OVERVIEW OF THE MIDOS PROCESS FOR SPONTANEOUS METAL DEPOSITION

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A unique spontaneous metal deposition process (MIDOS – Metal Immersion Deposition from Organic Solutions) using strongly polarizing, low electrically conductiving organic solutions, is being developed. A more noble metal ion in the organic solvent deposits by an electrochemical displacement reaction on the less noble metal substrate. Thin films and activation seed layers, including Cu, Ag, Pd, Au and Pt, have been deposited on a wide variety of substrates including Al, Cu, Ni, Fe and TiSiN. Processing from the organic solutions may offer some attractive alternatives for specific applications, such as for electronic materials and other high technology uses.

The MIDOS (Metal Immersion Deposition from Organic Solutions) process refers to a spontaneous metal deposition system similar to cementation or chemical displacement reactions.[1] The major difference is that organic solutions are used instead of an aqueous media of the type commonly employed. In addition, the organics used are not good ionic conductors, resulting in high resistance, strongly polarized, localized reactions. Because of these unique characteristics, the possibilities for conducting different types of electrochemical reactions in these organics may offer some attractive alternatives in certain specific applications. Examples of metal plating systems[2] that have been demonstrated to produce seed layers and thin films using this new concept are presented.

The spontaneous plating and production of a metal from an aqueous solution is the oldest, ambient temperature hydrometallurgical process known. One of the important initial examples of these reactions was the recovery of copper using metallic iron. The process was called cementation and involved the displacement of the less noble iron substrate by a copper ion dissolved in a sulfate electrolyte. In simple terms, the overall reaction might be given as,

$$Cu^{2+} + Fe = Fe^{2+} + Cu. \qquad (1)$$

in which copper is reduced and iron is oxidized. In an aqueous electrolyte the ions have an ordered sheath of water molecules as the surrounding species, but these are not usually included in the written chemical equation. In the MIDOS process the sheath is composed of organic species.

As a better fundamental understanding of the spontaneous, immersion reactions was obtained, the reaction mechanism was identified as being electrochemically driven. This meant that the overall reaction could be divided into anodic and cathodic half cells, which allowed the individual charge transfer reactions to be physically separated by some finite distance by adding the half cells, shown in (2) and (3) so that the net reaction (1) is obtained.

$$Cu^{2+} + 2e^{-} = Cu \qquad E^{o} = +0.34 \qquad (2)$$
$$Fe = Fe^{2}+ + 2e^{-} \qquad E^{o} = -0.44 \qquad (3)$$

The half cell with the more positive standard potential (Cu in this case) will be the cathode and the iron half cell with the more negative potential serves as the anode. The magnitude of the difference in potential between the two half cells indicates the tendency toward spontaneity or the driving force for the reaction.[3]

Spontaneous reactions might best illustrated using an Evans diagram, which incorporates both the half cell potentials and the theoretical reaction rates or kinetics using polarization curves. A generic polarization curve for a metal (M) is illustrated in Figure 1. An Evans diagram is obtained by combining the reduction arm of the copper polarization curve with the anodic arm of the iron curve. The intersection of the two lines implies the reaction is spontaneous and defines the mixed potential as shown in Figure 2. The value of log i at the mixed potential gives the current density or relative kinetics of the reaction.[4]

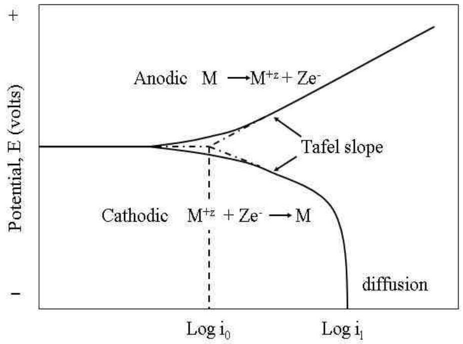


Figure 2. Generic metal polarization curve

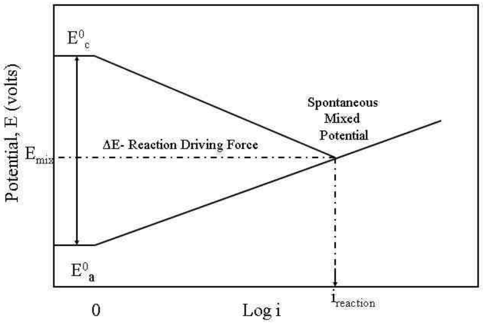


Figure 2. Evans diagram

MIDOS Concept

While immersion deposition using organic solutions is fundamentally similar to the model described above, there are some significant differences as well. The most obvious, and surprising, is that the organic solutions can sustain an electrochemical reaction even though they have very high resistance values and are poor ionic conductors, properties not usually associated with metal plating processes. However, it was shown that electrochemical reactions were possible in the organics, but limited to short range reactions with the anode and cathode located close together..

