Optimization of Cu Seed Deposition from Organic Solution on TaSiN Barrier Layers Using Design of Experiment (DOE) Methods

Jingye Li,[*1] Matthew J. O'Keefe,[2] Thomas J. O'Keefe[2] and David Drain[3]*

[1] *Cookson Electronics, Enthone, Inc., West Haven, CT*
[2] *Department of Materials Science and Engineering & Materials Research Center, Missouri University of Science and Technology, Rolla, MO*
[3] *Department of Mathematics and Statistics, Missouri University of Science and Technology, Rolla, MO*

The conditions for copper particle deposition on TaSiN barrier layers were optimized using design of experiments (DOE) methods. Copper particles were deposited spontaneously from an organic immersion bath for subsequent electroless copper deposition. Seeding time, copper concentration and organic additive concentration were selected as the main factors for a two-level full factorial experiment, augmented with center points. The total coverage by copper particles, median particle size and the standard deviation of the particle size were used as the responses. Statistical methods were used to estimate the effects of these factors and their interactions on the responses, and to identify optimal seeding conditions. A high density, uniform copper crystallite seed layer was deposited using the predicted optimal seeding conditions, and a smooth, shiny, adherent electroless copper film was readily obtained on the seed-activated layer.

Keywords: *Copper particle deposition, copper seed deposition, TaSiN barrier layers, preparation for electroless deposition*

Introduction

Copper is currently being used extensively in the manufacture of advanced silicon integrated circuits. Interconnects can be produced by activating the barrier layer followed by building up copper to the desired thickness with electroless deposition.[1,2] The activation of the barrier layer can initiate the electroless deposition and improve the uniformity and continuity of the copper coating. In this study, a novel method for copper metal crystal deposition from organic solution on the barrier layer was used as the activation step.[3,4] For this process, the solid metal barrier layer surface served as the reducing agent for copper ions, which deposited on the reaction surface by a chemical displacement mechanism. In previous studies, it was shown that the rate of deposition and morphology of the seed layer was directly influenced by the conditions used for deposition.[4] Because of these competing process factors and response tradeoffs, careful optimization is needed to obtain an appropriate balance among the experimental conditions. In this study seeding time, copper concentration and organic additive concentration are the main variables identified to produce the best seed layer properties: crystal size, density and uniformity.

While process optimization can be attempted using a variety of methods, such as changing one factor at a time, in this case a full factorial was selected as the best option. Full factorial experiments can detect factor interactions and are more efficient than one-factor-at-time experiments. These experiments cover all possible combinations of the main factors over a range of interest, allowing for estimation of both main effects and factor interactions. Analysis of variance (ANOVA) was used to assess the statistical significance of the various main effects and interactions. A series of contour plots was used to illustrate response surfaces and determine the optimal seeding conditions.

Experimental

Cu seeding process

All deposition experiments were conducted on unpatterned TaSiN (95% Ta, 4% Si, 1% N) diffusion barrier films sputtered on glass. The substrates were rinsed with deionized water and acetone and pre-etched with 25 vol% HBF_4 for 40 sec prior to seeding with copper. The detailed procedure for the organic seeding solution preparation can be found in Reference 4.

The seeding solution was maintained at a temperature of 35°C. The pre-treated TaSiN substrate was placed on the bottom of the seeding solution container and allowed to react from 5 to 30 sec with ultrasonic agitation. The specimen was then removed, washed and placed into an electroless Cu coating bath for 2 min. The electroless Cu bath used in these experiments contained 6 to

* *Corresponding author:*
Dr. Jingye Li
Enthone Inc.
350 Frontage Road
West Haven, CT 06516

8 g/L $CuSO_4$, 40 g/L EDTA and the pH was adjusted to 12.5. The reducing agent was 10 to 20 g/L glyoxylic acid and 75 ppm 2'2'-dipyridyl was added as a stabilizer.

A Hitachi S-4700 field emission scanning electron microscope (SEM) was used to characterize the surface morphology. A Varian SpectrAA-50 flame atomic absorption spectrometer was used to analyze the copper ion concentration. Scion Image software, by Scion Corporation, was used for particle size analysis. Minitab 14 statistical software, by Minitab Inc., was used for the DOE design and analysis of experimental results.

