (or height). Section 4.3 contains additional details on nucleation density for the samples. It is noted that all the plots contain error bars with an 80% confidence interval based on two samples per point.

4.2.1 Conductivity

Figure 4-1 gives the surface conductance measured on the four-point probe as a function of time and additive used (pretreated and treated). These data are the raw data measured on the four-point-probe mechanism and the values do not account for surface thickness of conductivity. Because none of the non-APTES treated surfaces exhibited measurable conductivity, they were not included in the graph. In this graph, the MPS-pretreated samples leveled off in that increased time did not increase the surface conductance, while the surface conductance of PDS-treated samples continued to increase. The PDS-pretreated and DPS-pretreated samples did not exhibit any surface conductance until being plated for 30 minutes.

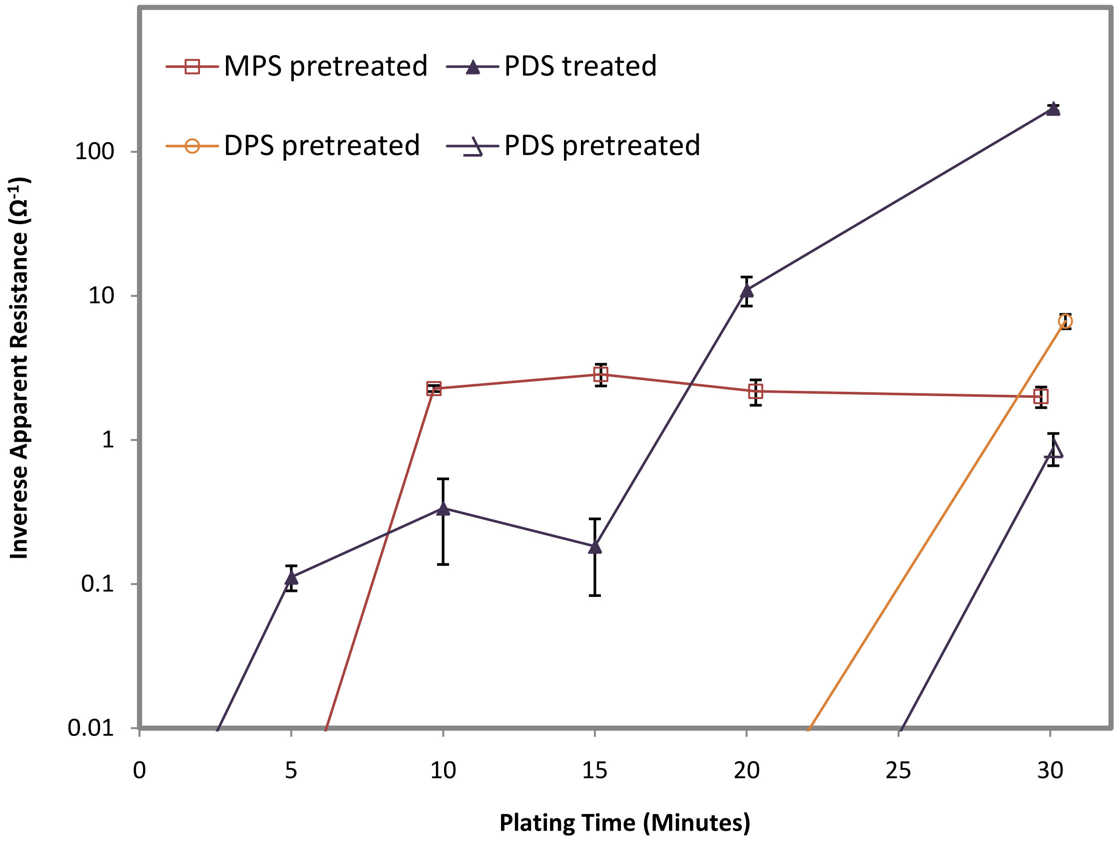


Figure 4-1: Inverse Apparent Resistance of pretreated and treated samples over time. Lines between points are to guide the eye. In some cases the error bars are smaller than the symbol size. The upper and lower limits of the vertical axis are the resolution limits of the four-point probe.

Figure 4-2 is a graph showing the calculated conductivity from the raw data for the four additive-modified samples with detectable conductivity. The greatest conductivity achieved was $8.12 \cdot 10^6$ S/m which is in very good agreement with the bulk conductivity for palladium of $9.48 \cdot 10^6$ S/m. By the end of the 30 minute plating step, all four additive-modified samples showed significant conductivity.

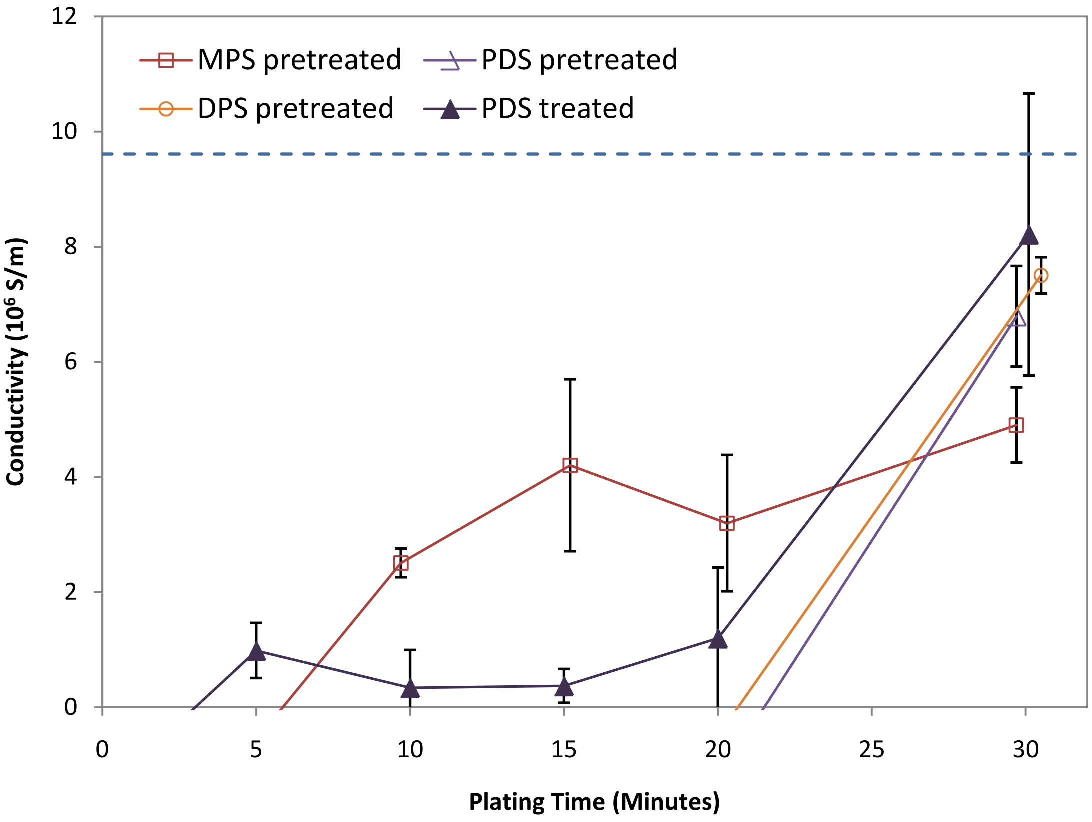


Figure 4-2: Sample Conductivity for different additive pretreatments and treatments. Lines between points are to guide the eye.

4.2.2 Selectivity

The selectivity of the samples was determined by making a ratio of nucleation density of the APTES-coated substrates to the nucleation density of non-APTES-coated substrates, holding all other variables constant. This ratio shows at a particular time the selectivity toward metallization we could expect for a patterned surface containing both APTES-coated and bare silicon oxide regions. A graph of these ratios is shown in Figure 4-3. The PDS-treated samples exhibited the greatest amount of selectivity. There is great variability on those samples that seem to exhibit little selectivity, and this is possibly due to the difficulty in determining accurate nucleation density on non-APTES-coated surfaces. Metallization increases with plating time at different rates on different surfaces, so the selectivity ratio can fluctuate and even decrease.

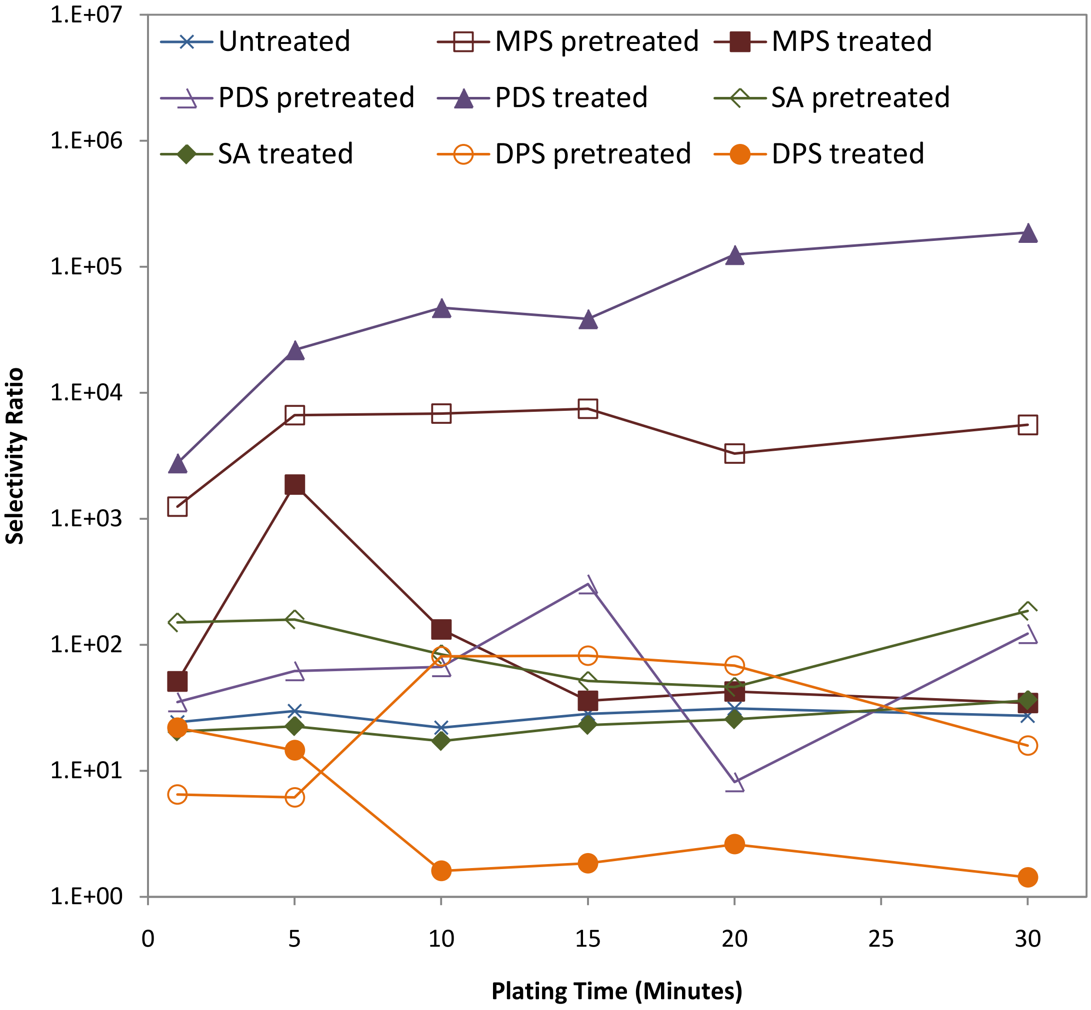


Figure 4-3: Selectivity of the additive-modified surfaces. Selectivity is the ratios of the APTES-coated surfaces over the non-APTES-coated surfaces. Lines are included to guide the eye.

