Plating Under Reduced Pressure

J. W. Dini
T. G. Beat
W. C. Cowden

Lawrence Livermore National Laboratory
Livermore, CA

L. E. Ryan
W. B. Hewitt

TRW
Redondo Beach, CA

For AESF SUR/FIN 92
Atlanta, Georgia
June 1992

ABSTRACT

Plating under reduced pressure was evaluated for both electroless nickel and electrodeposited copper systems. The objective was to reduce pitting of these coatings thereby further enhancing their usage for diamond turning applications. Cursory experiments with electroless nickel showed reduced porosity when deposition was done at around 500 torr. Detailed experiments with electrodeposited copper at around 100 torr provided similar results. Scanning tunneling microscopy was effectively used to show the improvement in the copper deposits plated under reduced pressure. Benefits included reduced surface roughness and finer and denser grain structure.

*This work was performed under the auspices of the U. S. Dept. of Energy by LLNL under contract No. W-7405-Eng-48.
The American Electroplaters and Surface Finishers Society, Inc. (AESF) is an international, individual-membership, professional, technical and educational society for the advancement of electroplating and surface finishing. AESF fosters this advancement through a broad research program and comprehensive educational programs, which benefit its members and all persons involved in this widely diversified industry, as well as government agencies and the general public. AESF disseminates technical and practical information through its monthly journal, Plating and Surface Finishing, and through reports and other publications, meetings, symposia and conferences. Membership in AESF is open to all surface finishing professionals as well as to those who provide services, supplies, equipment, and support to the industry.

According to the guidelines established by AESF's Meetings and Symposia Committee, all authors of papers to be presented at SUR/FIN® have been requested to avoid commercialism of any kind, which includes references to company names (except in the title page of the paper), proprietary processes or equipment.

Statements of fact or opinion in these papers are those of the contributors, and the AESF assumes no responsibility for them.

All acknowledgments and references in the papers are the responsibility of the authors.

Published by the
American Electroplaters and Surface Finishers Society, Inc.
12644 Research Parkway • Orlando, FL 32826-3298
Telephone: 407/281-6441 • Fax: 407/281-6446

Copyright 1992 by American Electroplaters and Surface Finishers Society, Inc. All rights reserved. Printed in the United States of America. This publication may not be reproduced, stored in a retrieval system, or transmitted in whole or part, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise without the prior written permission of AESF, 12644 Research Parkway, Orlando, FL 32826-3298.

Printed by AESF Press

SUR/FIN® is a registered trademark of the American Electroplaters and Surface Finishers Society, Inc.
**Introduction**

Precision machining (also termed single point diamond turning or just diamond turning) is accomplished by combining the very hard and sharp edges obtained from certain crystalline (usually diamond) tools with extremely precise machine tools (either liquid or gas bearing) operating under closely controlled environmental conditions to produce finished or nearly finished optical surfaces. This technology removes some of the difficulties in forming optical surfaces encountered in conventional grinding and polishing, specifically for that family of materials both physically and chemically compatible with diamond tools. Because these tools are so hard and sharp, no cutting edge contact area is presented to the material. This promotes the cutting process by restricting it to a thin shear plane with a minimum of contact stress or friction and results in a process that minimizes material deformation. The result is a specular finish required for optical surfaces and a contour that is an exact copy of the tool path(1).

The materials that can be successfully diamond turned are limited in number(2). Therefore, coatings such as electroless nickel, and electrodeposited copper and gold are particularly important for diamond turning applications. Requirements include void free, low stress, fine-grained deposits, with no inclusions.

Although many successful applications of these coatings have been reported, problems occasionally arise, and they are often in the form of pitting. Pits that remain in the finished coating result in a void on a mirror surface or a “pip” in a molded surface. Both of these are degrading to optical performance(2,3). This type of problem is one of the key issues occurring with electroless nickel deposits. With copper electrodeposits, a phenomenon referred to as "black spots" has been occasionally obtained. These are small, localized defects noted on electroplated copper after single point diamond turning. Analysis of these spots has revealed oxides, sulfates and chlorides, materials which are components of the plating solution. This leads to the speculation that the most likely cause of these defects is a void or pit exposed by the diamond cutting tool.

In an effort to completely eliminate pitting from electroless nickel and electroplated copper coatings we decided to evaluate reduced pressure deposition. We felt the pitting was caused by gas bubbles formed on the surface during coating and that by using reduced pressure during the coating process these bubbles would be continuously swept from the surface. The purpose of this paper is to present the results of this study.
Why Use Reduced Pressure?