The concept of using organic solutions with these seemingly undesirable organic electrolyte characteristics for use in electrochemical reactions developed in a rather unexpected way. The original goal of the research was to find a way to selectively separate cations present in metal liquid/liquid or solvent extraction processes. Most all the organic extractants and solvents used in these operations are poor electrical conductors and the metal ion separations are based on a chemical driving force difference for the ions to transfer between an aqueous and organic phase. For example a cation may be loaded from a dilute aqueous solution (transfer from aqueous to organic) at a high pH and then stripped or removed using an acidic, low pH (transfer to the aqueous from the organic) solution. In this case, changes in hydrogen ion concentration, or pH, will shift the equilibrium or stability of the metal ion between the aqueous and organic phases.

There are four types of organic extractants used to carry out the desired solvent extraction reactions and they include:

1. Solvating extractants – (TBP or tri-n-butyl phosphate)
2. Cation exchange extractants – (DEHPA-di(2-ethylheyl) phosphoric acid)
3. Chelating extractants – (Lix64-liquid ion exchange)
4. Anion exchange extractants – (Alamine - 336 tri-n-octylamine)

The ability to purify, concentrate and recover cations using solvent extraction is well documented, but the mechanism for metal ion separation is always based on a chemical driving force. With the MIDOS concept an alternative electrochemical driving force is introduced, which allows localized spontaneous redox reactions to occur allowing the direct deposition of metals in the organic by an immersion displacement mechanism.

As shown previously for aqueous immersion plating, a simple expression for plating from organics would be:

$$\text{R-M}_2 + \text{M}_1^{o} \rightarrow \text{M}_2^{o} + \text{R-M}_1 \qquad (4)$$

The reaction is shown schematically in Figure 3. The R represents one of catagories of organic extractants listed above and the equation (4) indicates that both metals M_1 and M_2 must be soluble in the reacting solution. The simplified flow sheet for the MIDOS process is given in Figure 4. After loading from the aqueous solution, M_1 is solubilized by means of the stabilizing organic R extractant and will serve as the more cathodic or noble species, which is reduced and deposits in metallic form. The extractant (R) chosen must also form a stable chelate with the less noble or anodic species M_2, which is oxidized and dissolves into the solution.

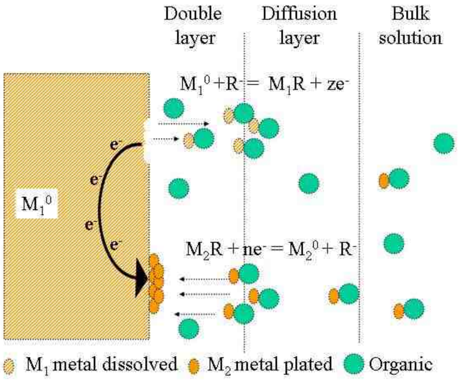


Figure 3. Schematic illustration of a MIDOS reaction

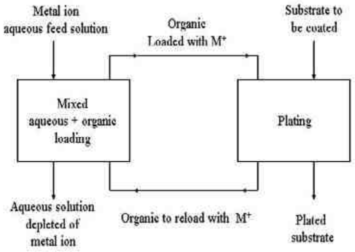


Figure 4. Generic flow sheet for MIDOS process

Process Parameters

There are many options in choosng the R extractant and the range of organics that are potentially applicable to a given M_1/M_2 system is large. Some examples of metal ion/metal substrate plating systems that have been demonstrated using the organic solutions is given in Table 1. One or more of the four types of organic extractants described previously were used in plating these metal systems.

The generic MIDOS plating bath consists of single or mixed organic extractants, chosen to be compatible with the metal/ion systems involved. An organic diluent, for example kerosene or other appropriate organic, is also used at concentrations between 20% to 90% of the final solution to control solution properties, such as viscosity. Organic and/or inorganic additions can be used to enhance the plating process or the properties of the metal phase deposited, similar to aqueous processes.