Experimental design

The high and low level values for the factors given in Table 1 were selected based on previous screening tests. The total surface coverage of the copper seed crystals, the median copper particle size and the particle size standard deviation were chosen as the main experimental outputs.

Two replicates were made to provide an error estimate for an analysis of variance. The total of 18 test specimens required was separated into two blocks, with a complete replicate and a center-point in each block. Each block was processed separately. After the first two blocks were completed, some additional treatment combinations were tried as part of a D-optimal design as a third block. The run order within each block was randomized.

The statistical model under consideration was defined as follows:

$$Y = \beta_0 + \alpha_1 Z_1 + \alpha_2 Z_2 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_{11} + \beta_{22} X_{22} + \beta_{33} X_{33} + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \varepsilon \quad (1)$$

- Y: output; X_1: Time; X_2: Cu concentration; X_3: organic additive concentration; $X_i X_j$: interaction of i and j factors.

- The Z_i are dummy variables indicating block membership as follows: $Z_1 = 1$ when sample is in Block 1, and zero otherwise; $Z_2 = 1$ when sample is in Block 2, and zero otherwise. If both Z_1 and Z_2 are both zero, the sample was in Block 3.

- α_1, α_2, β_0, β_1, β_2, …, β_{23} are unknown parameters to be estimated.

- ε are random error terms, assumed to be independent, identically and normally distributed with zero mean.

Results and discussion

Initial model analysis

Figure 1 shows the SEM pictures of copper seed crystals deposited on TaSiN substrates from the first block of the experimental design. The difference in copper seed morphology between each setting is quite apparent. For example, with increasing time, the copper nuclei continue to grow and agglomerate, resulting in the highest level of coverage (Figs. 1e, f and g). With a low concentration of the organic additive, the copper nanoparticle density and average size are relatively low (Figs. 1a, c and e). A very dense, uniform copper seed crystal layer was obtained with the middle point (Fig. 1i). As expected, there are some variations in morphology for the same experimental conditions between blocks but the general trend of each main factor's effects on the morphology is the same regardless of block.

Table 1

Factor levels for the experiment

Factor (units)	Factor level		
	Low (-)	Center (0)	High (+)
A: Time (sec)	5	12.5	20
B: Cu^{+2} concentration (ppm)	50	175	300
C: Organic additive (vol%)	5	17.5	30

The initial statistical analysis results by *p*-values are shown in Table 2. The decision guideline used for effect significance was to decide the effect was significant only if the *p*-value was 0.05 or less.

Based on the *p*-values in Table 2, the relative significance of the parameters on the outputs is given. For surface coverage the three main factors and the quadratic effect of the Cu concentration (Cu*Cu) all show a statistically significant effect on the response. For size median, only the copper concentration shows a significant effect. The factors with *p*-values less than 0.20 are retained in the refined model because of their apparent explanatory power and near-significance. The other factors, such as organic additive concentration, which have higher *p*-values, do not have significant effects. Figure 2 shows the examples of main effects (a) and the interaction plots between main effects (b) for the outputs, which visually illustrate the relative significance of the main effects and their interaction.

Refined model analysis

By leaving out insignificant effects, a more parsimonious model was formulated as shown in Table 3. The re-calculated *p*-values for the factors of the refined model are shown in Table 3. A residual analysis to evaluate compliance with the assumptions necessary for a valid ANOVA was also done, and the results lend credence to the validity of the ANOVA assumptions.

Using Minitab, the model coefficients, α_1, α_2, β_0, β_1, β_2, etc., can be estimated for each of the outputs. The final model can be expressed as:

$$Y_{\text{Surface coverage}} = 0.644 - 0.036Z_1 + 0.019Z_2 + 0.088X_1 + 0.122X_2 + 0.143X_3 - 0.271X_{22} + \varepsilon \quad (2)$$

$$Y_{\text{Size median}} = 29.89 - 4.04Z_1 + 2.76Z_2 + 3.29X_1 + 6.13X_2 - 5.23X_{12} + \varepsilon \quad (3)$$

$$Y_{\text{Log particle size standard deviation}} = 1.012 + 0.041Z_1 + 0.039Z_2 + 0.105X_2 + 0.082X_3 + 0.119X_{22} - 0.057X_2X_3 + \varepsilon \quad (4)$$