There are a number of steps a coater can take to reduce porosity of a deposit. These include use of a wetting agent in the solution, cathode movement, agitation-with or without air, use of a mixer to stir the solution, and ultrasonics. Over the years we have evaluated all of these techniques with varying degrees of success. A paper published in the Proceedings of Interfinish 80 (4) and subsequently elsewhere (5,6) on hard chromium plating under reduced pressure caught our attention. Claims of this work were that reduced pressure (about 450 to 480 torr) made it easier for hydrogen bubbles to get loose from the surface of a metal, especially from grooves and other uneven places on the surface. Corrodkote tests results, shown in Figure 1, reveal that deposits produced under reduced pressure were considerably less porous than those produced under normal atmospheric conditions. Figure 2 shows porosity of various chromium deposits as a function of pressure reduction and the flow rate of the solution. In all cases, a reduction in porosity was obtained when deposition was performed at about 380 torr. Other benefits claimed for reduced pressure chromium deposition included higher density, a smaller crack density, improved adhesion and work safety advantages since the solution is enclosed within the chamber and chromium mist does not escape to the atmosphere (4,5,6).

A literature search revealed that two U.S. patents have been granted on use of reduced pressure during deposition for the purpose of removing gas bubbles from the surface of parts during the coatings process (7,8).

Experimental Details

Electroless nickel and electrodeposited copper coatings were evaluated under reduced pressure conditions. Both types of coatings were produced by using proprietary solutions. The electroless nickel experiments were done in a desiccator (4 liter capacity) reduced in pressure by means of a water-ring pump as shown in Figure 3. Low carbon steel samples, 1 by 1.5 by 0.020 inch were plated on both sides. Thickness varied from 0.5 mil to 2.5 mil in 0.5 mil increments.

The copper deposits were produced in a 40 liter box tank designed specifically for this work (Figure 4). A water ring pump was used with this system. With each coating system, air was introduced to control pressure. The air also provided agitation and mixing of the solution. Table 1 provides details on all copper samples. Thickness varied from 0.5 to 9.0 mil. After plating, some samples were heated at 250°C for 1 hour and some were heated and single point diamond turned (SPDT).
Figure 1: Corrodkote test results showing the effect of reduced pressure on porosity of electrodeposited hard chromium (Reference 4). Top panel plated at 450 to 480 torr, porosity 2%, Middle sample plated at 400 to 450 torr, porosity 8%, Bottom sample plated at 760 torr in SRHS solution, porosity 100%.
Figure 2: Average porosity vs pressure reduction and flow-rate of the solution for chromium samples plated in sulphate, flouride and SRHS solutions (Ref. 4). For conversion, 50 kPa = 380 torr.
Figure 3: Set-up for doing reduced pressure electroless deposition.
Figure 4: Set-up for doing reduced pressure electrodeposition of copper.
Table 1

**Electrodeposited Copper Samples***

<table>
<thead>
<tr>
<th>Sample Set</th>
<th>Sample #</th>
<th>Plating Conditions</th>
<th>Thickness (inch)</th>
<th>Post-Plating Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TORR</td>
<td>AMPS (mid)</td>
<td>Time (min)</td>
</tr>
<tr>
<td>A</td>
<td>1</td>
<td>763</td>
<td>1.16</td>
<td>38</td>
</tr>
<tr>
<td>A</td>
<td>2</td>
<td>763</td>
<td>1.16</td>
<td>19</td>
</tr>
<tr>
<td>A</td>
<td>3</td>
<td>97-140</td>
<td>1.16</td>
<td>38</td>
</tr>
<tr>
<td>A</td>
<td>4</td>
<td>60-110</td>
<td>1.16</td>
<td>19</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>764</td>
<td>1.33</td>
<td>465</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>764</td>
<td>1.33</td>
<td>465</td>
</tr>
<tr>
<td>B</td>
<td>3</td>
<td>764</td>
<td>1.33</td>
<td>465</td>
</tr>
<tr>
<td>B</td>
<td>4</td>
<td>56-130</td>
<td>1.33</td>
<td>465</td>
</tr>
<tr>
<td>B</td>
<td>5</td>
<td>56-130</td>
<td>1.33</td>
<td>465</td>
</tr>
<tr>
<td>B</td>
<td>6</td>
<td>56-130</td>
<td>1.33</td>
<td>465</td>
</tr>
</tbody>
</table>

* All samples were plated in the same 40 liter solution.

** All heat treating was at 250°C for 1 hour.
Both electroless nickel and electrodeposited copper coatings were evaluated by use of standard metallographic techniques while scanning electron microscopy (SEM) and scanning tunneling microscopy (STM) were also used to evaluate the copper deposits.