The final organic solution may also be formulated to be either one or two phases. Low concentrations of water may be present, usually in a range of 0.1% to 5%. The values are dependent on the saturation levels for the organics involved and the fact that water can be added intentionally to give the desired morphology of the plated metal. Etching of the metal substrate may be a pre-treatment step or accomplished in the organic solution by providing in-situ etching or surface activation. The plating reactions are relatively rapid, with times of 10 seconds to 1 minute being sufficient for most applications.

The temperature of the plating bath is usually about 20^o to 30^oC, but may be slightly higher. The deposition reactions are conducted in air at ambient pressure. Under some circumstances an inert environment (e.g. nitrogen or argon) may be used if any of the ions present are susceptible to oxidation.

An electrochemical displacement reaction is proposed as the mechanism for plating. However, in certain instances, deposition appears to have characteristics similar to electroless plating. This obviously depends on the formulation and make-up of the bath and the anodic and cathodic reactions occurring, and additional research is needed to verify the actual mechanism involved.

The morphology and properties of the metals deposited can be altered to fit the application not only because of the wide range of choices available but the ability to mix the various organic extractants for the composition the organic solution.

Table 1
Examples of Metals/Substrates Plated Using MIDOS Process

Metals Plated

Cd Pb Ni Co Sn

Cu Ag Au Pd Pt

Substrates

Al Mn Zn Fe Ni Cd Ag Au

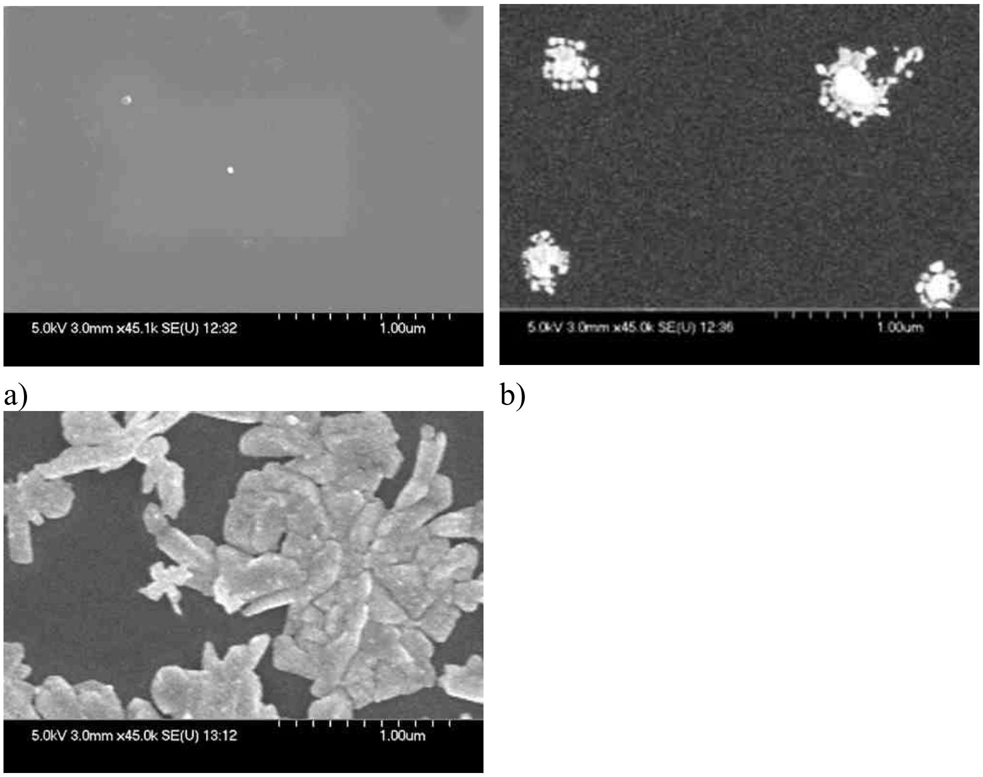
Ta TaN Ti TiN TiSiN TaSiN WSiN

MIDOS Process Parameter Effects

Ag deposition on thin film TiSiN on Si Wafer

Silver crystal seed layers are reported to act as a catalyst for Cu electroless deposition on a TiSiN thin film on a Si wafer substrate.[5] Screening tests showed that Ag could also be plated using the MIDOS process. A series of tests were then conducted to determine the effects of selected operating variables on the MIDOS deposition of Ag on a TiSiN starting substrate and the results are described in the following sections

