Electrochemical Impedance Monitoring of Copper Damascene Chemistries

Alan Zdunek\textsuperscript{a}, Delia Nieto Sanz\textsuperscript{b}
\textsuperscript{a} Air Liquide Chicago Research Center, Countryside, Illinois
\textsuperscript{b} Air Liquide Centre Recherche Claude Delorme, Les Loges en Josas, France

Claude Gabrielli, Philippe Moçoteguy, Hubert Perrot
CNRS, Laboratoire Interfaces et Systemes Electrochimiques, Paris, France

Hung Ming Chen, Satish J. Parulekar
Illinois Institute of Technology
Department of Chemical and Environmental Engineering, Chicago, Illinois

Abstract

This paper describes electrochemical impedance spectroscopy (EIS) measurements performed on copper damascene plating chemistries during non-production plating experiments and on process tool baths during copper metallization to characterize changes in the plating bath condition. The results show that the shape of the impedance scan is sensitive to changes in the steady state of the bath chemistry, bleed/feed operation, and process perturbations, and may be an indicator of the overall bath quality. Further development of this method, as an online monitor to track the overall bath quality and its incorporation into a copper bath management and delivery system, are also discussed.

Introduction

The promising electrical properties and capability to deposit copper into submicron features by superconformal deposition have brought copper electroplating technology into the mainstream of the semiconductor metallization process. However, the ability to perform superconformal deposition of copper in vias and trenches depends strongly on specific organic additives to the copper sulfate/sulfuric acid-based electroplating bath. Achieving a defect-free deposition requires a precise maintenance of the concentrations of additives and additive byproducts. Monitoring or controlling these is therefore crucial to guaranteeing the properties of the copper deposit.

The roles of bath ageing and additive degradation are of considerable interest since these can affect the quality of the copper deposit and ultimately influence copper bath chemical management schemes [1].
Additionally, changes in the overall bath quality influenced by manufacturing conditions, additive degradation, and byproduct accumulation, can profoundly affect the copper deposit and these are not presently controlled. State-of-the-art copper interconnect plating tools use online monitoring to quantify bath component concentrations to achieve tighter bath control. Presently, bath quality is maintained by bleeding part of the solution about 10% each day. A more quantitative determination of bath quality would enable out-of-spec bath conditions to be readily measured, identified and controlled, and more accurate preventative maintenance performed.

While quantifying bath ageing and measuring byproducts has been reported, optimization of bath quality management remains difficult, partly due to the proprietary nature of copper bath formulations [2-4]. Electrochemical impedance spectroscopy (EIS) was proposed as a possible method for following bath quality during wafer processing [1]. Laboratory experiments involving simulated bath ageing revealed that the impedance technique can track copper bath ageing during and after plating [1]. Furthermore, these results appeared to correlate well with deposit morphology and thus maybe a reliable indicator of the overall quality of the bath during plating operation [5]. EIS measurements were also made on plating bath solutions taken from production copper deposition tools at a semiconductor manufacturing fab [6,7]. EIS was able to distinguish between different bath compositions, as well as between different process perturbations.

In this paper, impedance measurements were made on copper damascene plating chemistries during non-production plating experiments and on additional process tool baths during copper metallization. The non-production plating experiments allowed out-of-spec bath conditions with recovery back to a steady state to be characterized without manufacturing production constraints and the risk of wafer loss. The production tests were performed to further demonstrate that EIS can detect differences in production bath chemistries including changes attributable to process perturbations and maintenance functions.

**EIS Method**

Electrochemical impedance spectroscopy, is used commonly in electrochemical characterization, battery and fuel cell research, and corrosion measurements [8-12]. EIS is a steady-state technique capable of observing phenomena in electrochemical systems whose
relaxation times vary over many orders in magnitude [8]. The EIS technique applies a small-amplitude sinusoidal voltage to a working electrode at a number of discrete frequencies, \( \omega \), ranging from 0.01 to 62,500 Hz as shown in Figure 1. At each of these frequencies, the resulting current exhibits a sinusoidal response, \( I(\omega) \) that is out-of-phase with the applied sinusoidal voltage signal. The electrochemical impedance, termed \( Z(\omega) \), is the frequency-dependent proportionality factor between the voltage signal and current response [10]:

\[
Z(\omega) = \frac{V(\omega)}{I(\omega)}
\]

\( Z(\omega) \) is a complex-valued vector quantity with real and imaginary components, whose values are frequency-dependent:

\[
Z(\omega) = Z_{\text{Real}}(\omega) + j Z_{\text{Imag}}(\omega)
\]

The real and imaginary impedance components can be plotted against each other to generate a Nyquist plot with characteristic semicircle shapes as shown in Figure 2. This plot is derived from a model of copper deposition that accounts for organic additive effects [1]. Each point on the plot is the impedance at one frequency, and each semicircle is characteristic of a single time constant. The ohmic, or electrolyte solution resistance, is determined at the high frequency intercept on the real (horizontal) axis. The first semicircle diameter (Loop 1) gives the charge transfer resistance, which is related to the rate of the electrochemical reaction. In systems where additives are present and influence the deposition process, additional semicircles and inductive loops on the Nyquist plot can be observed (Loop 2 to Loop 4) and are related to ion-additive complexation, adsorption mechanisms, or additive degradation processes. The semicircles above the horizontal axis are capacitive, while those below are inductive since capacitors and inductors have only an imaginary impedance component.