Table 2
Observed p-values for the experimental design

Term	Coverage	Size Median	Log Size Std. Dev.
Constant	0.000	0.000	0.000
Block 1	0.293	0.174	0.415
Block 2	0.754	0.169	0.439
Time	0.006	0.139	0.328
Cu	0.001	0.005	0.007
Organic additive	0.000	0.760	0.041
Time*Time	0.532	0.268	0.210
Cu*Cu	0.038	0.721	0.074
Organic additive*Organic additive	0.853	0.802	0.443
Time*Cu	0.366	0.436	0.416
Time*Organic additive	0.516	0.712	0.805
Cu*Organic additive	0.683	0.351	0.178

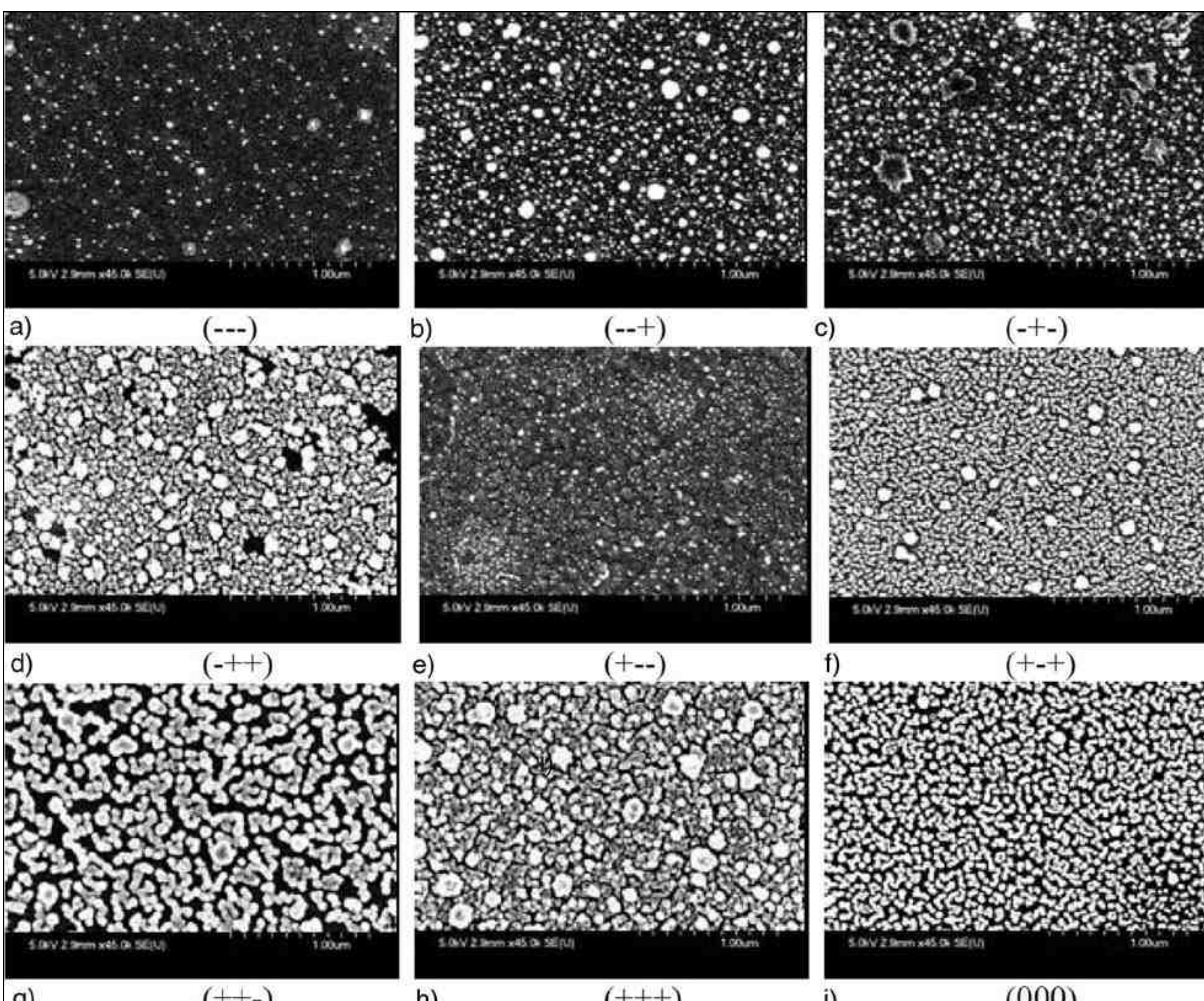


Figure 1—SEM of Cu seeds deposition on TaSiN according to the design of experiment for the variables time, Cu concentration and organic additive concentration, respectively.

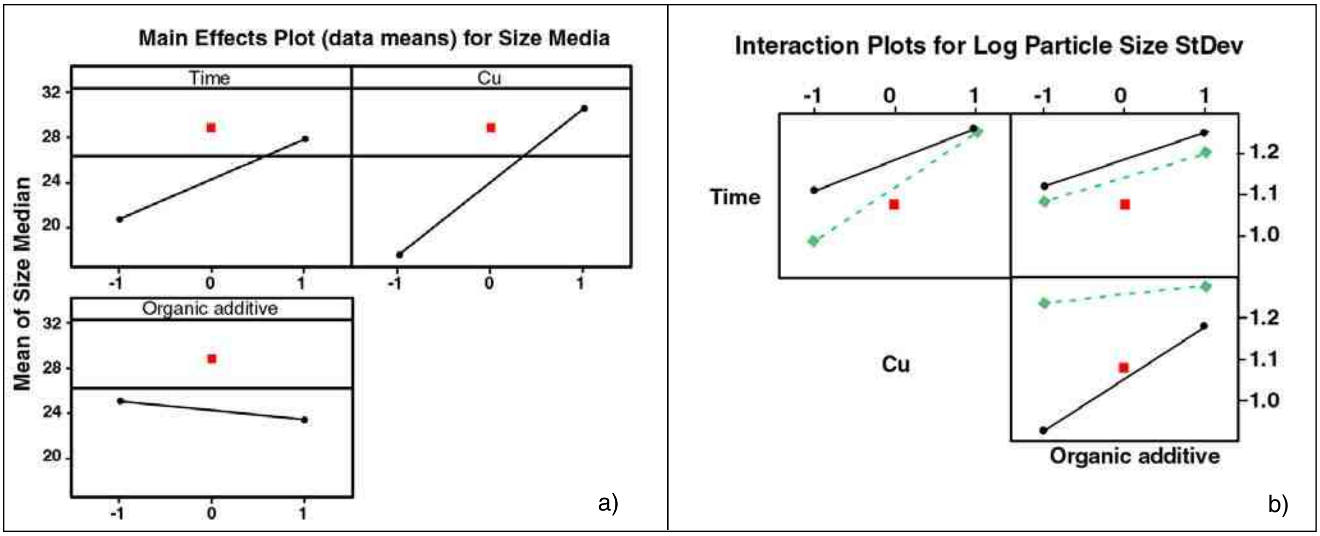


Figure 2—(a) Main effects plot and (b) Main effects interaction plot (Log particle size standard deviation) of the Cu crystal deposition on TaSiN.

Optimizations

Contour plots were constructed based on the above equations to assist in identifying the optimal seeding conditions. As shown in Fig. 3, when the organic additive concentration is held constant at the lower level, an intermediate level of copper concentration and longer seeding time would give a higher copper seed density. Similar contour plots can be generated based on other prediction equations and different factor combinations. With the same combination of copper and time by equation (2), higher organic additive concentration will provide higher copper seed surface coverage and higher particle size standard deviation.

Comparing the SEM morphologies shown in Fig. 1 and the output data with different experimental settings, the optimal limits for this design output should be: total copper surface coverage ≥ 70%, median particle size ≤ 25 nm with standard deviation ≤ 10 (Log standard deviation ≤ 1.00).