1. Two phase additive effect - Silver (to 500 ppm) was loaded into the organic solution from an aqueous solution containing silver nitrate. A 2v% aqueous etching solution was added into the organic solution to provide in-situ etching. The aqueous etch did not completely dissolve into the organic phase, resulting in a two-phase, emulsified seeding solution. Next a soluble metal cation and organic additive were also added and the seeding of Ag on TiSiN was increased as shown in Figures 1 a, b and c.



a) b)

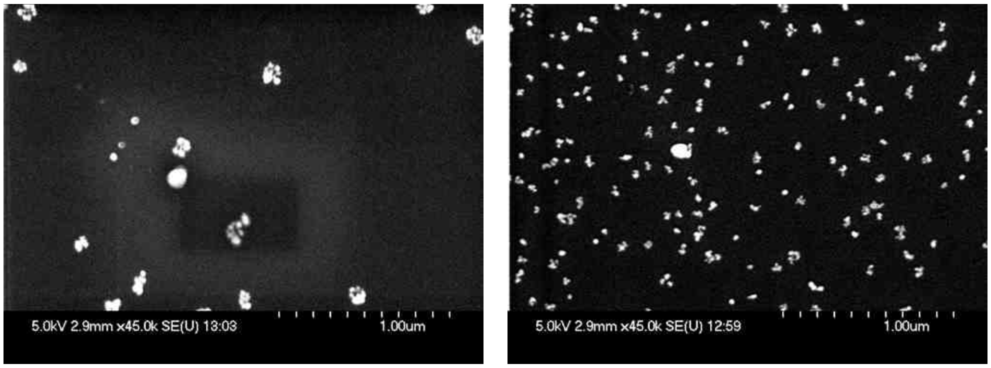
c)

Figure 1. *a) Ag + in-situ etchant b) Ag + in-situ etchant + metal cation c) Ag + in-situ etchant + metal cation + organic additive.*

Without the metal cation and organic additive there was negligible Ag found on the TiSiN surface as seen in Fig. 1a. With the metal cation added, some large particles were found as shown in Fig.1b, but coverage was poor. With organic additives alone, no obvious particle deposition was found, however, with both metal cation and organic additives in the organic bath, high density metal deposition was found, as shown in Fig. 1c. Chemical analysis using energy dispersive spectroscopy (EDS) verified that the particles are silver with 24wt% surface concentration.

2. One phase and etchant effect - To increase the particle uniformity and density of the Ag seed, the quantity of aqueous etching additive was reduced to maintain a single organic phase of the seeding bath.

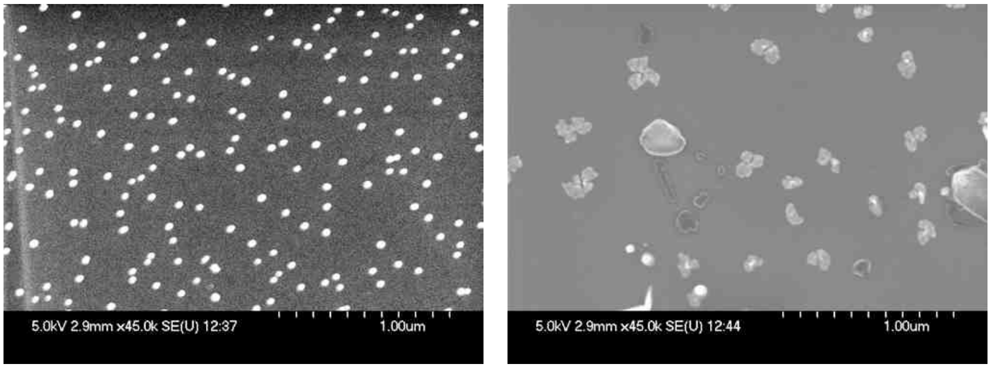
Two different kinds of etching additives, A and B, were tried for in-situ etching, and their concentration was decreased by a factor of 20 compared to that used in the two-phase solution. Comparing Fig. 2a and 2b, etchant B is more efficient for TiSiN surface activation, and gives a denser and more uniform crystal deposition than etchant A. The results show that the proper choice of the type and concentration of the activating etch will affect the nature of the Ag seed obtained.