**EIS Setup**

The EIS equipment consists of a potentiostat and frequency generator/analyzer for imposing and acquiring the electric signal, as well as an electrochemical cell and ancillary components [rotating disc electrode (RDE) assembly, reference electrode, counter electrode] for conducting the experiments on the bath solutions. A small DC current was imposed on the system in addition to the AC current signal that was varied in frequency from 0.01 Hz to 62,500 Hz.
For each frequency: $Z(F) = \frac{\Delta E}{\Delta I} = |Z|e^{j\phi}$.

Figure 1. AC voltage signal imposed on an electrochemical system and the resulting AC current and impedance.

Figure 2. Calculated impedance scan from the model (from Reference 1).
**Experimental**

**Non-Production Plating Bath**

Electrochemical impedance spectroscopy measurements were performed while plating 200-mm, non-patterned wafers in a non-production (laboratory) wafer-plating tool. Figure 3 shows a photograph of the wafer plating tool and the “in-situ” impedance monitor setup. Silicon wafers were plated in a plating cell that contained a rotating wafer platter and a copper anode. The wafer-plating tool had a total copper bath solution volume of 70 L that recirculated from the plating cell to a reservoir tank. The plating bath used was a commercially available, low-acid, copper sulfate bath containing chloride ion and three organic additives, an accelerator, suppressor and leveler. Concentrations of copper, chloride, acidity and the three additive were monitored in the reservoir tank using an online concentration monitor (Real-Time Analyzer (RTA)), from Technic, Inc.

200-mm wafers were plated using a current density of 20 mA/cm$^2$ for 4 hours each day during the test period. The total charge accumulated (amp-hr), during plating was recorded during the test. EIS measurements were made during the plating cycle and before and after any bath addition or removal was performed. During the first phase of the test, the additives were compensated to maintain a nominal concentration level. However, the bath solution was not removed (i.e., no bleed/feed). The first phase allowed bath degradation, or by-products to increase while still maintaining the additive levels at the “in-spec” nominal levels. The second phase of the measurements added a bleed/feed operation. Typically, 10% of the bath was removed, and fresh inorganic solution and additives were added to the bath. This had the effect of diluting the by-products and bringing the bath back to a steady state condition.

**Production Plating Bath**

Electrochemical impedance spectroscopy measurements were performed on plating bath solutions from six copper plating tools during copper deposition manufacturing. A proprietary acidic copper sulfate bath with chloride ion and three additives (A,B,C) was used in the production tools. The process tools were followed using EIS measurements during a ten-day campaign to determine the steady state stability of the bath solution as a function of processing
time. Copper bath solutions were periodically obtained from the 6 process tools from a sampling port in each of the tools.

Figure 3. Photograph of the laboratory wafer plating tool and in-situ EIS monitor.

**Results for Non-Production Plating Bath**

Table 1 lists the experimental conditions for the bath ageing experiments. There is no additive compensation for the first two sets of experiments. From the 3rd through 10th ageing experiments, the three additives, suppressor, accelerator and leveler, are restored to their nominal values in each experiment. From 11th through 15th experiments, a 10% volume bleed and feed algorithm has been adopted with additive compensation. Figure 4 shows the depletion and compensation of the accelerator, suppressor, and leveler during the test period. Throughout the 700 hours of ageing process, however, the copper, acidity and Cl⁻, remained at a constant level and were not compensated.

**EIS Results**

Figure 5 shows the impedance scan for the first and second ageing experiments. The impedance spectrum is composed of 2 capacitive loops and two inductive loops. Since we started with a totally fresh solution without any byproduct originally present in the electrolyte, the changes in the impedance spectrum were not significant even though the consumption of the accelerator and leveler was nearly 50% and that of suppressor was 20%.
<table>
<thead>
<tr>
<th>Number of ageing</th>
<th>Accumulating ageing current (Amp-hr)</th>
<th>Additive Compensation</th>
<th>Bleed &amp; Feed</th>
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<tbody>
<tr>
<td>1</td>
<td>25.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>51.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>76.4</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>101.6</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>127.4</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>152.6</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>177.8</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>203.0</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>228.2</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>253.4</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>11</td>
<td>278.6</td>
<td>X</td>
<td>(Volume increases to 70 L, no bleeding)</td>
</tr>
<tr>
<td>12</td>
<td>303.8</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>13</td>
<td>329.0</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>354.2</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>379.9</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

Table 1. Experimental conditions for the non-production wafer plating and bath ageing.

Figure 4. RTA concentration monitoring data for the suppressor, accelerator and leveler.
Figure 5. Initial impedance scans without additive compensation or bleed/feed.