4.2.3 Average Height

In our experiment we determined the height of the conductive samples as a proxy for minimum line width or diameter of the metal crystallites. Figure 4-4 shows the heights of the conductive samples, that is, samples with an apparent resistance below 100 Ω on the four-point probe measurement. The PDS-treated and MPS-pretreated samples each showed increasing height for nearly the entire plating time. However, both samples exhibited a relative leveling off of deposit height after the initially rapid growth. This decrease in deposition rate could be due to consumption or degradation of additive during the plating process.

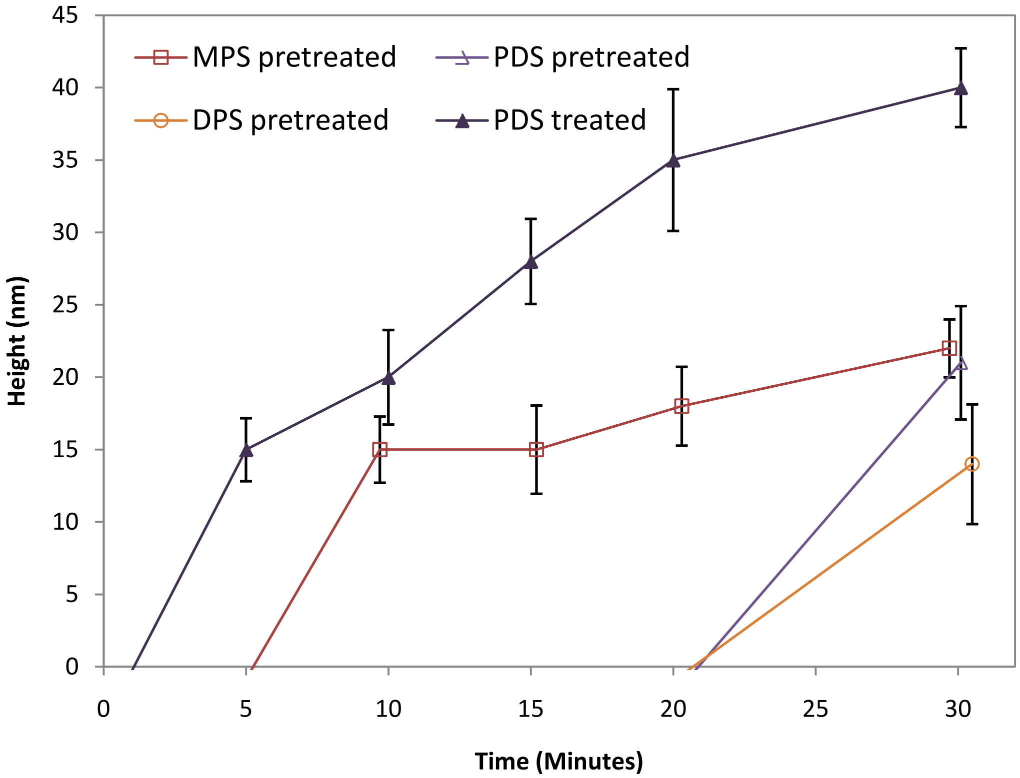


Figure 4-4: Height of conductive samples as measured by AFM

In Figure 4-5 are some sample images showing the deposit uniformity of the “best case” plated surfaces. It should be noted the metal crystallites exhibit similar dimensional size and relative uniform coverage, both desirable features for conductivity. There are some areas where the metal crystallites begin to stack on top of others, but those areas are limited in scope at the times observed.

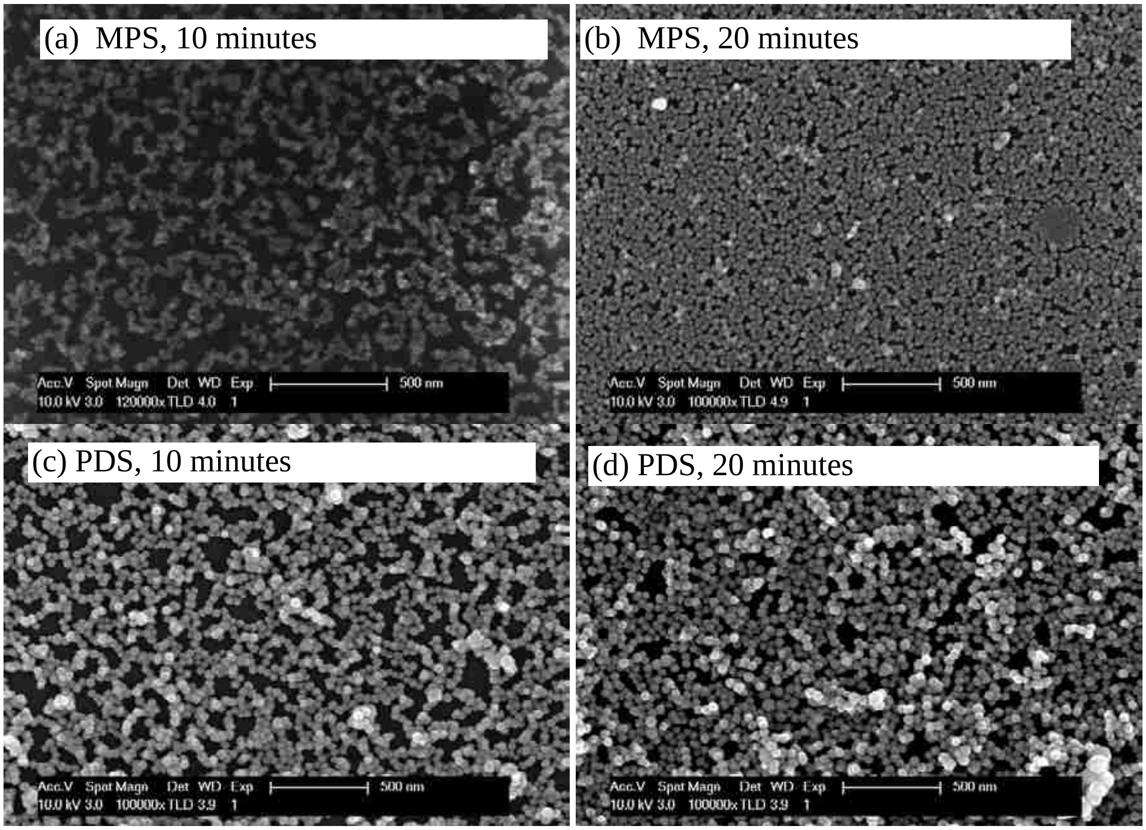


Figure 4-5: Plating on APTES coated substrates

4.3 Individual Experiments

This section describes each individual additive-variation experiment and particularly shows the observed nucleation densities and some corresponding sample images.

4.3.1 Plasma cleaned, non-APTES-coated substrate

To determine selectivity of the metallization we needed to determine the nucleation density on samples that were not treated with APTES. We expected that there would be a little metallization due to the stochastic nature of electroless plating, but we nevertheless followed the same counting and analysis procedures. Below is a series of graphs and images that show the effect of the additives on metallization of a non-APTES-coated substrate.

Non-seeded Surfaces

As a control experiment, we decided to see the effect of the additives in the plating process if the samples were treated with the additives, but not seeded. Below in Figure 4-6 shows the nucleation density effects from these experiments. The DPS-treated surfaces had the greatest nucleation density, but it should be noted that it is still a very small density on the order of $10^{-2}/\mu m^2$, which is about five times less than corresponding seeded samples. Due to such a small nucleation density, none of these samples exhibited any conductivity. The overall metallization curves in these samples are trending upward as plating time increases, but still the overall metallization is small.

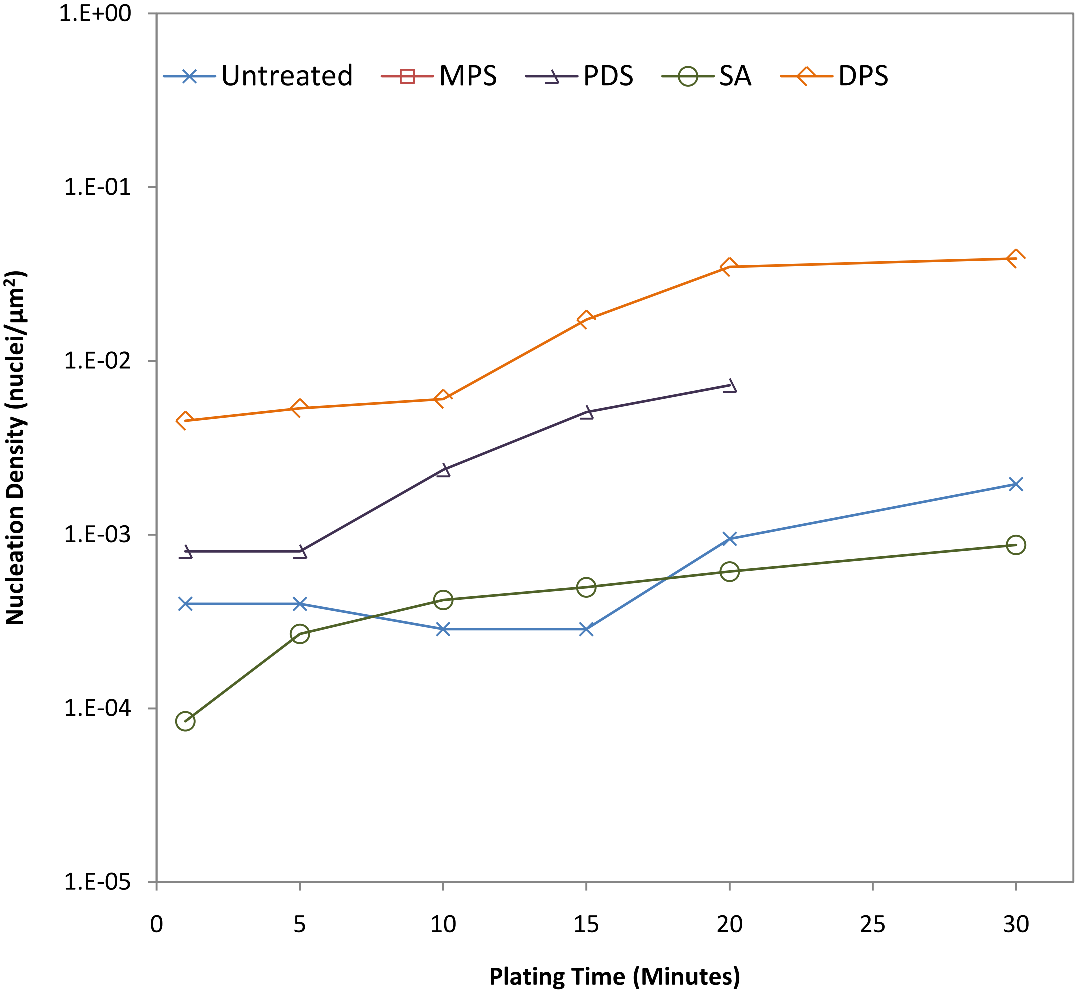


Figure 4-6: Nucleation Density of additive-treated, unseeded surfaces. Lines between points are to guide the eye.

In Figure 4-7 there are a few images showing the nucleation density of these samples. As can be seen in the images, there is very little metallization occurring.