a) Etchant A b) Etchant B

Figure 2. *Effect of etchant type on Ag seeding of TiSiN.*

3. Time effect – Metal deposition using the MIDOS process is a dynamic and reversible process. Nucleation, growth and re-dissolution will occur with time, to differing degrees, depending on plating conditions. As a result, the morphology of the metal seed is time dependent. As shown in Fig. 3a, after 30 sec reaction a uniform, dense Ag seed was present on the TiSiN. However, after 1 min seeding, as shown in Fig. 3b, many small seed particles dissolved. Some particle growth and agglomeration occurred simultaneously results in a decrease in the density of larger Ag seed crystals. These results show that a longer reaction time may not necessarily result in a denser seed layer and final morphology of the surface depends not only on the deposition rate but the re-dissolution rate as well.

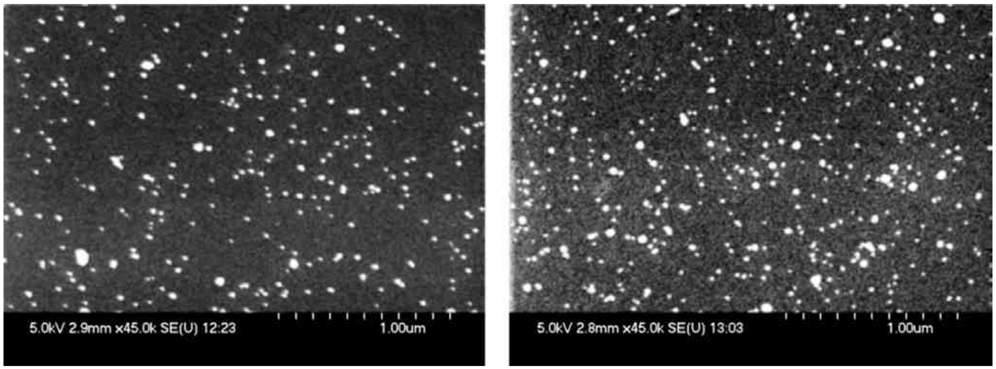


a) b)

Figure 3. *Ag seed crystal distribution after a) 30 seconds b) 1 minute*

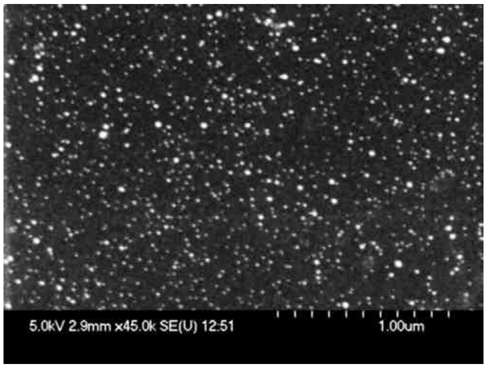
4. Ag and Ag-Cu Seeding - In order to increase the total aqueous additive solubility and maintain the solution uniformity, the organic content of the solution was increased and the dilutent was decreased. The density and particle size improved, as seen by comparing Figures 3a and 4a. Seeding time was 30 sec. in both cases. When Cu ion was added to this solution the seed density increased nearly 50% as seen from Figure 4b. Using the same plating conditions,

the seeding time was reduced to 10 sec an even denser and more uniform morphology was obtained, as indicated in Fig. 5.



a) b)