Figure 6 shows the impedance scans for the 3rd through 10th ageing experiments where additive compensation is performed while plating. During this test period, the plating bath was continuously aged up to 253 amp-hr total plating charge. Since there is no removal of the bath solution (no bleed/feed), the byproducts gradually accumulated in the bath during the ageing process. Many interesting changes were observed in the impedance scans. At the lowest frequency, 0.01 Hz, both the $Z_{\text{Real}}$ and $Z_{\text{Imag}}$ increased while the bath ageing continued, or in other words, the diameter of the inductive semicircle increased. After the 8th ageing experiment, the diameter of the inductive loop did not change significantly. It was concluded that bath degradation, with additive compensation and without a bleed/feed reached a saturation state at this stage and a proper bleed and feed operation would be needed for prolonging the bath life.

Figure 7 shows the impedance scans for the 10th through the 15th ageing experiments where additive compensation and a 10% bleed/feed mechanism were performed. After one bleed/feed operation and at the 11th ageing run, the inductive loop expanded, indicating that the byproducts were still influencing the impedance scan. However, after a 19 L bath dilution and another
bleed/feed, the EIS scans at the 12th and 13th ageing experiments showed that a steady state had been reached in the low-frequency inductive loop. Except for the EIS scan at the 14th ageing, the inductive loop before and after bleed & feed was confined to a limited range and thus appeared to be at a pseudo-steady state. This suggests that the bleed & feed permits keeping the byproducts at a certain low level.

The results reveal that the low frequency range of the EIS scan is sensitive to the bath ageing process, since changes occurred despite maintenance the additives at a constant level in the bath. This sensitivity could be exploited further to develop a monitor that tracks bath ageing during wafer plating. After a certain value of the Z_{Real} or Z_{Imag} or inductive loop diameter has been reached, indicating a detrimental amount of byproducts, a maintenance function such as a bleed/feed operation could be started. The value in such a scheme is that bleeding the bath would be carried out only when needed, reducing thereby the consumption of the copper bath and additives.

Figure 6. Impedance scans during bath ageing with additive compensation.
Production Plating Bath
Six production plating baths were followed using EIS measurements during a one-month period. Several pertinent results will be described here. EIS scans for two production tool baths are shown in Figure 8. One of the most striking results was the very good overall stability of the bath with time. In addition, Figure 9 shows EIS scans while following the production start of a completely new bath (Tool 6). EIS measurements were performed at the time when the additives were added and also during the first operating days. In Figure 9, a slight shift in the impedance spectra is observed as the bath is initially stressed (i.e., dummy wafers are plated to condition the anode). Also when wafer production is started, the EIS scans are mainly characterized by the decrease in the size of the inductive loop. EIS scans were also performed during an anode change and cleaning operation. Figure 10 shows the evolution of the impedance spectra recorded before, during, and after an anode change. Two sets of impedance shapes were observed: a set corresponding to measurements performed before and during the anode change and a set corresponding to measurements performed after the anode change. The steady state was slightly
affected by the anode change. In addition, the change of anode corresponds to an increase in the size of the inductive loop. Indeed, the three plating cells in the tool were emptied before the anode change and the corresponding amount of fresh bath has been supplied to the bath after the change to keep the total bath amount the same. However, it is not certain whether the observed changes in the steady state are due to the anode change or due to the partial renewal of the solution.

**Summary**

Impedance measurements were made on copper damascene plating chemistries during non-production plating experiments and on process tool baths during copper metallization. The non-production plating experiments show that the impedance scan is sensitive to bath ageing and byproduct formation, especially in the low frequency, inductive loop range of the measurement spectra. Furthermore, bleed & feed of the bath also changes the EIS spectra in the low frequency range with the impedance scans following the change in the bath steady state during ageing and byproduct dilution. On the other hand, the EIS measurements performed during production measurements also indicated that the reach of steady state in production bath and therefore the maintenance operations could be possibly characterized by the EIS technique. The results from these experiments suggest that the EIS technique may be a good candidate to track bath ageing and to control byproduct buildup, as well as to provide a baseline for production operations, such as new bath starts, anode changes, and other maintenance functions. Ultimately, development of the impedance method as an online sensor could have broad implications of lower chemical consumption and cost-of-ownership.
Figure 8. Impedance spectra recorded on two different bathes: Tool 1 (left graph) and Tool 6 (right graph).

Figure 9. Impedance scans after a new production start, Tool 6.
Before anode change:
- 09/04/2004 08h42 ($t_0 + 24$ mn)
- 09/04/2004 13h52 ($t_0 + 22$ mn)

During anode change:
- 13/04/2004 08h21 ($t_0 + 53$ mn)

After anode change:
- 13/04/2004 15h52 ($t_0 + 20$ mn)
- 13/04/2004 18h00 ($t_0 + 17$ mn)
- 14/04/2004 09h39 ($t_0 + 19$ mn)

![Graph showing impedance scans](image)

**Figure 10.** Impedance scans on Tool 2, before, during and after an anode change.

**Acknowledgements**

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**References**