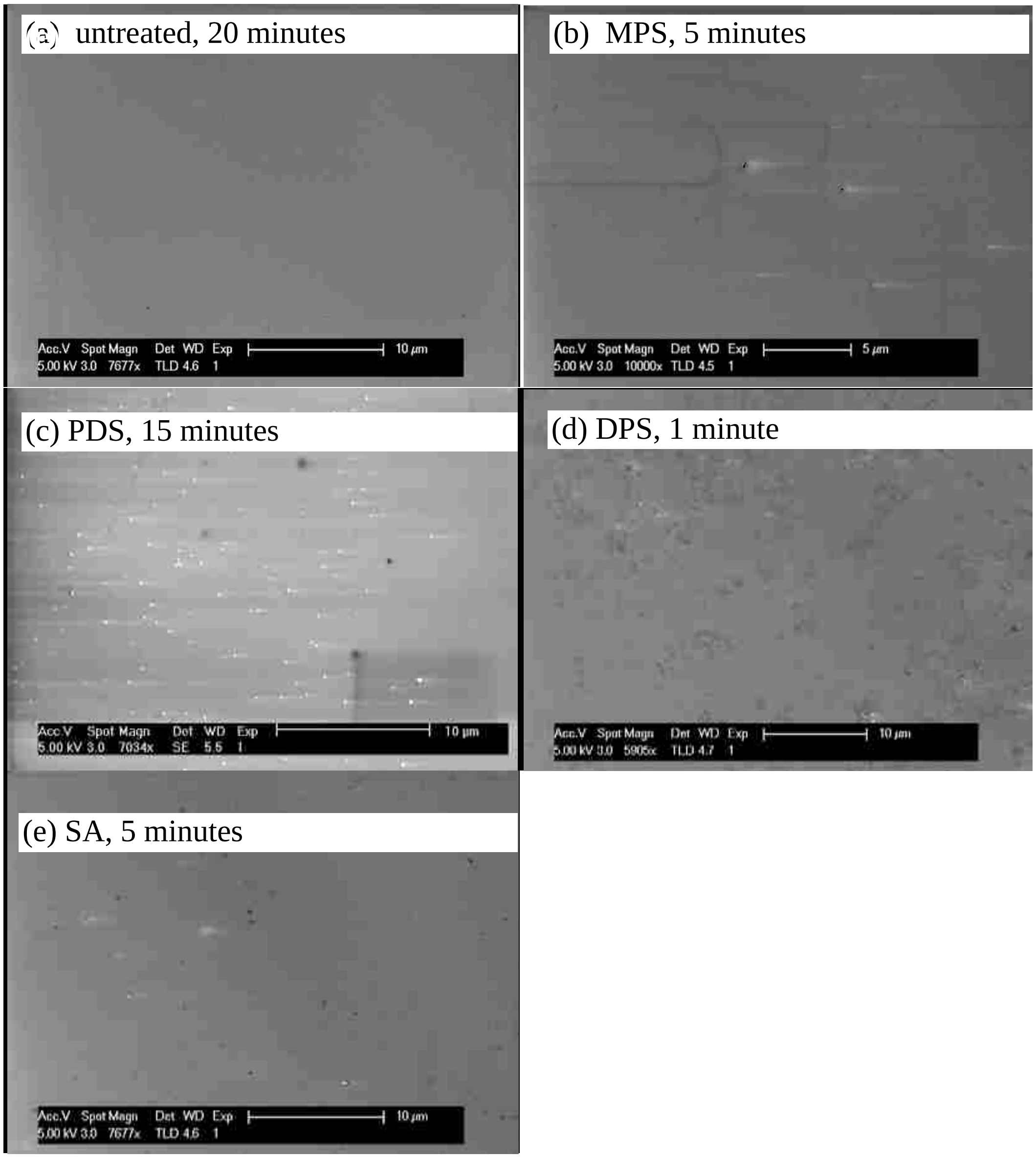


Figure 4-7: Unseeded samples that were treated with additive and plated. Plating times for each sample and additive are indicated for each image.

Pretreated Surfaces

The next set of samples were pretreated with the additives, seeded, and then plated for various times to see the effect of pretreating the surfaces in the absence of an aminosilane on the surface. These samples also exhibited very small densities, but there was an increase from non-seeded surfaces. As shown in Figure 4-8 the greatest density was from PDS-pretreated samples. The greatest density though was still on the order of $10^{-1}/\mu m^2$. None of these samples exhibited any conductivity.

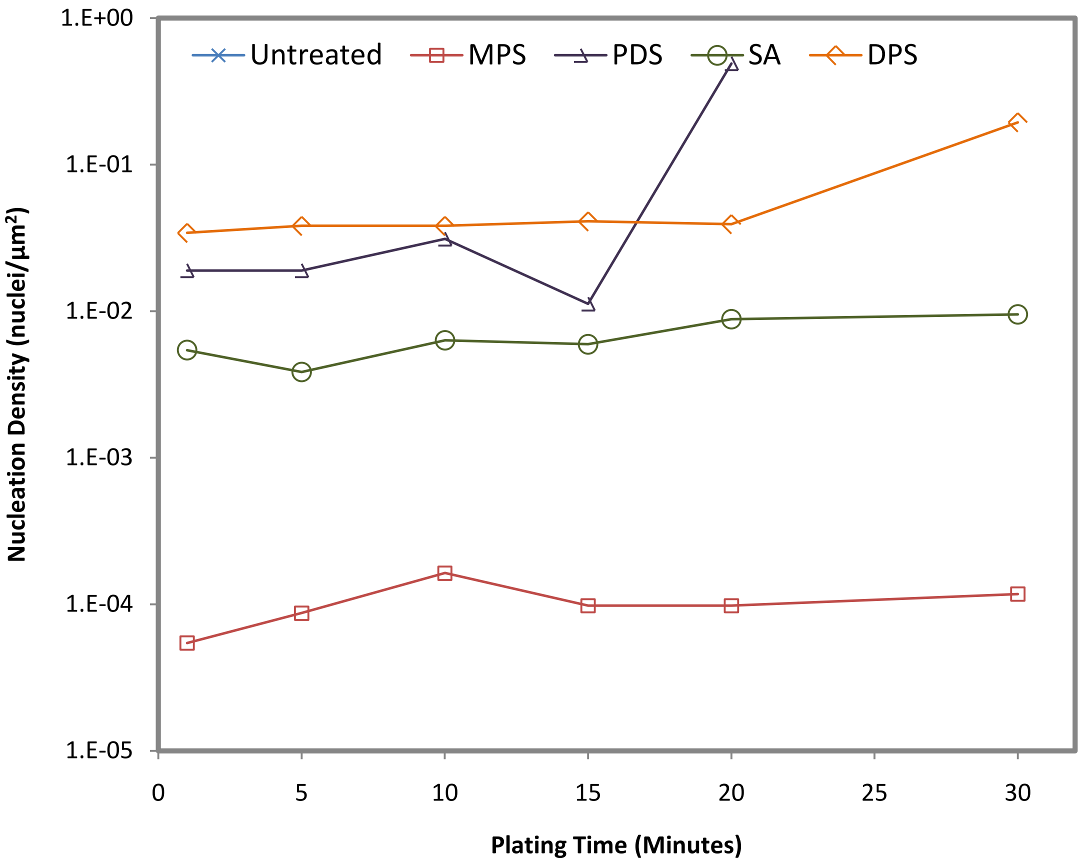
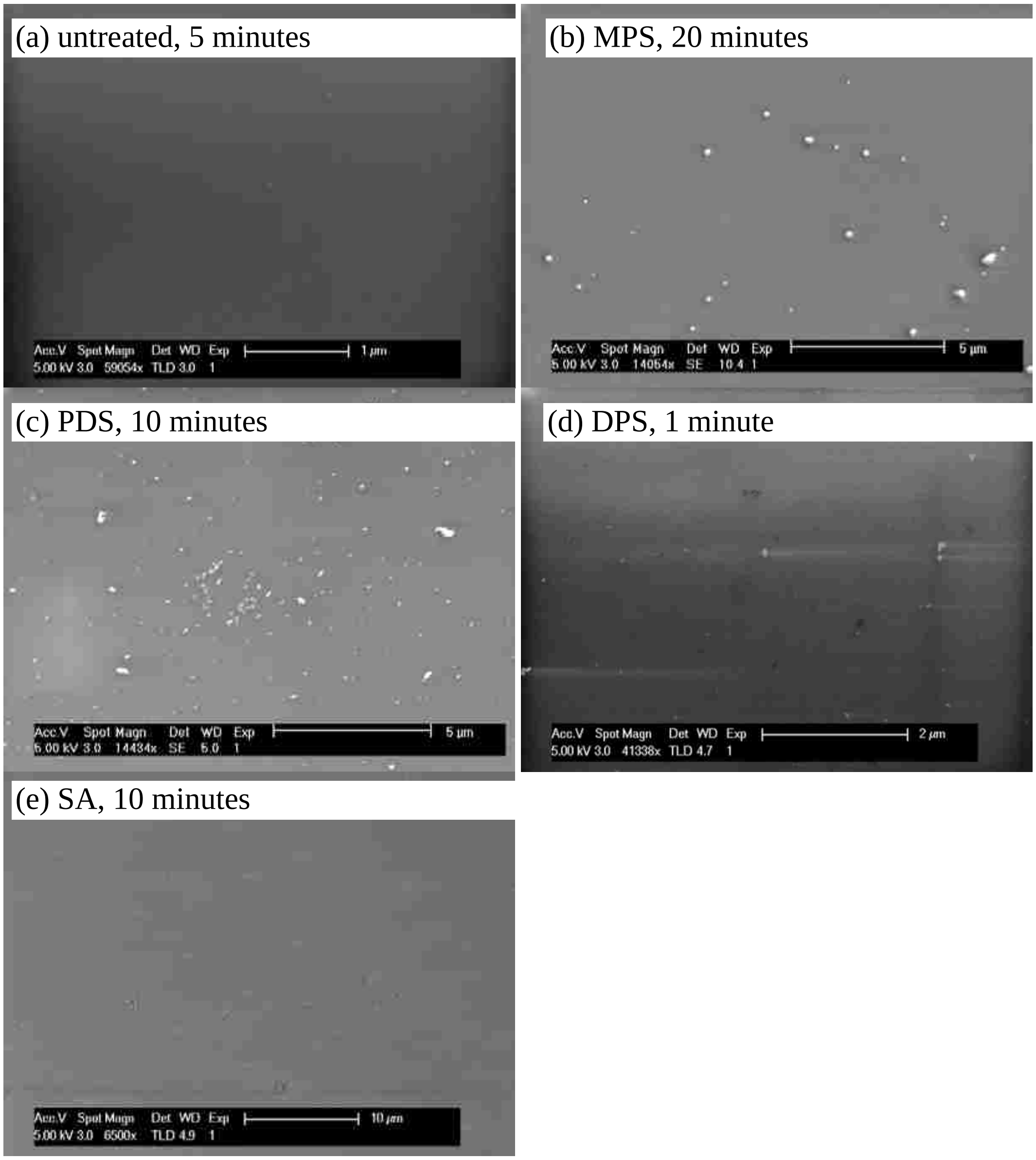


Figure 4-8: Nucleation density of non-APTES-coated pretreated samples. Lines between points are to guide the eye.

Figure 4-9 shows a series of images showing the nucleation density on the surface of these samples. Plating is visible on these surfaces, but the scale is large and so the amount of metallization is comparably small.


(a) untreated, 5 minutes

(b) MPS, 20 minutes

(c) PDS, 10 minutes

(d) DPS, 1 minute

(e) SA, 10 minutes

Figure 4-9: Additive-pretreated non-APTES-coated samples. Plating times and additive are indicated for each sample image.

Treated Samples

The next experiment was conducted so that the samples were treated with the additive after completing the seeding process. The graph in Figure 4-10 shows the nucleation density of these samples. In this case the samples that were treated with DPS exhibited the greatest nucleation density, but again the amount was overall small and there was no conductivity exhibited in these samples. The samples in this experiment reached a comparative leveling off of metallization and showed little or no subsequent increase over times observed.