Results

Electroless Nickel

The results obtained with the electroless nickel deposits are shown in Figure 5 and tabulated in Table 2. Information in the table clearly shows the benefit derived from reduced pressure deposition. In Figure 5 the top set of panels, code numbers 110 to 114 were plated at 89°C and a pressure of 500 torr. Thickness increased in 0.5 mil increments from sample 110 which was 0.5 mil thick to sample 114 which was 2.5 mil thick. The bottom set of panels was plated at 89°C and 760 torr and the thicknesses correspond to those in the set shown above them in Figure 5. For example, sample 115 was 0.5 mil thick and sample 119 was 2.5 mil thick.

Very little pitting was evident on any of the samples deposited at reduced pressure (500 torr). By comparison, pits were evident on all samples plated at atmospheric pressure (760 torr). Generally, the pitting increased as thickness increased, e.g., panels 117 (1.5 mil) and 118 (2.0) exhibited the most pitting, and then seemed to decrease somewhat for the thickest coating (sample 119, 2.5 mil thick).

Electrodeposited Copper

With either optical or scanning electron microscopy it was not possible to distinguish differences between the copper deposits plated under atmospheric conditions and those plated under reduced pressure. Therefore, surface examination was limited only to that conducted with the scanning tunneling microscope. With this approach, the atomic contours of a specimen are measured by the electrons' tunneling current across the microscope's tip and the sample's surface.

Examination of the four samples in set A from Table I revealed three consistent feature differences between atmospheric and reduced pressure deposits, namely, with reduced pressure there was: 1-reduced surface roughness, 2-finer and 3-denser grain structure. Figure 6 shows representative areas on these four samples. Measurements were made normal to the surface. Figures 7-10 are 750 x 10,000 x 10,000 angstroms STM plots of the surface profiles of these samples. These show tighter, smoother structures (closer peak-to-peak spacing and shorter peak-to-peak valley heights) for the reduced pressure plated copper.
The reduced pressure plated sample A-4 (60 to 110 torr, 0.5 mil thick) was cross sectioned and examined using STM. Figure 11, the plot from this profile, illustrates that the plating structure remains dense throughout the electrodeposited copper.

Similar results were obtained with sample set B from Table 1. All reduced pressure samples consistently exhibited smoother and denser structure. Figure 12 shows STM plots for both heat treated (250°C for 1 hour) and single point diamond turned samples, B-3 and B-6. Although the average surface roughness is about the same, e.g., 137 angstroms for the atmospheric produced sample and 111 angstroms for the reduced pressure sample, STM reveals a denser structure with less peak-to-valley distances for the reduced pressure deposit. When several less dense areas on the atmospheric samples were examined and measured with the tunneling current, these voids showed spacings and depths of about 250 angstroms.

One sample from a series of parts plated in a large (4500 liter) tank as described in reference 9 was examined. This was selected because it represented our best attempt at the time to control solution chemistry, plating parameters (current density, agitation, additive concentration, etc.) and size effects for a full scale part. It had not been heat treated nor diamond turned. Figure 13, the STM plot for this sample, clearly shows that it was the roughest and least dense of all the samples examined.

Discussion

The tests that were run with both electroless nickel and electrodeposited copper clearly show that benefits are derived when reduced pressure is used during the deposition process. There are a number of key application issues that need further investigation and these are detailed in Table 3. Unfortunately, funding for further work on this project has not been made available so presently the program is on a holding pattern.

Summary

Plating under reduced pressure has been shown to improve electroless nickel and electrodeposited copper coatings. With electroless nickel, reduced porosity was obtained when deposition was done at around 500 torr. Detailed experiments with electrodeposited copper at around 100 torr provided similar results. Scanning tunneling microscopy clearly showed that copper deposits plated under reduced pressure exhibited reduced surface roughness and finer and denser grain structure.
References:


5. Anon., "Vacuum Chamber Improves Chromium Electroplating", Products Finishing, 48, 82 (July 1984)


Table 2

Influence of Reduced Pressure Deposition on Pitting of Electroless Nickel Deposits

<table>
<thead>
<tr>
<th>Deposit thickness (mil)</th>
<th>Number of Pits/inch</th>
<th>Deposition Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>760 torr*</td>
</tr>
<tr>
<td>0.5</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>1.0</td>
<td>17</td>
<td>0</td>
</tr>
<tr>
<td>1.5</td>
<td>23</td>
<td>0</td>
</tr>
<tr>
<td>2.0</td>
<td>27</td>
<td>1</td>
</tr>
<tr>
<td>2.5</td>
<td>19</td>
<td>2</td>
</tr>
</tbody>
</table>

* These are the bottom samples in figure 5; sample 115 was 0.5 mil thick and each successive sample was 0.5 mil thicker than the preceding sample.