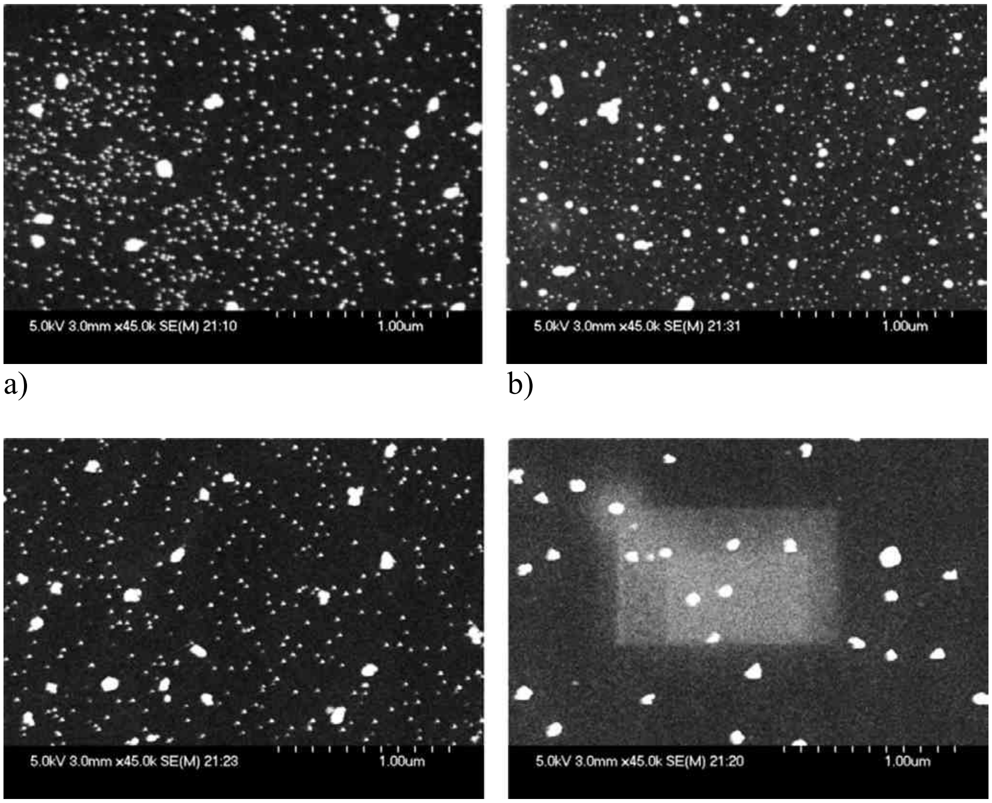
Figure 4. *Effect of (a) increased organic content and (b) increased organic content and Cu additive on Ag seed.*



Ag-Cu10 sec 50T5D45K 0.1HF

Figure 5. *Time effect for Ag-Cu seed.*

5. Diluent effect on Ag deposit - Diluents are used to adjust the extractant concentration and the viscosity of the organic seeding solution. It is preferred to use organic diluents with lower flash points than kerosene for the organic seeding bath. Such diluents include SX-1 (paraffins 86%, aromatics 13%, olefins 1%), and SX-11 (iso-paraffins 100%). Due to their chemical nature, different diluents can change the Ag seed morphology and give a different time effect, as shown in Fig. 6.



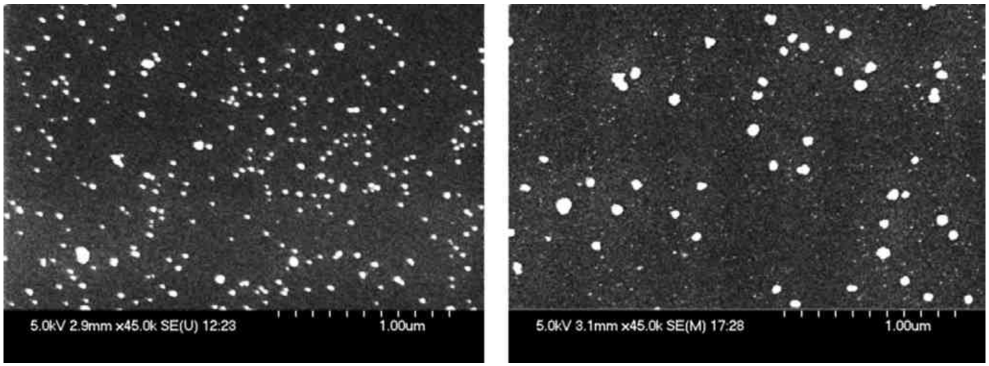
a) b)

c) d)

Figure 6. *Time effect for Ag seed with different diluents. a) SX-1 dilutent, 10 sec deposit b) SX-1 diluent, 30 sec deposit c) SX-11 diluent, 10 sec d) SX-11 diluent, 30 sec.*

Compared to the seed morphology with kerosene as the diluent , given previously, there is an obvious bi-modal structure in the Ag seed crystal with SX the series as the diluent, as shown in Fig. 6a (SX-1) and 6c (SX-ll). Comparing Fig. 6b vs. 6d, the time effect with different diluents is not the same. With SX-1, a longer seeding time will enhance the bi-model structure by decreasing the smaller particle sizes and increasing the larger ones. With SX-11, the bi-modal structure was eliminated but at the expense of dissolving all the small seed particles.

