

Optimization of Silver Powder Production through Factorial Experimentation

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Abstract

High purity silver powders are a key building block for the production of conductive pastes and adhesives used by the microelectronics industry to manufacture a wide variety of products, such as sophisticated semiconductor packages, flexible membrane touch switches, RFID antennae, the rapidly growing photovoltaic/solar cell marketplace, printed electronic (PE) applications, etc. The physical properties of the powder, especially apparent density and specific surface area are critical to performance and quality in these products. Through a series of factorial experiments, Metalor has been able to understand and mathematically model the effects of key process parameters that control physical properties of the powder they supply to their microelectronics customers. In particular, estimating interaction effects was important to the success of our project. This paper describes the design and analysis of these experiments as well as the implementation of the results which led to a 2X improvement in product quality and process control in our precipitation processes.

Key words: Design of Experiments, Minitab, Statistical Analysis, Silver Powder, Silver Flake, Factorial

Introduction

Conductive adhesives have now been used for more than three decades in microelectronic packaging industry. Silver filled organic polymers are the most common type of conductive adhesive. The most common form of conductive filler is silver flake.

An explanation of the process for manufacturing silver flake is helpful in understanding

its influence on the performance of conductive adhesives. The first step in the process is to produce silver powder. Powder is made by a number of techniques, including chemical precipitation, electrolytic deposition and melt atomization. Most commercial suppliers of microelectronic grade silver flake precipitate silver powder by reducing silver nitrate solution with a variety of agents. This method yields powders that range in size from 0.5 μ to 10 μ , with shapes that are irregularly crystalline or dendritic (FIGURE 1, Caption: Silver powder at

5000X). Flake manufacturers adjust and control the precipitation reaction to produce powders with desired properties. Next, silver powder is converted to flake by mechanical milling. Size and morphology of the silver powder are the most important factors that influence the properties of subsequent silver flake. Care is taken to select powders that will produce flake with particular attributes. The selected powder is placed into either a ball mill or an attritor, along with milling media, lubricant and solvent. Physical properties of the flakes can be altered by changing the milling conditions. Even though there are many variables in the production of the silver flake the most critical parameter is the starting powder (McNeilly 1999).

Controlling manufacturing processes of the silver powder so that it produces products that meet our customers' expectations and specifications is often difficult. Understanding and quantifying how the process inputs affect the output is critical to process control. Sometimes we can rely on our first principle's knowledge of the process, but often our process response defies our predictions. In this situation, a factorial experiment does an excellent job of demonstrating the impact of each experimental variable on the response. In addition, proper analysis of the experiment results provides a mathematical model that quantifies the effect of each variable, allowing you to determine the input settings to adjust the process to the desired target. Metalor was able to use a well-designed factorial experiment to better understand the silver powder production process. Implementation of the results resulted in a 2X improvement in product quality and control in their precipitation process. Since they incorporated several useful techniques in the design and analysis of their experiment, it serves as an excellent example of the power of designed experiments as applied to any manufacturing process.

As mentioned earlier, high purity silver powders are one of the most important factors in producing silver flakes for use in conductive pastes by the microelectronics industry. Figure 2 shows the combination of reactants fed to the Rx vessel and the resulting solid silver powder filtered from the process. The physical properties of the powder, especially apparent density and specific surface area,

are critical to performance and quality in these products. These two properties are also difficult to predict or control in production. Using a designed factorial experiment, Metalor set out to determine the effects of reaction temperature, ammonium and stir rate on the physical properties of the powder produced.

Design

The full factorial experiment and results are shown in Figure 3. Notice that just a high and a low setting for each input variable are tested. This allows one to estimate the main effect of the input as well as any interactions with other variables with the least number of experiment runs. Due to the high cost of experimentation in production, the experiment was executed in a prototype lab at about 1/500 scale. This avoided the common occurrence of canceling the planned factorial experiments altogether due to the high expense.

Due to the proprietary nature of the process and experiment results, the names, values and units on the responses and experimental variables have been changed. However, the analysis and results from the experiment have not.