Upon examining the entire set of response contour plots (not shown here), the optimal condition for seeding time was determined to be at its higher end, and Cu/organic additive concentration must be in the lower level. Several experimental runs were made within these ranges. When converted into actual values, the final optimized conditions were Cu = 137 ppm, time = 20 sec and organic additive = 12.5 vol%.

Confirmation by experimental runs

Using the optimized seeding conditions, a dense and uniform copper crystal seed layer was deposited from the organic on TaSiN as shown in Fig. 4a. The surface coverage for Fig. 4a is about 75.4% with a medium of particle size 23.6 nm and a Log particle size standard deviation of 0.801. An electroless copper coating was made on the substrate processed using the optimal conditions and a uniform, adherent copper film was deposited in 2.0 min, as shown in Fig. 4b.

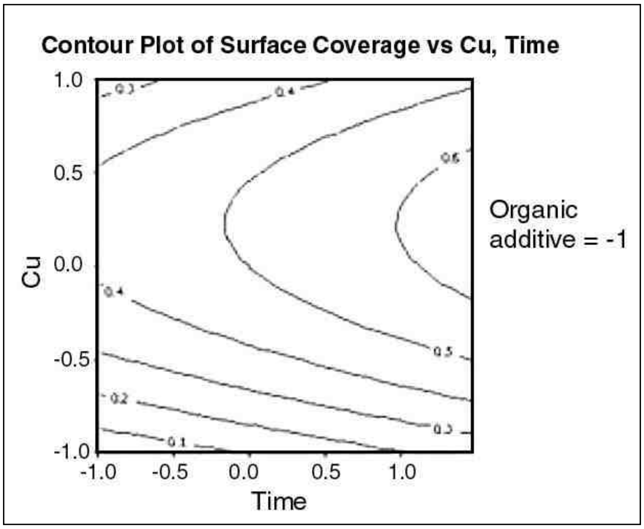


Figure 3—Contour plot analysis of the Cu seed deposition on TaSiN barriers.

Table 3

***p*-value of the refined experimental statistical analysis**

Term	Coverage	Size Median	Log Size Std. Dev.
Constant	0.000	0.000	0.000
Block 1	0.324	0.054	0.380
Block 2	0.608	0.179	0.404
Time	0.003	0.059	
Cu	0.000	0.001	0.007
Organic additive	0.000		0.029
Time*Time		0.054	
Cu*Cu	0.001		0.195
Cu*Organic additive			0.142
NOTE: Block 3 = -(Block 1 + Block 2)			

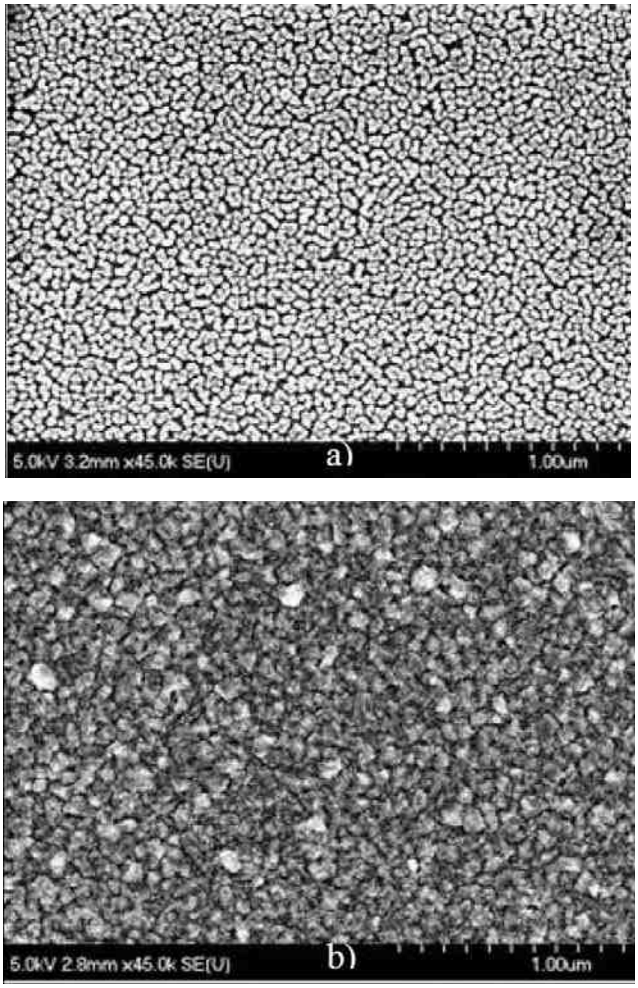


Figure 4—SEM of electroless Cu coating on TaSiN with optimized seeding conditions: (a) seeded TaSiN with the optimized condition, (b) 2 min electroless Cu plated on (a).