6. Ag-Pd two-step deposition - silver seed was first deposited on TiSiN using the one phase bath containing 300 ppm Ag (see Fig. 7a). Then the Ag seeded substrate was rinsed and put into a second bath containing 70 ppm Pd. As seen in Fig. 7b, the seed density and particle morphology changed after the second seeding step, and EDS analysis shows both Pd and Ag are present on the substrate. The composition was determined to be Pd 1.7wt% Ag 5.2 wt %, showing that seed crystals consisting of more than one metal are possible.

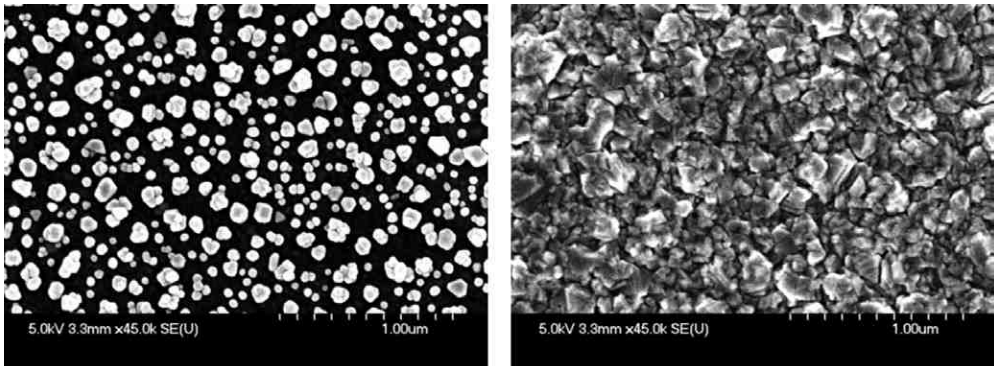


a) b)

***Figure** 7. a) Ag seed 30 sec b) Ag seed plated for 2 min in 70 ppm Pd bath containing organic additive*

Cu deposition on TaSiN

TaSiN is a promising candidate as a barrier layer for silicon wafers. Build up of the conductive Cu can be by electroless deposit on a metal seed activated TaSiN barrier. Fig. 8a shows the Cu seed deposited from a two phase organic solution; EDS and XPS verified the particles are Cu with a surface concentration about 12wt%. A complete and uniform electroless Cu layer was deposited on a similar Cu seeded substrate as shown in Fig. 8b.



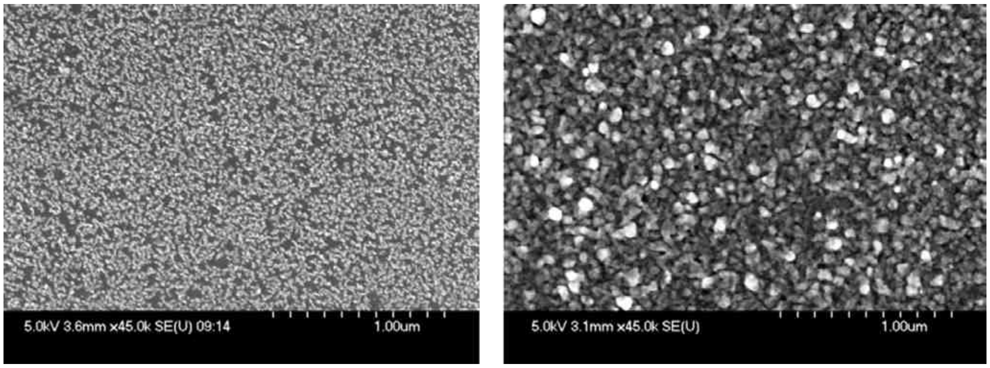
a) Cu seed (500pm) from two phase organic

b) after 2min electroless

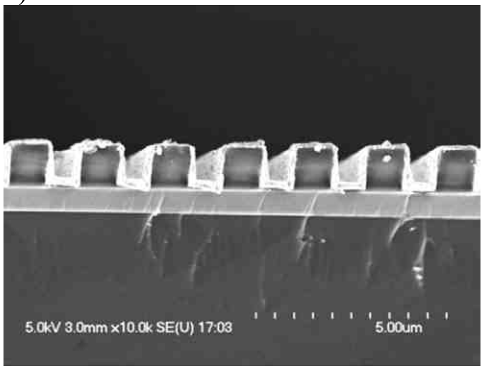
***Figure 8.** Electroless Cu coating on Cu seeded TaSiN barrier layer.*