Proper planning is key. This experiment design incorporates several best practices that can ultimately lead to successful experiment results. These best practices are worth reviewing in more detail.

1. Replication. There are 8 unique combinations of high / low settings for three experiment variables. In this experiment each combination was run twice. This assured the experimenters they would have enough data to have a high probability of detecting a 15% change or more in their responses, which was a high enough resolution for their needs.
2. Center points. As seen on a main effects plot, two level factorial designs take advantage of the assumption that once you measure the response at the high / low input levels, everything that happens in between is linear; therefore, you don't have to waste measurements at settings between the high

and low. Just two runs at the center of the high and low values (center points) provide enough data to check this assumption of linearity. If the response is not linear, additional runs may be added to the original experiment allowing you to model this curvature.

3. Control runs. Normal production settings were chosen as the center of the input variable settings. Therefore, the center point runs represent familiar process operation and if evenly spaced throughout the experiment, also serve as control runs. Since executing factorial designs requires strong and frequent adjustment of the process, these control runs provide valuable confirmation that the process is stable, except for the experimental variable changes.
4. Bold variable settings. The high and low settings for the experiment variables were selected as far from the production center as was practical. Exploring conditions very different from everyday operation increases the probability of learning something new about your process. Also, by maximizing the range of the variable settings, the size of the effect is increased. This makes it easier to detect the effect above and beyond the normal variation (noise) of the process.
5. Interaction effects. When the effect on the response of one variable changes depending on the settings of another variable, the two variables are said to “interact”. Interactions between process variables are common and are vital to developing a full understanding of a process. Even though it is difficult for process experts to determine which interactions are occurring based on everyday operation, a full factorial experiment allows you to identify and quantify the interactions that are active in the process.
6. Monitoring covariates. Plans were made to record the settings of variables that could impact the response, but were not controllable during the experiments. Recording these variables allows them to be incorporated in the analysis as covariates.

Often this can salvage results that would not have otherwise lead to solid / correct conclusions.

In short, this experiment was set for success before the first data point was collected. For more information on experiment design and analysis, Montgomery (2005) is a very popular text, but Hamada & Wu (2001) or Box, Hunter & Hunter (2005) are also excellent resources.

Analysis

The first goal of the analysis is to determine the main effect of each of the three input variables by comparing the average response when the input was at its high level with the average response when the input was at its low level. This comparison is shown graphically in Figure 3 with apparent density as the response. It appears that apparent density goes up as stir rate increases, goes down as ammonium increases and is not greatly affected by temperature. Since the response at the midpoint of each of these graphs, the center point shown in red, seems to be approximately on the straight line connecting the high and low level response, our assumption of a linear response between the high / low levels appears to be true.

However, the main effects plot does not always tell the complete story. If an interaction between two variables is active, the main effect of one variable depends on the setting of another variable. For example, the active interaction between ammonium and stir rate is shown in Figure 4. Clearly, the drop in apparent density with an increase in stir rate is much stronger when the ammonium level is 2 than when the ammonium level is 30. For a complete understanding of the effect of stir rate on apparent density, one must also measure the interaction effects of stir rate with other input variables. Factorial experiments have the benefit of providing estimates of interactions between input variables in addition to their main effects. In this DOE experiment, there were several interactions active in the process, thus the importance of this benefit.

So how do we take advantage of our newfound understanding of what drives apparent density? Complete analysis of the data would include statistical tests comparing the size of each factor's effect to the noise in the data, creation of a mathematical model for the response as function of statistically significant factors, and an analysis of the difference between each data point and the model's prediction for that data point (residuals) to validate the model. Details are beyond the scope of this article, but can be easily carried out with statistical software as described by Montgomery (2005). The result of this analysis was the following equation which can be used to predict the apparent density for any process conditions of interest:

$$\text{Apparent Density} = 34.8 - .35 * \text{Ammonium} - .19 * \text{Stir Rate} + .004 * (\text{Ammonium} * \text{Stir Rate})$$