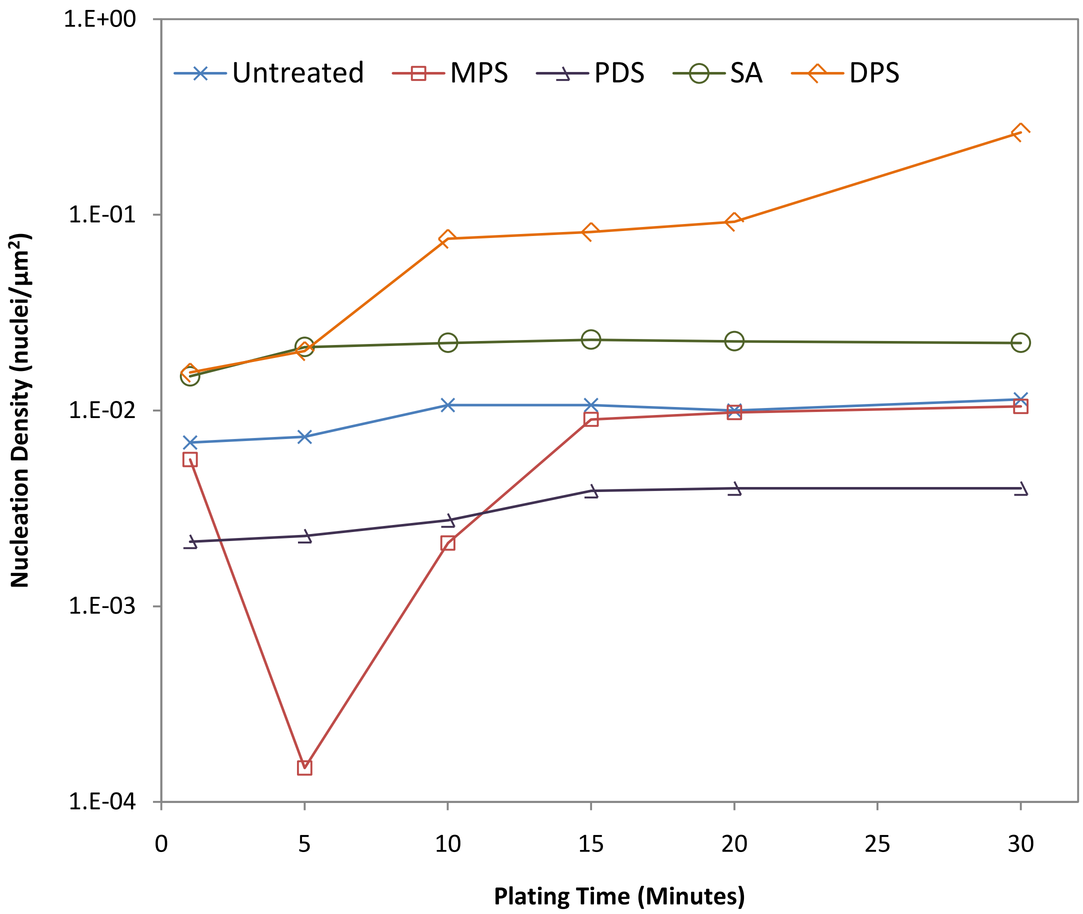


Figure 4-10: Nucleation density of non-APTES-coated samples that were seeded, additive treated, and plated. Lines between points are to guide the eye.

Figure 4-11 shows some sample images that illustrate the nucleation density.

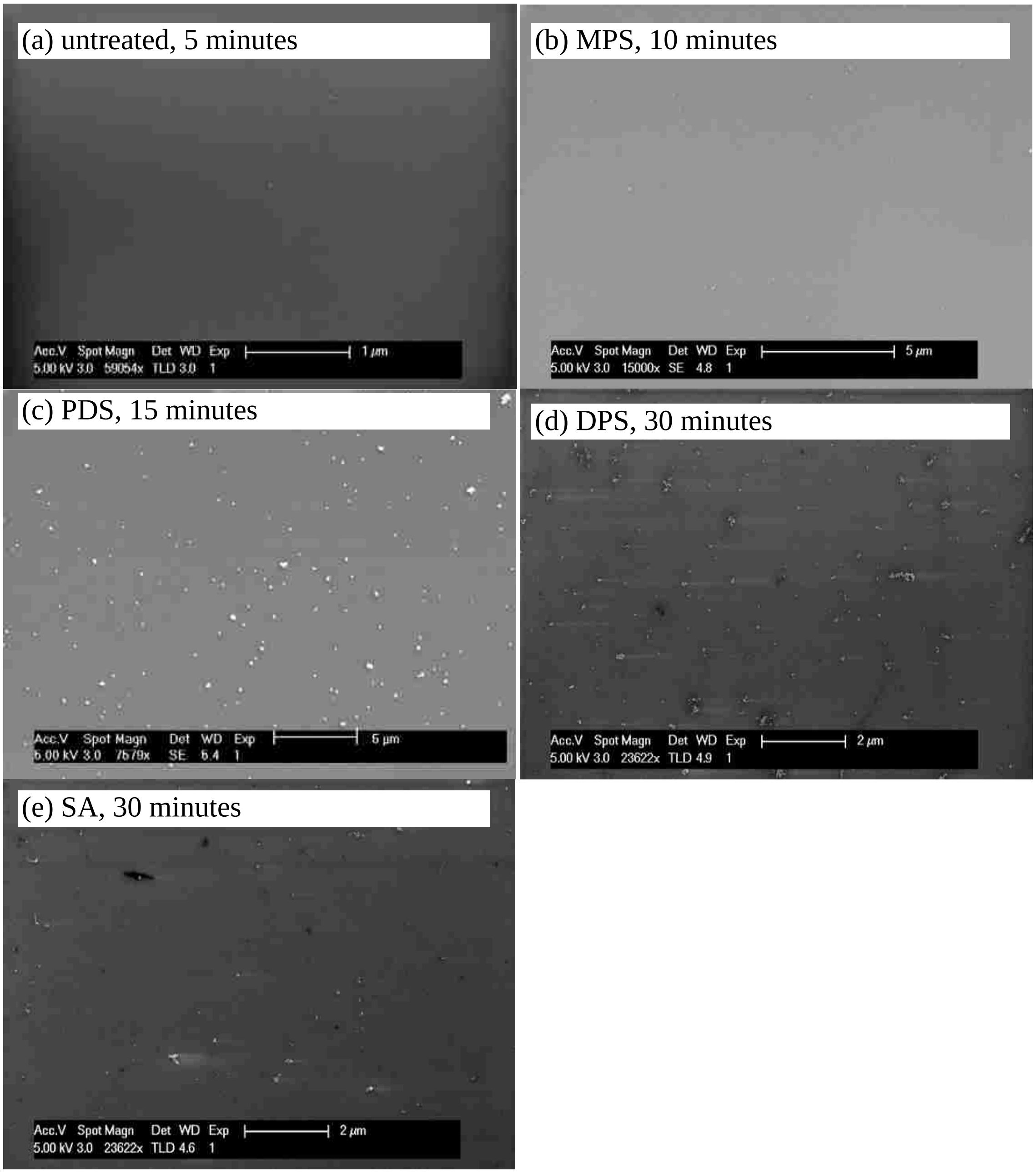


Figure 4-11: Additive-treated non-APTES-coated samples. Plating times and additive are indicated for each sample image.

4.3.2 APTES-Coated Surfaces

APTES was chosen as the aminosilane that was coated on the substrate for the purpose of metallization. It provides an amino group on the surface that can attract the negatively charged metal complex and can mirror the reaction that could be expected in metallization of DNA. APTES also easily binds to the silicon dioxide substrate through a vapor deposition reaction in a silane reactor, allowing us to make a well-controlled amine-covered surface. In this section we illustrate the effectiveness of the additives on an APTES-coated surface through a series of graphs and images. The following experiments were carried out in the same manner as the ones noted above in Section 4.3.1.

Unseeded Surfaces

We took a set of samples that had APTES coated on the surface and treated them with an additive and plated them without a seed layer. The graph in Figure 4-12 shows the nucleation density seen from this series of experiments. In this experiment the untreated surfaces showed the greatest amount of nucleation density, which is unexpected. However, in every case the density is very small with the largest density on the order of $10^{-2}/\mu m^2$ and none of the samples exhibiting any electrical conductivity. As with nearly every other experiment where the relative amount of metallization was small, the trends showed that a significant amount of metallization occurred rapidly (time less than one minute), followed by slow subsequent increase in metallization.

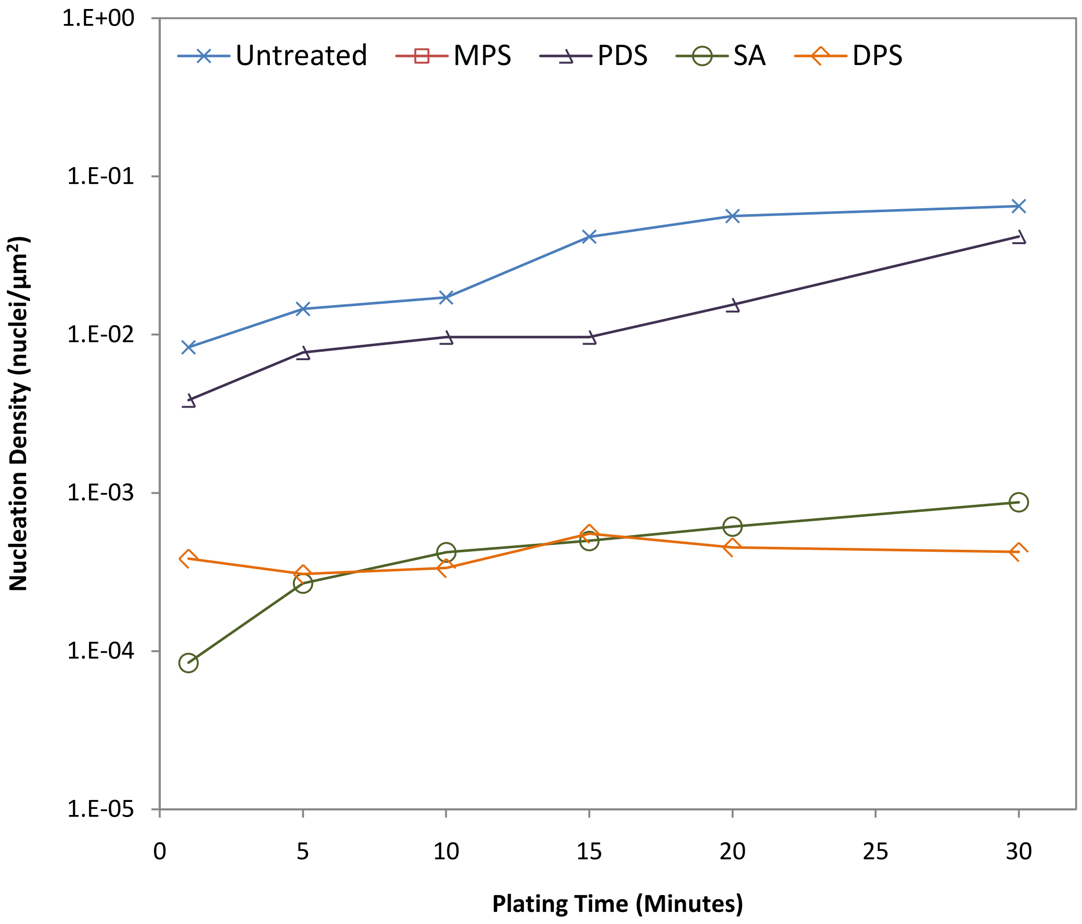


Figure 4-12: Nucleation density of APTES-coated, additive-treated, unseeded surfaces. Lines between points are to guide the eye.

Figure 4-13 shows a series of images that illustrate the nucleation density seen for these samples. The samples exhibited limited metallization with the use of a seed layer, even on APTES-coated substrates.