Summary

The results show that designed experiments are an effective way to investigate the linear and quadratic effects of multiple factors and their interactions for the deposition of copper seed layers from an organic solution on TaSiN. Three factors were considered: copper concentration, organic additive concentration and reaction time. The response values were total coverage of copper particles, median particle size and the standard deviation of the particle size. The copper concentration was the main factor for all the three outputs. Higher copper concentration results in higher surface coverage, larger particle size and less uniformity of the particle size. The organic additive concentration was a main factor influencing surface coverage and standard deviation of the particle size. Increasing the organic additive concentration gives a higher surface coverage of the copper seeds, but decreased particle size uniformity. The longer the seeding time, the higher the surface coverage and the particle size. Optimum values were determined to be Cu = 137 ppm, time = 20 sec, organic additive = 12.5 vol%. This optimum was verified by confirmation experiments.

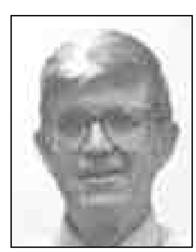
References

1. M.-A. Nicolet, *Applied Surface Science*, **91** (1-4), 269 (1995).
2. Y. Hara, Y. Yoshida & H. Toida, *Electrochemical and Solid-State Letters*, **5** (5), G36 (2005).
3. J. Li, M.J. O'Keefe & T.J. O'Keefe, *J. Applied Surface Finishing*, **1** (2), 166 (2006).
4. J. Li, S. You, M.J. O'Keefe & T.J. O'Keefe, *J. Electrochem. Soc.*, **153** (10), C722 (2006).
5. D.C. Montgomery, *Design and Analysis of Experiments*, 6th Ed., John Wiley & Sons, New York, NY, 2004.

About the authors

Dr. Jingye Li is a Research Chemist at Cookson Electronics - Enthone Inc. in West Haven, Connecticut. Before that, he was a Research Engineer at Delphi Research Labs in Shelby Township, Michigan. He has a B.S. in Applied Chemistry from Fudan University (Shanghai, China) (1996) and Ph.D. in Metallurgical Engineering from the Missouri University of Science and Technology (2005). His research interests are in the areas of metal thin film deposition, materials surface characterization and nano-particle codeposition in metal matrices.

Dr. Matthew O'Keefe is a Professor of Metallurgical Engineering and Director of the Graduate Center for Materials Research at the Missouri University of Science and Technology, Rolla, MO. He has a B.S. and Ph.D. from the Missouri University of Science and Technology (1985) and University of Illinois (1993), respectively. Dr. O'Keefe's research interests are in the area of surfaces, interfaces, thin film and coating deposition, and characterization of materials.



Dr. Thomas J. O'Keefe (1935-2008) was Curators Professor Emeritus in the Department of Metallurgical Engineering and Senior Investigator in the Materials Research Center at the Missouri University of Science and Technology, Rolla, MO. Dr. O'Keefe's main research interests were in the area of non-ferrous electrometallurgy, corrosion and deposition processes for metals in both inorganic and organic solutions.

Dr. David Drain teaches undergraduate and graduate statistics courses at Missouri University of Science and Technology. Before teaching, he spent 23 years as an industrial statistician. He most recently worked at Intel Corporation for 14 years before joining the university as an Assistant Professor in 2003. Dr. Drain holds a Ph.D. in Industrial Engineering from Arizona State University, an M.S. in Applied Statistics, an M.A. in Mathematics and a B.S. in Mathematics from Bowling Green State University. His research interests include design of experiments, process optimization for noisy processes and applications of statistics in the semiconductor industry.