The same analysis was carried out using specific surface area as the response to generate an equation to predict the specific surface area for any process conditions. Using both of these equations, we can find the process run conditions that produce powder with an apparent density below 14 as well as a specific surface area between 0.5 and 0.7. In addition, the equations identify which inputs need to be most tightly controlled to keep the response stable over time. These two equations were used to generate Figure 5, an overlaid contour plot where the process conditions that meet the apparent density specification as measured and the process conditions that meet the specific surface area specifications are identified on the same contour plot. The area of overlap shown in white identifies the process variables needed for both responses to meet specifications. Whereas any settings in this region should work, it is common to select the settings that are most practical or would also benefit the operation in some other way.

By implementing the process settings recommended by the experiment and monitoring the process over time, the experiment results and benefits

to the process are confirmed. Control charts of process performance after implementation for both responses are shown in Figure 6. They illustrate the 2X decrease in process variation leading to a higher quality powder meeting the customer's specifications.

Conclusions

Understanding a manufacturing process based on first principles can often be a difficult task. Following a number of experiment design best practices, Metalor executed a factorial experiment which allowed them to quantify the effects of each process input on their two responses of interest. Based on this understanding, they were able to adjust the process to meet customer specifications for both key quality characteristics and better control their process, decreasing variation by about 50%. Their approach is generally applicable and can be used to improve product quality and process control in most manufacturing operations.

References

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Appendix

Table 1. Experiment Design

Run Order	Ammonium	Stir Rate	Temperature	Density	Surface Area
1	2%	150	8°C	7.54	0.69
2	2%	150	8°C	6.66	0.67
4	30%	150	8°C	12.46	0.52
5	2%	100	8°C	14.68	0.40
6	30%	100	8°C	15.12	0.42
3	16	125	24°C	12.88	0.42
7	30%	100	40°C	12.65	0.57
8	30%	150	40°C	14.96	0.41
9	30%	150	40°C	14.96	0.41
11	2%	100	40°C	10.95	0.58
12	2%	150	40°C	8.84	0.75
13	2%	150	40°C	8.03	0.68
10	16	125	24°C	13.36	0.43
14	30%	100	8°C	17.48	0.41
15	2%	100	40°C	17.68	0.43
16	30%	100	40°C	15.96	0.54
17	30%	150	8°C	12.62	0.36
18	2%	100	8°C	15.18	0.43