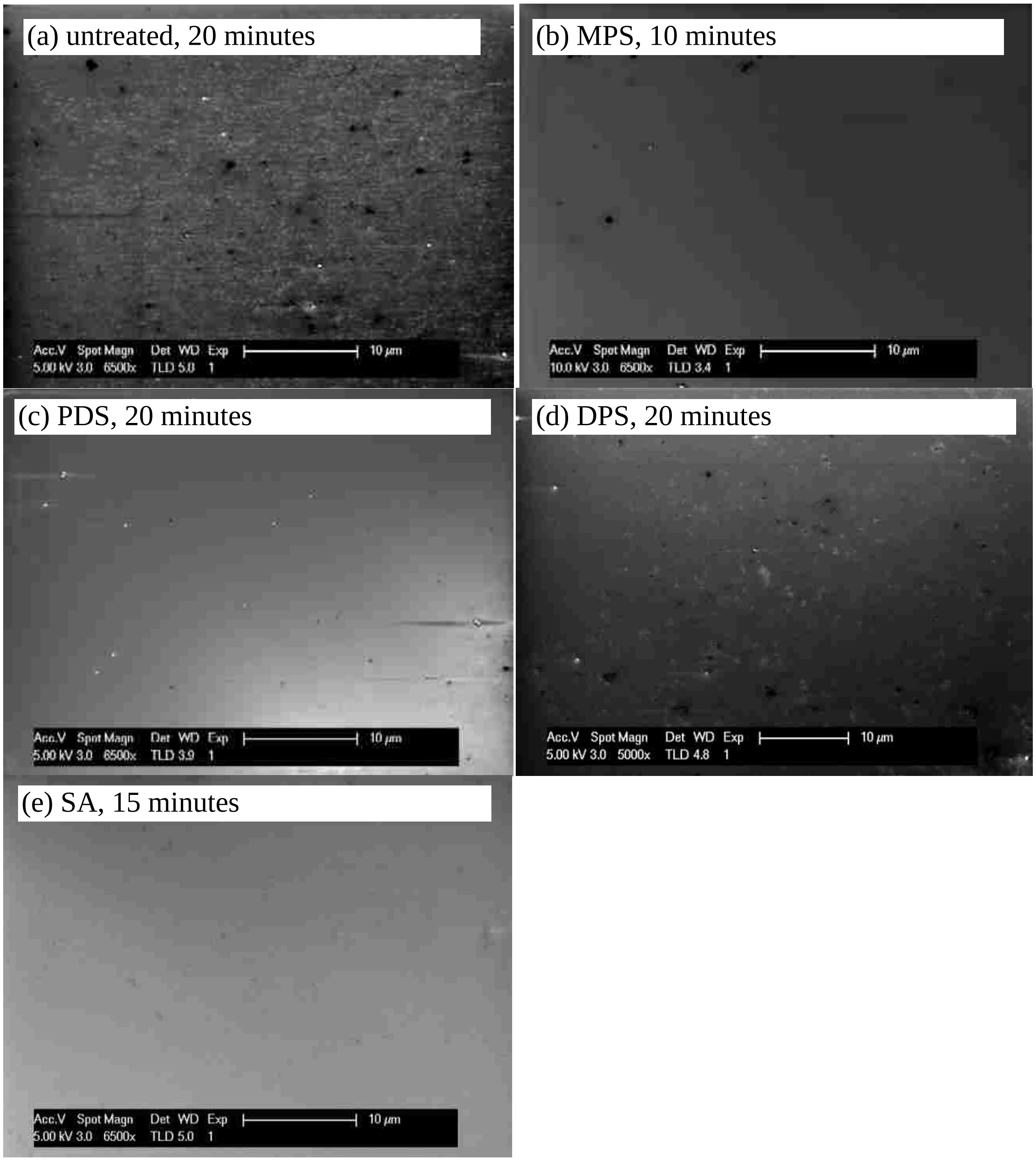


Figure 4-13: SEM image of APTES-coated, additive treated, unseeded samples plated for times indicated. Plating times and additive are indicated for each image.

Pretreated Samples

For another set of experiments we took APTES-coated substrates and pretreated them with an additive, and then seeded and plated to see the effects of pretreatment in the metallization of the surfaces. In these samples MPS exhibited the greatest influence on the metallization as is seen in Figure 4-14 . The MPS-treated samples also exhibited conductivity which is shown in section 4.2.1. Again, the nucleation density generally trends upward in these samples, but there was a degree of leveling off, where the samples did not significantly increase in metallization once reaching a certain density.

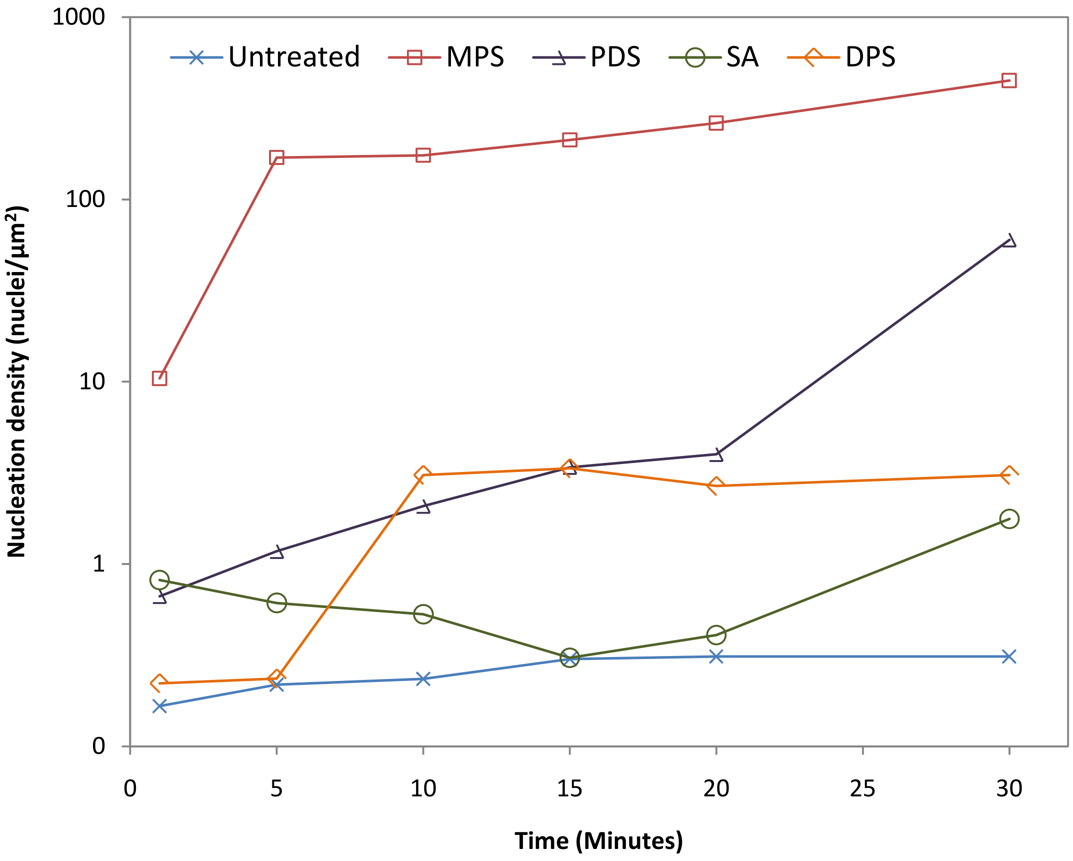


Figure 4-14: Nucleation density of APTES-coated, additive-pretreated, seeded and plated samples. Lines between points are to guide the eye.

Figure 4-15 shows sample images from the above experiments. The increasing metallization is apparent as more and more white areas are visible on the surface of the samples.

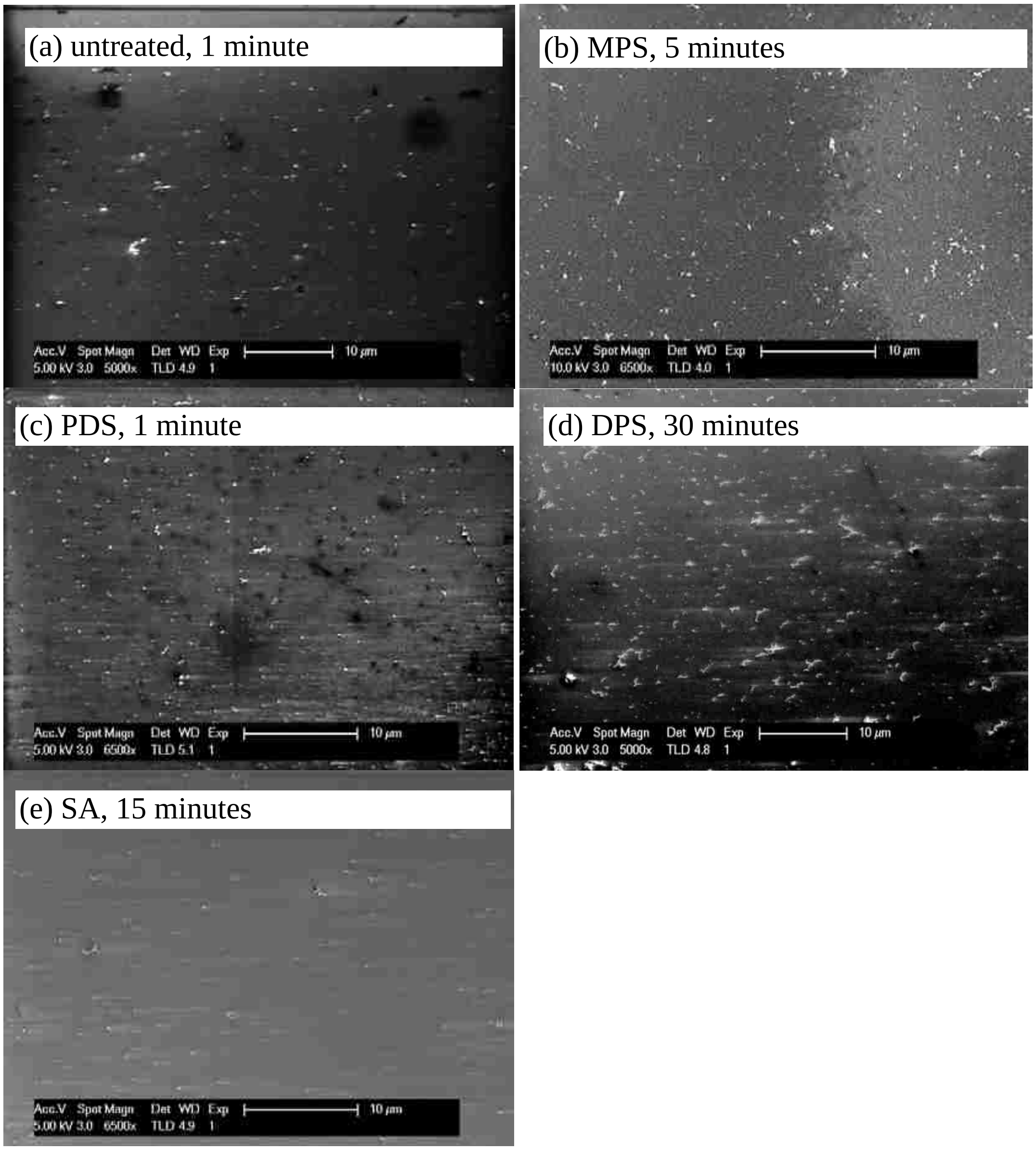


Figure 4-15: APTES-coated, additive-pretreated and seeded samples. Plating times and additive are indicated for each image.

Figure 4-16 shows additional enlarged images of MPS-pretreated samples. As the metallization increases with time, the crystallites enlarge and grow together and begin to fill in the unmetallized gaps creating a more uniform metal surface. Up to around ten minutes plating time the crystallites mostly form a monolayer. By 20 minutes plating time, there appears to be some stacking of crystallites. Based on the size of the metal crystallites these appear to be single crystals.