Pd-Cu co-deposition on TiSiN

Similar to Ag deposition, incorporating a metal cation such as Cu, into the organic bath, can also increase the density of Pd deposition on a TiSiN barrier layer. As shown in Fig. 9a, a high density and uniform metal seed layer was made on TiSiN with Pd-Cu co-deposition. EDS and XPS show both Cu and Pd are present (Pd 5.41w%, Cu 1.22w%). A smooth, shiny Cu electroless film was obtained on this seed layer, as shown in Fig. 9b. When the Pd-Cu co-deposited seed was used to electroless Cu coat a patterned wafer (4:3 feature) a conformal, uniform layer was obtained as shown in Fig. 9c.



a) Pd-Cu seeded b) electroless Cu coated



Cross section of Cu electroless coating on
patterened TiSiN after prior seeding with Pd-Cu.

Figure 9. *Electroless Cu coating on Pd-Cu seeded TiSiN barrier layer.*

<u>Alternative Applications</u>

In addition to using the MIDOS process for making final product seed layers or thin films, the concept is also applicable in environmental control and the scavenging or purification of electrolytes. Depending on the impurity ion present, there is a possibility that it can be selectively separated from the bulk electrolyte by extracting it into a suitable organic. The concentrated impurity could then be recovered in solid form directly in the organic solution using the MIDOS concept, which eliminates the need for another aqueous solution and allows direct recovery of the metal. In concentrated form the metal is easily handled and can be more easily treated.

It is not mandatory that the cathodic step in the electrochemical reaction give a solid product as was described previously. For example, a half cell reaction could involve a decrease in valence, then both the product and reactant would be ions,

$$M_1^{+3} + e^- = M_1^{+2} \qquad (5)$$

Reactions of this type have also been demonstrated using the MIDOS concept and include:

$$Fe^{3+} + e^- = Fe^{2+} \qquad (6)$$
$$Ce^{4+} + e^- = Ce^{3+} \qquad (7)$$

The ferric/ferrous reaction is particularly interesting in that it provides the opportunity to remove ubiquitous iron impurities that can be readily recovered in a soluble or easily handled form. The Fe^{3+} is difficult to selectively separate and recover from aqueous solutions, particularly in terms of an efficient, collectable form that does not, in itself, present an environmental problem. The MIDOS concept can be applied to solve the problem by selectively extracting the Fe^{3+} into the organic phase and then reducing it electrochemically to Fe^{2+} directly in the organic phase.[5]

The Fe^{3+} is strongly extracted into the organic, but it so stable that removal in this form is difficult. For example, for the effective removal and stripping of the Fe^{3+} it is necessary to use 6N HCl. However, if the Fe^{3+} is reduced to Fe^{2+} directly in the organic using a less noble metal, such as Zn, Al or even metallic iron, removal is much easier. The Fe^{2+} can then be stripped or separated in concentrated form using a dilute acid (H_2SO_4, HCl, etc) at pH values of 1.4 to 2, which is much more desirable than using very strong acids.

This specific application has been demonstrated at the laboratory and pilot plant levels. A sulfate solution containing Zn^{2+} and Fe^{3+} was treated with DEHPA to load the Fe^{3+} into the organic. The Fe^{3+} was converted to Fe^{2+} directly in the organic using metallic Zn powder. The Fe^{2+} was then stripped into a concentrated $FeSO_4$ solution that could be used for water treatment. Other recovery methods included electrolysis to form pure iron and evaporation to produce $FeSO_4$ crystals.[7]

Summary

An overview and description of the MIDOS process and examples of selected metal ion/metal systems used to plate seed layers or thin films was presented. The MIDOS concept is similar in theory to aqueous immersion displacement reactions. The major unique aspect of the MIDOS process is that spontaneous electrochemical reactions can be readily conducted in very poorly conducting organic media used in the process. A large number of organics are available that are capable of sustaining these plating reactions, which provides a much greater choice for selection of an extractant. This, in turn, allows a variety of theoretical plating systems to be designed that are potentially capable of giving metal seed layers and thin films with unique properties or that offer alternative process options. The concept is also applicable in environmental control applications. Laboratory studies have shown that metal deposition from organics may offer some novel alternatives to standard aqueous processing in selected applications and the ability to tailor the electrolyte could be useful in designs novel plating systems.

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