** These are the top samples in figure 5; sample 110 was 0.5 mil thick and each successive sample was 0.5 mil thicker than the preceding sample.
Figure 5: Electroless nickel samples deposited at atmospheric conditions and under reduced pressure. The top set of panels, code numbers 110 to 114 were deposited at 89°C and 500 torr. Thickness increased in 0.5 mil increments from sample 110 which was 2.5 mil thick. The bottom set of panels was plated at 89°C and 760 torr and the thicknesses correspond to those in the set shown above them.
Figure 6: STM images of four copper samples from Set A in Table 1.

Sample A-1, 940 Å Surface Roughness
1.0 mil thick, 763 torr.

Sample A-2, 803 Å Surface Roughness,
0.5 mil thick, 763 torr.

Sample A-3, 468 Å Surface Roughness
1.0 mil thick, 97 to 140 torr.

Sample A-4, 496 Å Surface Roughness
0.5 mil thick, 60 to 110 torr.
Figure 7: STM plot of 1.0 mil thick copper deposited at 763 torr.

Nanoscope II
Parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bias</td>
<td>100.1 mV</td>
</tr>
<tr>
<td>Setpoint</td>
<td>0.49 nA</td>
</tr>
<tr>
<td>Z</td>
<td>100.0 A/V</td>
</tr>
<tr>
<td>XY</td>
<td>272.3 A/V</td>
</tr>
<tr>
<td>Samples</td>
<td>400/scan</td>
</tr>
</tbody>
</table>

Cu MIRROR #1
Data taken Fri Nov 02 13:44:39 1990
Buffer 3(13:44:39(F)), Rotated 0°, XY axes [nm], Z axis [nm]
Figure 8: STM plot of 0.5 mil thick copper deposited at 763 torr.

Cu MIRROR #2
Data taken Fri Nov 02 11:55:23 1990
Buffer 4(101A.006), Rotated 0°, XY axes [nm], Z axis [nm]

Nanoscope II
Parameters:
- Bias: 100.1 mV
- Setpoint: 0.49 nA
- Z: 100.0 A/V
- XY: 272.3 A/V
- Samples: 400/scan
Figure 9: STM plot of 1.0 mil thick copper deposited at 97 to 140 torr.

Cu MIRROR #3
Data taken Thu Nov 01 15:57:51 1990
Buffer 2(101A.004(F)), Rotated O°, XY axes [nm], Z axis [nm]

Nanoscope II
Parameters:
Bias 100.1 mV
Setpoint 0.49 nA
Z 100.0 A/V
XY 272.3 A/V
Samples 400/scan
Figure 10: STM plot of 0.5 mil thick copper deposited at 60 to 110 torr.
Figure 11: STM surface profile of sample shown in Figure 10 (0.5 mil thick copper deposited at 60 to 110 torr).
Figure 12: STM surface profiles for samples B-3 and B-6 in Table 1 (B-3 deposited at 764 torr, heat treated at 250°C and diamond turned, B-6 deposited at 56 to 130 torr, heat treated at 250°C and diamond turned).
Figure 13: STM surface profile plot of a part plated in a 4600 liter solution at 760 torr.

LARGE COPPER STRIP
Data taken Mar Dec 12, 1990
Buffer 4117, 0.56 cm
XY axes (nm), Z axis (nm)

Nanoscope II
Parameters:
25.4 A/V
400 scan

XY Samples 1000
500
Table 3

**Issues Remaining to be Addressed Regarding Low Pressure Deposition**

<table>
<thead>
<tr>
<th>Variables</th>
<th>Tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>Deposition rate and uniformity</td>
</tr>
<tr>
<td>Flow</td>
<td>Mechanical properties</td>
</tr>
<tr>
<td>Current density</td>
<td>Hardness</td>
</tr>
<tr>
<td>Brightener concentration</td>
<td>Metallography</td>
</tr>
<tr>
<td>Electrolysis time</td>
<td>Diamond turning characteristics</td>
</tr>
<tr>
<td>Rotation</td>
<td>Permeation</td>
</tr>
<tr>
<td>Scalability</td>
<td>Corrosion tests</td>
</tr>
<tr>
<td></td>
<td>Scanning tunneling microscopy</td>
</tr>
<tr>
<td></td>
<td>Differential scanning calorimetry</td>
</tr>
</tbody>
</table>