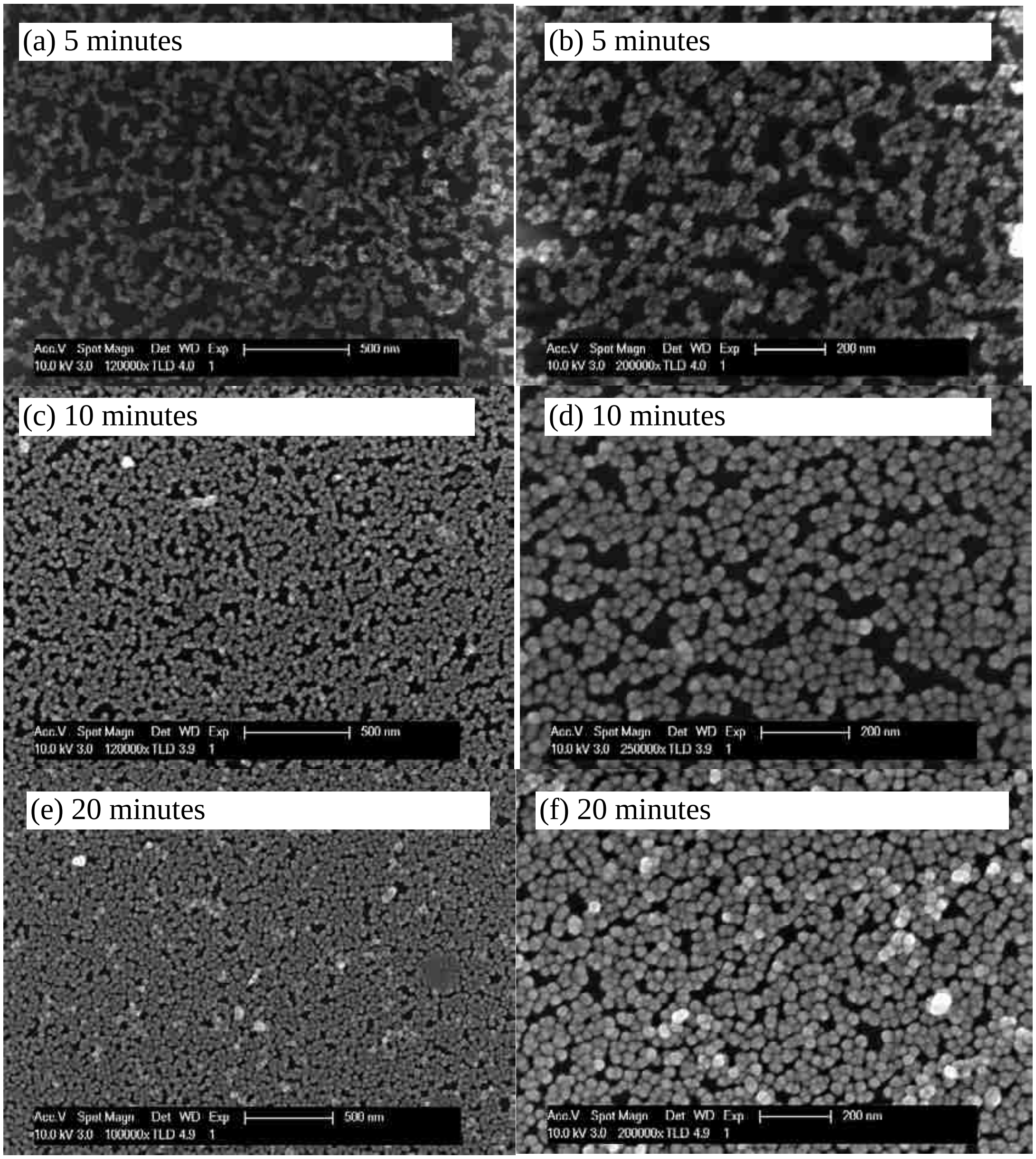


Figure 4-16: MPS-pretreated samples plated. Plating times and scales are indicated for each sample. These images appear to show single crystals bonded together.

Additive Treated Samples

The final set of experiments in this work involves APTES-coated surfaces that are seeded, treated with an additive, and then plated. In this set of experiments, PDS-treated samples exhibited the greatest amount of nucleation density while the other additives showed relatively little effect on the nucleation density of the samples. The PDS-treated samples were the only ones to exhibit conductivity, in contrast to pretreated samples in which PDS, DPS and MPS samples exhibited conductivity following plating. The PDS-treated samples continually increased nucleation density with time, while other additives leveled off and showed very little increase in nucleation density. For PDS-treatment either additional seeds are formed during the plating step, or seeds that are less favorable for growth nevertheless begin to grow.

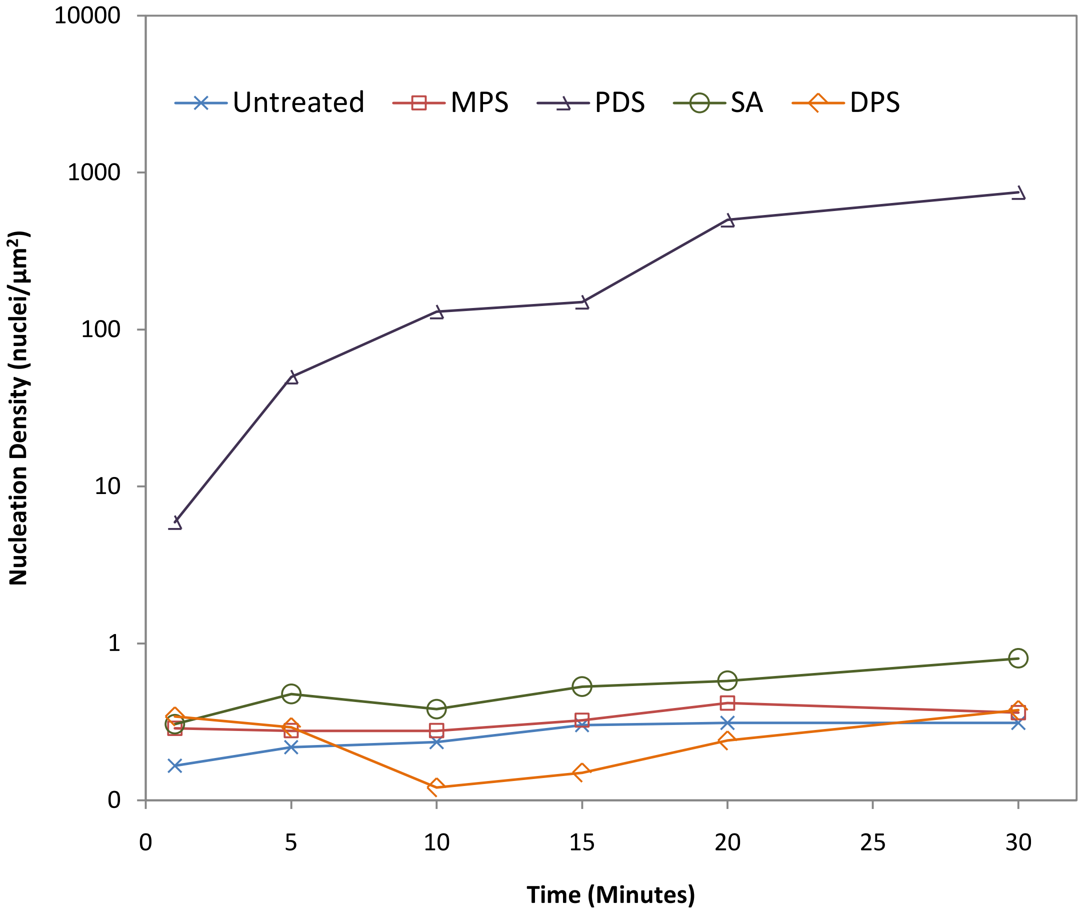
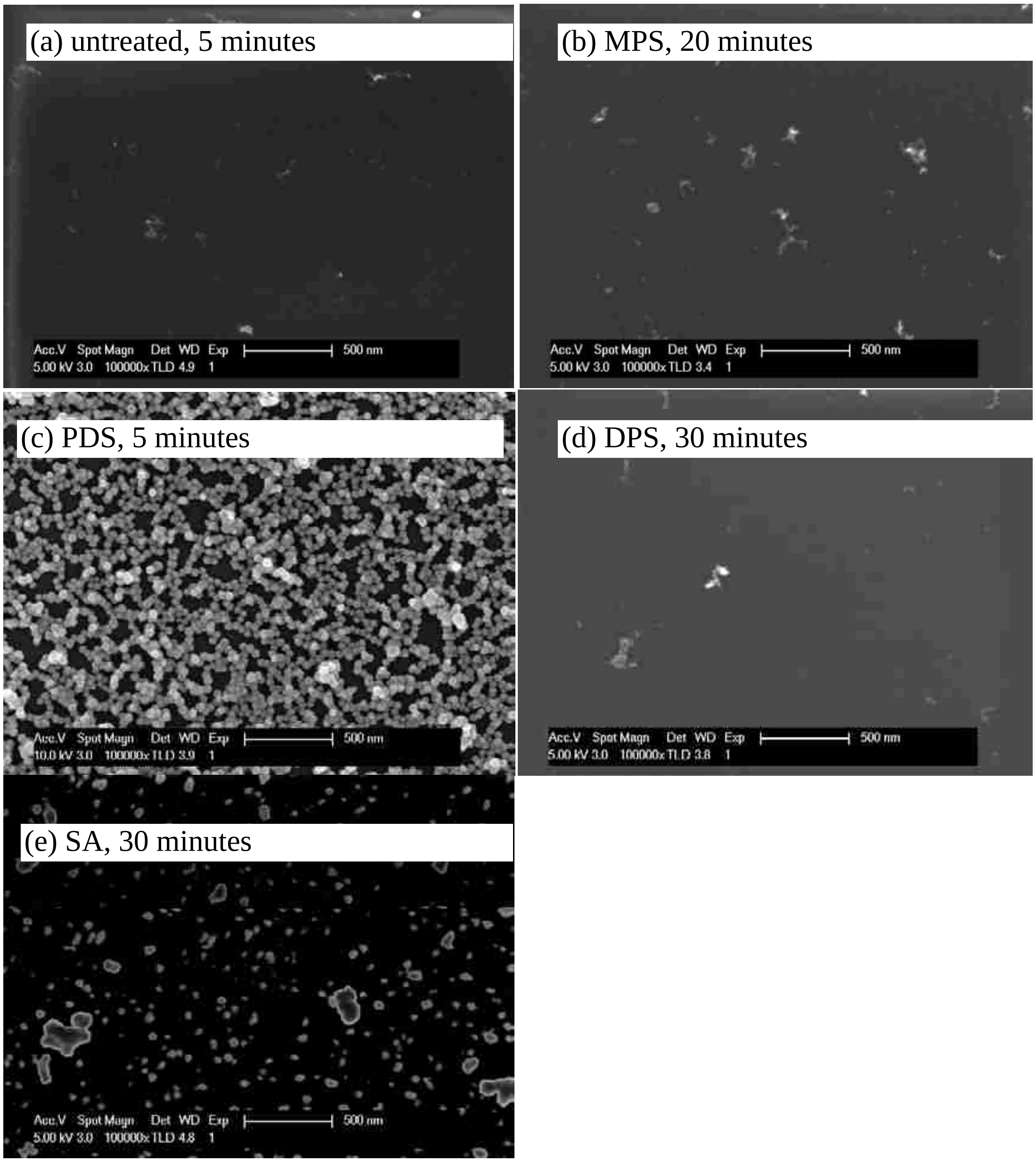


Figure 4-17: Nucleation density of samples APTES coated, seeded, treated with an additive and plated.

The images in Figure 4-18 show the metallization of these samples. The PDS sample image shows near uniform metallization on the surface after only five minutes of plating. The samples other than PDS-treated appear to show little to no plating; rather they show precipitates or other irregular surface structures that cannot produce conductivity.