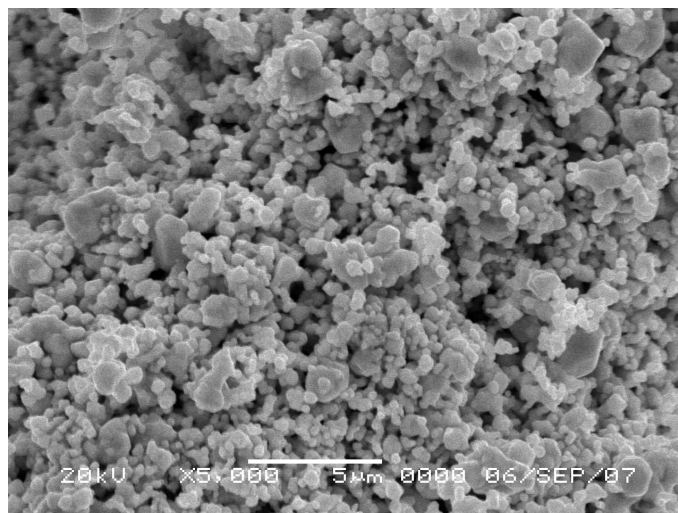


Figure 1 SEM of Silver Powder

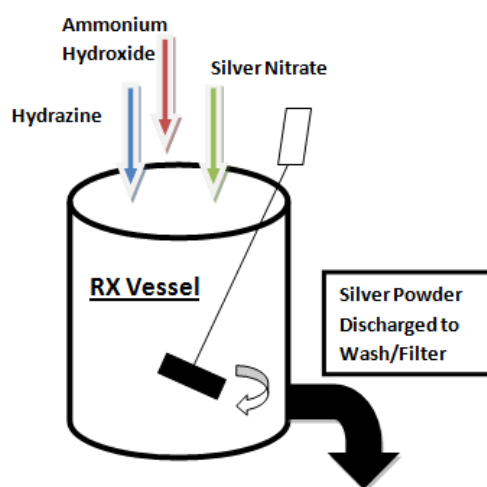


Figure 2 Silver Powder Production Process

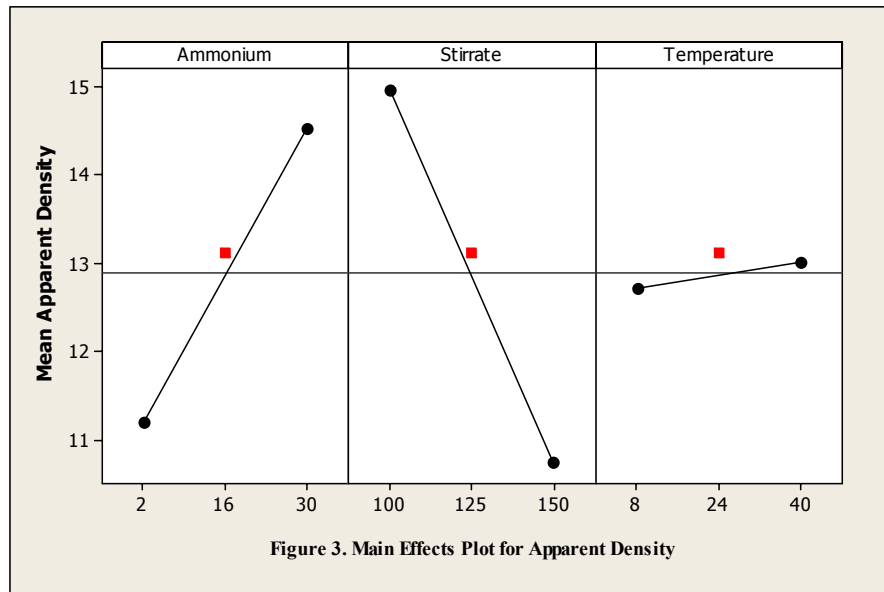


Figure 3 Main Effects Plot for Apparent Density

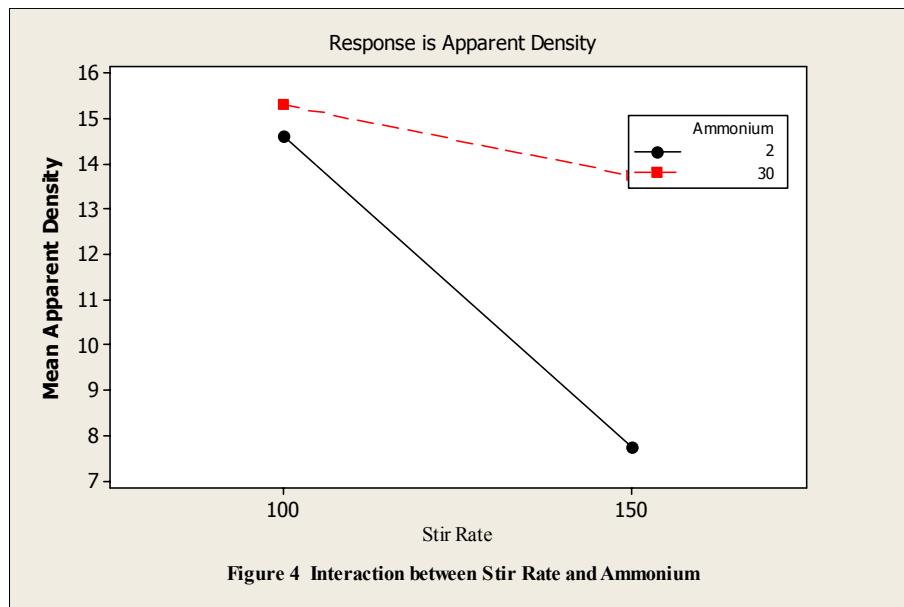


Figure 4. Interaction between Stir Rate and Ammonium

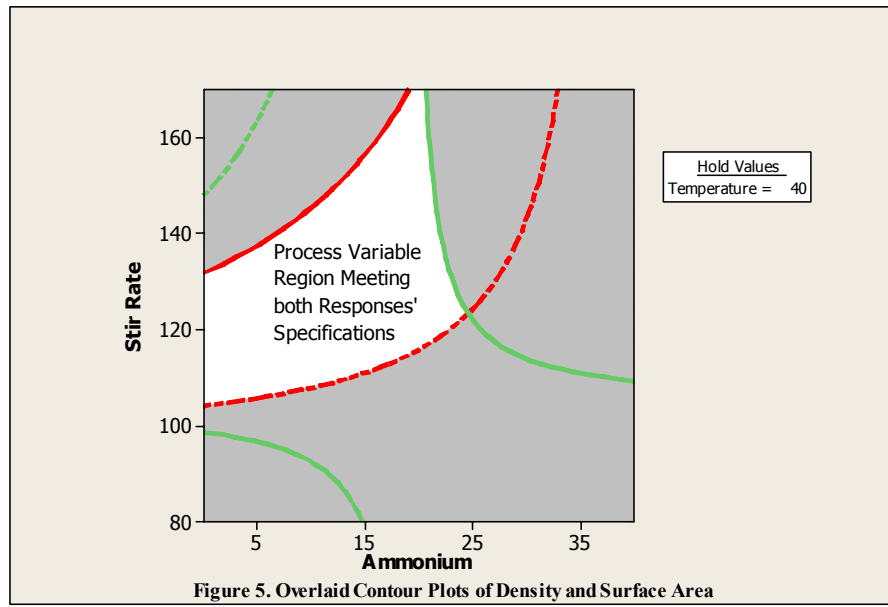


Figure 5 Overlaid Contour Plots of Density and Surface Area

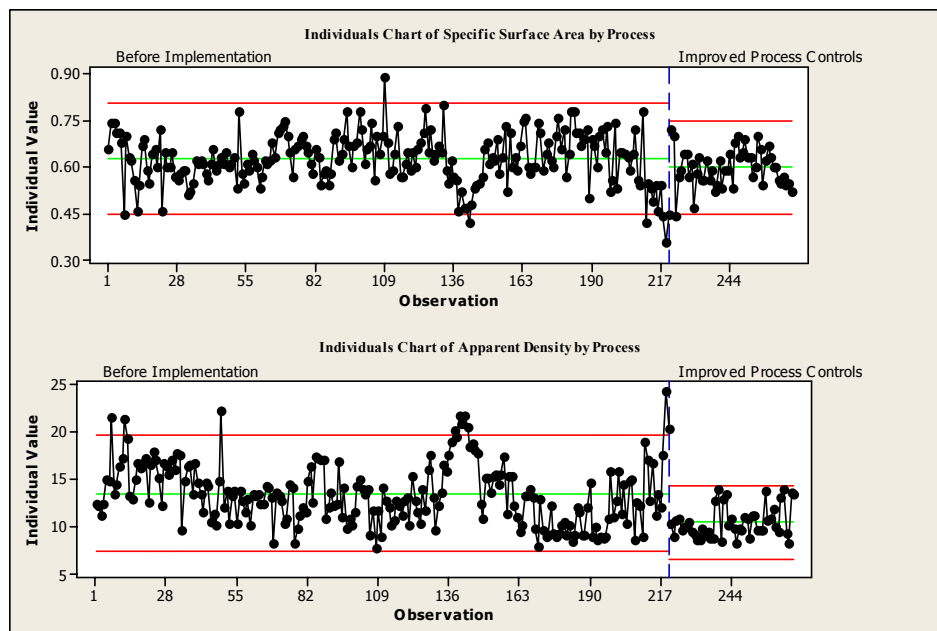


Figure 6 Apparent Density and Surface Area control charts by process