(a) untreated, 5 minutes

(b) MPS, 20 minutes

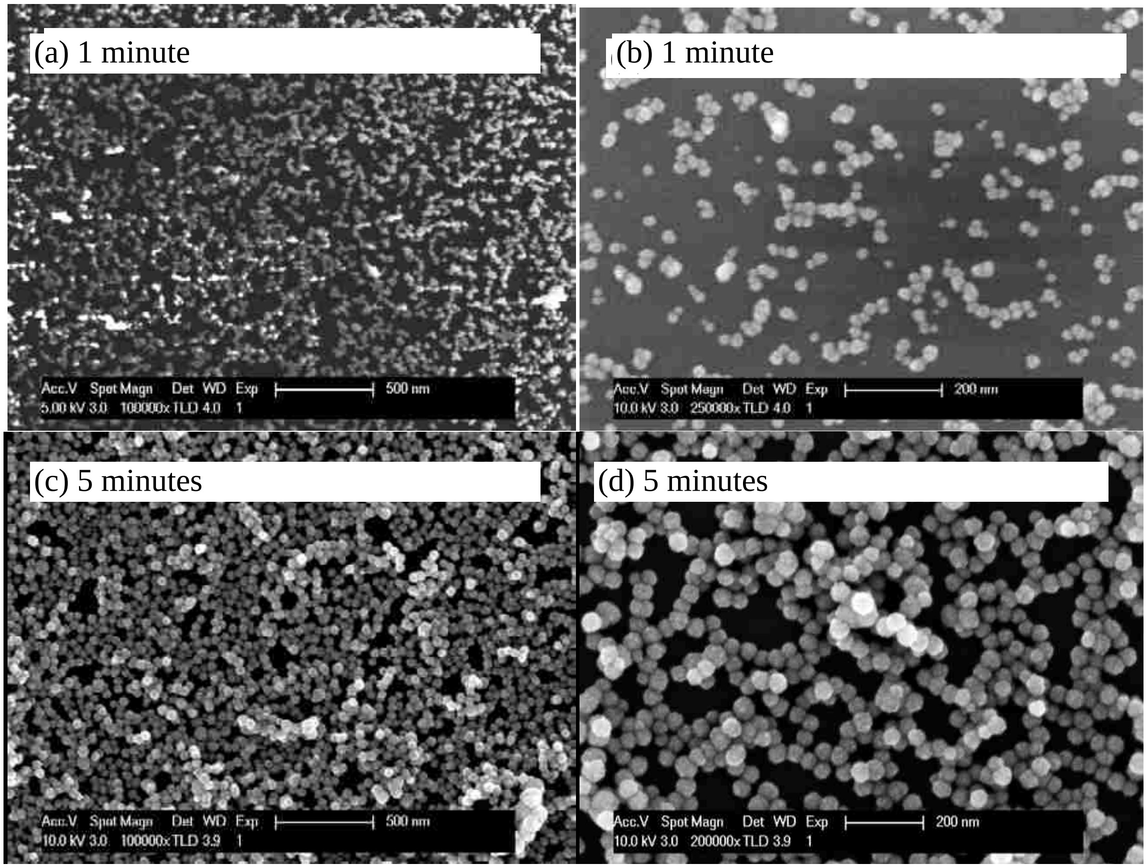
(c) PDS, 5 minutes

(d) DPS, 30 minutes

(e) SA, 30 minutes

Figure 4-18: APTES coated, seeded, additive treated samples plated for times indicated. Plating times and additive are indicated for each sample image.

In Figure 4-19, enlarged images of PDS-treated samples show the growth of the metal clusters over time. At shorter times not all the seeds are visible, but at longer times those smaller seeds begin to plate at the expense of larger crystallites, which is not what would be expected to occur. Due to surface tension, the larger metal complexes would generally attract further metallization, favoring increasingly large metal deposits to form on the surface; instead of many uniform-sized metal deposits as seen in these images. Moreover, the surface chemistry can be quite complicated. Additives can be either accelerating or inhibiting deposition depending on bath conditions [50]. In this case conditions favor the formation of nearly uniform crystallites on nearly all the exposed surface.



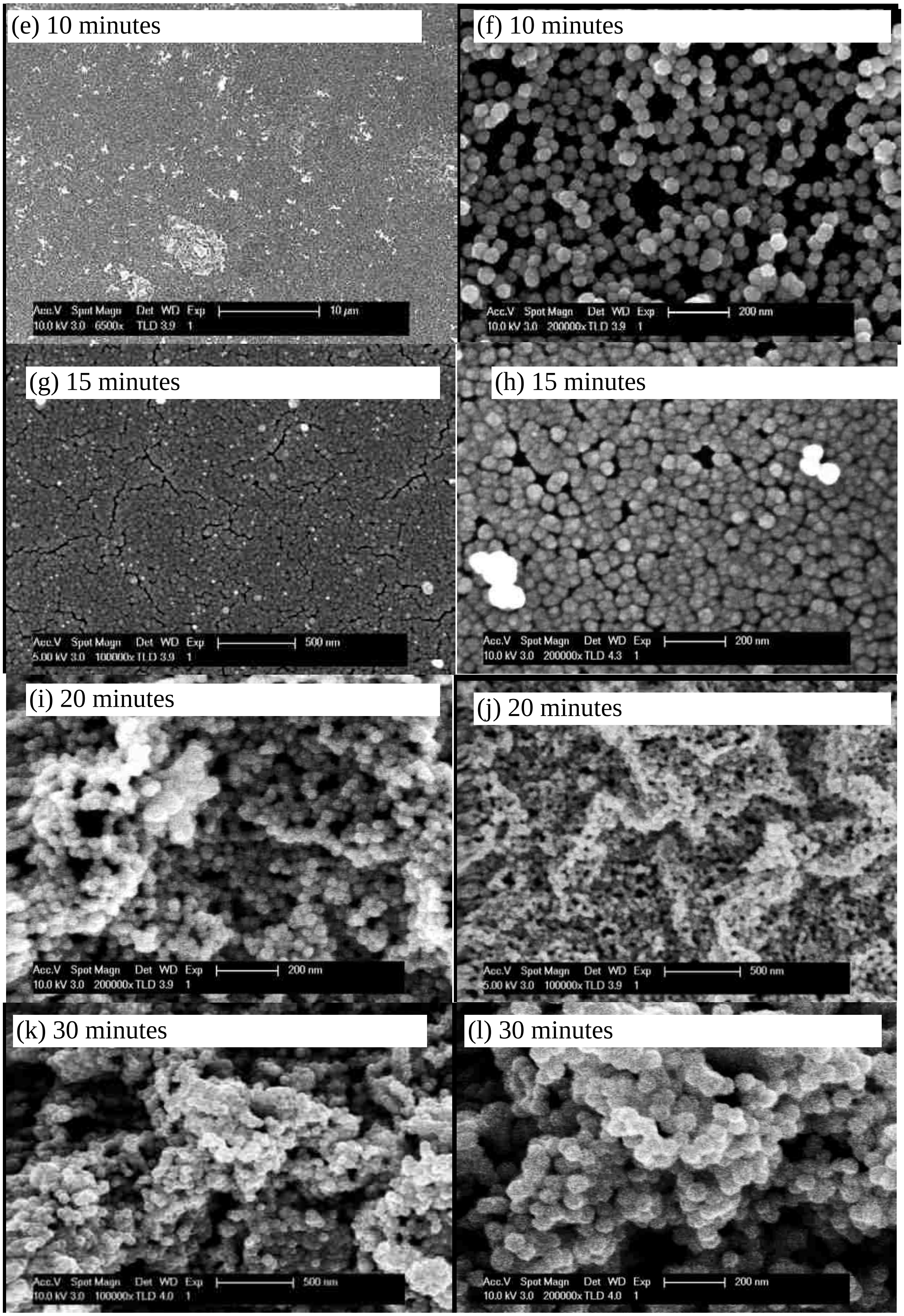


Figure 4-19: SEM images of PDS-treated samples. Plating times are indicated for each sample image.

4.4 Preliminary Observations for DNA Metallization

The ASCENT group is working to combine *top-down* and *bottom-up* methods to achieve nanoscale electronic devices. Within the group, there is work progressing on metalizing DNA to integrate into circuit structures. While this study did not specifically attempt to bind metal to DNA, the use of additives could help overcome many of the difficulties associated with binding metal to the DNA structures. The additives tested here are not the only additives available that could support metallization on DNA.

Within the group there is also work to use AFM scribing to create nanoscale features that can also be metallized. Ongoing work has demonstrated functionalization and metallization in the scribed areas while non-scribed areas showed reduce metallization. The use of additives could easily contribute to this research by providing a means to achieve more uniform coverage of palladium metal in the scribed area with higher selectivity.

As part of this study we did a preliminary test of using the additives on a surface that was covered with DNA and then used plating additives as a pretreatment. Below are some images showing the preliminary test. The DNA was placed on a mica surface shown in Figure 4-20 with DNA heights of around 7 nm. The samples were pretreated with additives, seeded and plated with palladium for 20 minutes. In Figure 4-21 and Figure 4-22 the surfaces showed an increases height to (in some places) 350 nm. There is apparent metallization occurring in this preliminary test, but the metallization may be on the mica or the DNA-further testing is needed. A combination of methods could also achieve the overall metallization goals.

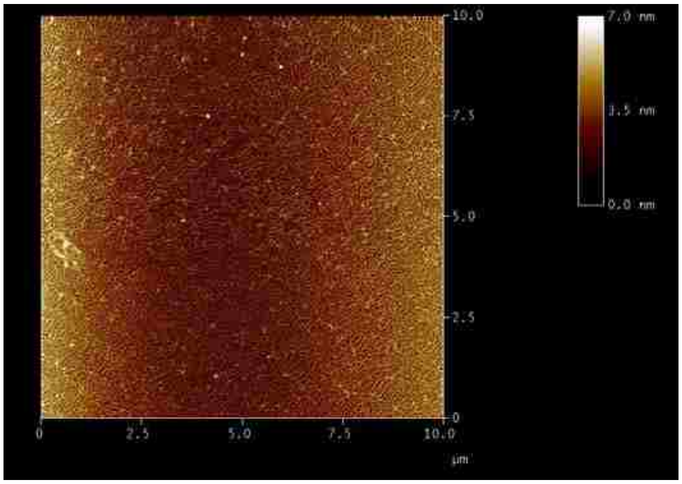


Figure 4-20: AFM image of DNA covered mica surface

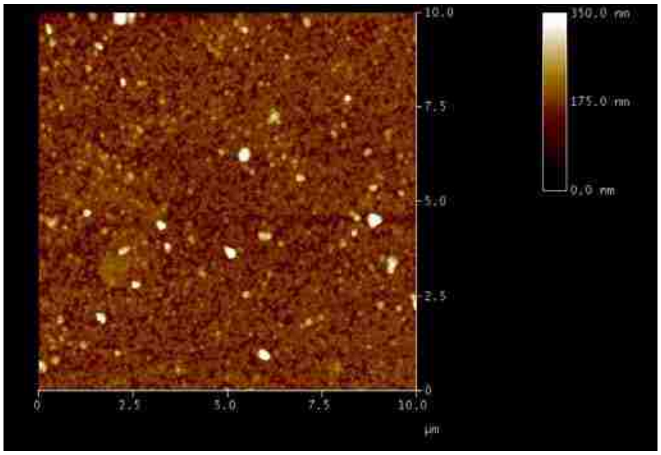


Figure 4-21: AFM image of DNA plated after pretreatment with PDS.

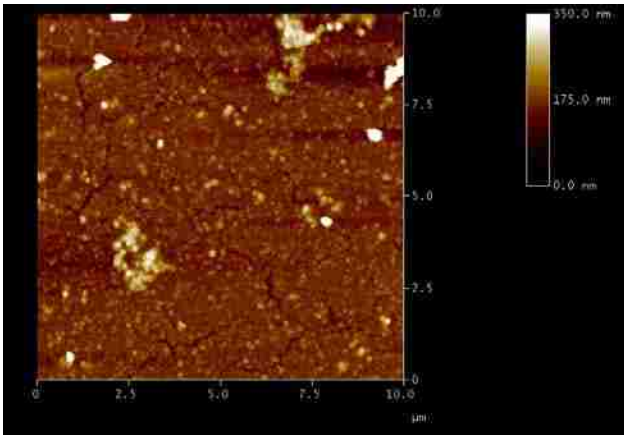


Figure 4-22: AFM image of plated DNA after being pretreated with SA.

4.5 Summary and Discussion

The results given above have shown the influence of additives on electroless plating of palladium under a number of different conditions. The results show that additives can significantly influence the seeding step and the plating step and their use can create conductive metallization on the surface of an APTES-coated insulating substrate. The results also show that additives can significantly increase the selectivity of the metallization. Additives are in no way a complete solution to the problem of using electroless plating for nanoscale devices, but constitute a promising step that can contribute to improved deposits.

4.5.1 Seeding

None of the additives showed any significant ability to promote plating on an unseeded surface. In fact, the untreated samples provided more metallization than untreated samples when no seed layer was present, an unexpected result that needs further investigation. Because none of the non-seeded samples had a large amount of metallization, it is difficult to make a mechanistic conclusion from this observation. However, we believe the additives interact with the seed layer in order to accelerate the plating process.

4.5.2 Additive Pretreatment

In a series of experiments we showed that the use of particular additives as a pretreatment prior to seeding increased nucleation density compared to an untreated sample in every tested case. MPS provided the greatest increase, causing the metal to reach a percolation threshold and allow for conductivity of the sample while the metallized layer was less than 20 nm thick. The percolation threshold is the degree of metallization needed for the metal crystallites to have sufficient continuity for the metal structure to conduct electricity on a macroscopic length scale [51]. PDS and DPS also caused the samples to have greater nucleation density and more quickly reach a percolation point, but the overall efficacy of these additives was much less than that of MPS for pretreatment. SA generates significant increase in nucleation density, but the deposit did not reach a conductive percolation threshold during the times investigated.

In the pretreatment, the MPS appeared to increase the seeding density of the sample. This may be explained by considering the thiol- and sulfonate functionality of the molecule. The sulfonate group is known to attract metal groups to the surface. The MPS molecule has a free thiol and sulfonate on its ends, so a possible mechanism is that the thiol group attaches itself to the surface of the substrate. The thiol groups have been shown to attach to aminosilane surfaces [52, 53]. Also, the chlorine atoms in the seeding solution will compete with surface sites, but they will preferentially attach to the oxide surface layer [42], leaving the amine groups available for thiol bonding. This leaves an exposed sulfonate group to attract metal coplexes to the surface. The additive is attached to the surface, but it moves freely enough to facilitate the binding and reduction of metal ions on the surface of the substrate, resulting in a more densely packed seeding layer. PDS, DPS and SA each have sulfonate groups as well to facilitate metal ions binding to the surface, but PDS and SA do not have a thiol group to bind to the surface for pretreatment. DPS has a thiol ester (not an S-H), but it is not located on a free end of the molecule and therefore is likely not as free to move along the surface if it binds to the surface using the thiol group.

4.5.3 Additive Treatment

Surfaces were treated with an additive after seeding and prior to the plating step. These experiments showed that, as with pretreatment, each additive treatment increased the metal nucleation density over that for untreated samples. PDS provided the greatest amount of metallization, with it easily producing a percolation point where the resulting conductivity approached that for bulk Pd metal. The selectivity ratio for PDS-treated samples was much better than for all other additives tested. Nevertheless, each of the other additives showed a significant selectivity and conductivity increase over untreated samples.

A possible mechanism for the effect of PDS is similar to that proposed for MPS. PDS has a sulfonate functionality on each end that attracts metal ions and is mildly attractive to metal [42]. The PDS molecule probably attaches to metal seed sites on the surface of the substrate and subsequently attracts more metal ions to the surface during the plating process. At the same time, PDS is probably fairly mobile on the surface. From our experiments it appears that surface-adsorbed PDS penalizes the growth of larger crystallites to allow for growth of a uniform crystallite layer. The other additives all contain sulfonate functionality, but not dual sulfonate functionality and so operate in a slightly different manner. The sulfonate group on one end binds to seeds on the surface, while the opposite end sulfonate attracts metal ions to bind to nucleation sites. The thiol group present in MPS may attach strongly to the seed-layer metal and then effectively block further reduction of metal ions, due to the high bond energy of the sulfur-palladium bond. SA has a free sulfonate group on one end, but an amine group on the other that does not facilitate binding to the seed layer. DPS has a free sulfonate group, but its other end has a methyl group that is not likely to easily bind to the metal seed on the surface.

For the samples with additive pretreatment and treatment, the rate of palladium reduction on the substrate could be explained by the Sabatier principle [54]. This principle states that for any heterogeneous reaction, there is a binding energy of species to the catalyst that is “just right” or allows adsorption and diffusion of reactants without impeding desorption of products. In this case, a weak interaction between metal ions and adsorbed additive would provide very little metallization, while too strong of an interaction would block metallization. In this system, the DPS and SA seem to exhibit too weak of an interaction, while MPS as a treatment is too strong.

Another observation is that the rate of metallization tapers off after an initially large rate. The cause could be as follows. Both additives are present at the surface of the substrate, but as metallization proceeds both additives could become consumed by incorporation into the deposit. The additive will then become less effective by chemical modification or reaction, or be desorbed by concentration driving forces. This may explain the leveling off of the thickness of the metal. An alternative explanation for this tapering off is that the metal bound to the surface increases, it will increase the radius of curvature. The radius of curvature will then reduce the available area for metal ions to reach the surface to bind to adjacent metal ions.

4.5.4 Time Analysis

The plating experiments in this study showed increased metallization with time. The time used for plating the sample is not that important. In fact, increasing the plating rate may lead to less selectivity. The important point is that additives can increase selectivity, conductivity and uniformity of the metal deposit in templated regions. If the use of an additive satisfies those requirements at a certain point in time then that particular additive at that particular plating time in the best choice of metallization protocol.

4.5.5 Conclusions

The use of electroplating additives with a sulfur- or sulfonate-containing functional group can provide an advantageous chemical interaction on the surface of the substrate that increases nucleation density, provides conductive metal on the surface and can improve overall selectivity of the metallization. Table 4-1 contains a qualitative summary of the main findings from this study. The cutoffs for determining the nucleation density differentiation between low/medium was 0.01 nuclei/μm^2 and for medium/high were 1.0 nuclei/μm^2. The cutoffs for selectivity were a ratio of 100 for low/medium and 1000 for medium/high. The conductivity was determined by the samples that exhibited resistance within the limits of the instrument.

Table 4-1: Qualitative Summary of Findings

		Desirable Qualities		
Treatment		Nucleation Density	Selectivity	Conductive
non-APTES coated	MPS Pretreated	Low	N/A	No
	MPS Treated	Low	N/A	No
	PDS Pretreated	Medium	N/A	No
	PDS Treated	Low	N/A	No
	DPS Pretreated	Medium	N/A	No
	DPS Treated	Medium	N/A	No
	SA Pretreated	Low	N/A	No
	SA Treated	Medium	N/A	No
APTES coated	MPS Pretreated	High	High	Yes
	MPS Treated	Medium	Medium	No
	PDS Pretreated	Medium	Low	Yes (after 30 min)
	PDS Treated	High	High	Yes
	DPS Pretreated	Medium-High	Low	Yes (after 30 min)
	DPS Treated	Low	Low	No
	SA Pretreated	Low	Low	No
	SA Treated	Low	Low	No

In this series of experiments, the disulfonate-containing additive PDS provided the highest nucleation density, highest conductivity and the best selectivity ratio. Overall, PDS provided the most desirable characteristics in the deposit. MPS provided great nucleation density when used as a pretreatment, but it still did not have reach conductivity close to that of the PDS treated samples. We recommend the use of PDS as an effective electroless plating additive for use in palladium electroless plating processes.

5 Conclusion

This chapter contains a summary of the conclusions and accomplishments of this project. It also discusses areas for possible future research and overall contributions of this work to the field of nano-templated metallization. Finally, it contains some lessons learned that may be of benefit to future researchers.

5.1 Experimental Conclusions

The use of additives can improve desirable deposit qualities for electroless plating methods. These interactions were studied for APTES-coated and non-coated silicon oxide substrates. We believe that this is due to the impact of additives on the chemical interactions on the surface. By using these interactions on the surface we can achieve nanoscale-thin, selective, and conductive deposits.

Overall, PDS-treated samples were the most selective and conductive for the tested conditions. The SEM images show improved uniformity in size of metal crystallites and also show that smaller seeds were favored for growth at the expense of larger crystallites, indicating that the additive is controlling the size distribution and morphology of the metallization on the surface of the substrate. Mechanisms were proposed, but further work is needed to confirm this hypothesis. In electroplating, it is known that certain molecules with the sulfonate functionality accelerate plating of metal in the surface. The dual sulfonate functionality present in the PDS molecule provides a probable mechanism for its ability to provide, selective, uniform, and conductive metal deposits on the desired substrate.

This study shows that the use of additives for electroless metallization of nanoscale features is an attractive and simple-to-implement technology.

5.1.1 Overall Scientific Contribution

As this project developed, it became increasingly clear that palladium metallization is not an extensively studied field, and there exists very little research involving additives for use in palladium deposition. Palladium is commonly used as a seed layer for many electroless plating methods. However, palladium itself provides for good conductivity and low oxidation. Thus, this work contributes to palladium metallization technology that will benefit research in developing nanoscale electronic devices.

5.2 Areas for Future Research

5.2.1 Seeding Processes

As mentioned in Chapter 1 and Chapter 2, there are various methods used for seeding. An interesting method is atomic layer deposition. This process can deposit thin layers of metal on a surface. This method could work for small nanoscale features as a seeding process. The use of the additives could then effect uniform metallization of the nanoscale features.

Also, there is an alternative of using colloidal seeding solutions in electroless plating solutions. Colloidal seeding solutions contain large metal complexes in solution that will then attach to the substrate. The use of additives with a colloidal seeding solution was not studied in this work, but it has potential to have similar effects if the colloidal metal particles meet the size requirements. However, colloidal particles may be too large to achieve metallization on the small scales desired in the ASCENT project.

5.2.2 Oxidation States of Palladium

In this work additives were applied to surfaces in a separate step from the seeding and plating steps. However, MPS and PDS seemed to exhibit a reaction or reducing mechanism when mixed directly with the seeding solution. MPS added to the Pd seeding solution would turn the solution dark red color, signifying the formation of a Pd-ligand complex in the seeding solution. PDS, on the other hand, would change the palladium seeding solution to a dark grey color, possibly indicating formation of colloids or precipitates. Investigating the oxidation and binding states of the Pd complexes would be useful to better understanding how MPS affects the seeding process. The NMR instrument at BYU does not currently have the capability to test for Pd oxidation states, but it is not too difficult to modify the NMR to get this information.

5.2.3 XPS

We wanted to get a quantifiable measurement of palladium metal on the surface of the wafer. The best method that was available to us was XPS. Unfortunately, the XPS instrument at BYU was broken for most of the experimental time available for this work.

We were not able to quantify the amount of metal on the surface through XPS scans. A step analysis, where the sample is tested on the XPS after each successive step, may be able to show if the additives are binding to the surface. On the other hand, the XPS sulfur peak and silicon peak are so closely positioned that it is not reasonably possible to differentiate the two peaks on the basis of sulfur atoms alone. If subsequent work could quantify the additive binding to the surface it may provide a clearer picture of the mechanism for the additive effect.

5.2.4 Alloys

As mentioned in Chapter 2, palladium is generally used as a seeding solution for plating of other metals. There is a possibility for the plating of an alloy to maximize oxidation-resistance and electronic conductivity. Searson at Johns Hopkins University developed a plating solution for copper-nickel alloys [16]. These alloys could benefit from the use plating additives to better control metallization of substrates by these alloys.

5.2.5 Organic Solvents

For this study, each of the additives was used in an aqueous solution, but there is potential to use these additives in an organic solvent. One of the great concerns of plating on DNA is possibly denaturing of the DNA through the metallization process. An organic solvent with additives could make the transition to plating of DNA easier. If the organic solvent avoids removing or damaging the DNA then it could possibly provide a means to use additives in the DNA plating process easier.

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