ElectroChemical Pattern Replication (ECPR) - metal printing for microelectronics

P. Möller[1], M. Fredenberg[2], P. Wiwen-Nilsson[2], L. Montelius[3], P. Leisner[4], M. Östling[1].

[1]Department of Microelectronics and Information Technology, Royal Institute of Technology, Stockholm, Sweden.

[2]Replisaurus Technologies, Isafjordsgatan 22B 5v, 164 40 Kista, Sweden

[3]Division of Solid State Physics, Lund Institute of Technology, Lund, Sweden

[4]School of Engineering, Jönköping University, and Acreo AB, Jönköping, Sweden

In this study, the capability of depositing copper structures at high rates using a novel electrochemical replication technique (ECPR) was demonstrated. The surface roughness and resistivity of deposited copper material were investigated as functions of replication current density and copper seed layer surface roughness. It was found that the average roughness decreased from 47 to 22 nm when increasing the current density from 4 to 14 A/dm^2. At the same time the resistivity of deposited copper decreased from 2.07 to 1.96 μΩ·cm with the increase in current density. The values for both surface roughness and resistivity are well in range with the results from similar studies using conventional electroplating processes. We suggest that the high deposition rates can be obtained without dendrite formation because of the effective mass transfer that is enabled by a very close electrode distance, and thus thin diffusion layers, in the local microcells formed when a patterned master electrode is compressed against a substrate with thin film of electrolyte in-between.

For more information contact:
Patrik Möller
Replisaurus Technologies AB
Isafjordsgatan 22B 5v, 164 40 Kista, Sweden
Phone: +46 701772101
Fax: +46 7526062
Email: patrik.moller@replisaurus.com

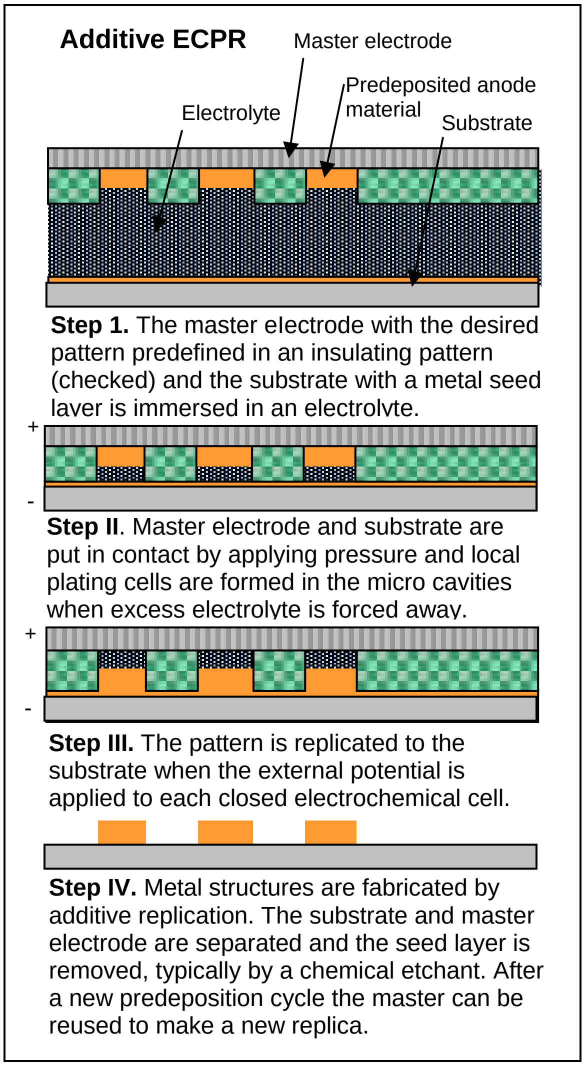
Introduction

The ever increasing demand for smaller, faster and less expensive electronic and biomedical microdevices calls for a continuous development of suitable materials and efficient manufacturing processes. Printing techniques have been shown as cost-efficient and reliable alternatives for fabrication of polymeric structures, with dimensions from several hundred micrometers to sub 10 nm. A number of different replication methods, such as microcontact printing (µCp)[1], hot embossing[2] and UV-molding (µTP)[3] have been demonstrated for the production of polymeric structures and are currently being used for R&D and pilot scale production for applications such as storage devices, MEMS and semiconductor applications. The polymeric structures fabricated using these nano imprint lithography methods can function both as permanent parts of a device and as pattern defining structures for subsequent pattern transfer processes like etching, lift off or electroplating. Electrochemical deposition has become the process of choice when the semiconductor industry is changing from aluminum to copper metallization.[4] Accurate control of deposit material properties, bottom up filling of high aspect ratio vias and competitive production costs are some reasons for that. ECPR is a new approach to do direct metallization without polymer processing, based on an electrochemical printing principle that combines the advantages associated with electrochemical deposition with the simplicity and productivity associated with printing techniques. This novel metal printing technique is targeting several promising application areas within microelectronics, such as wafer level redistribution, bumping, on chip passives, interposers and MEMS.

The ECPR process

In the ElectroChemical Pattern Replication process a template (master electrode), consisting of an electrically conducting electrode layer and one or more patterned layers of electrically insulating materials, is pressed against a substrate with an electrolyte applied between the two surfaces. (Fig 1.) When put in contact, excessive electrolyte is forced away from the master electrode/substrate interface and local electrochemical micro cells, filled with electrolyte, are formed according to the pattern of the master electrode. When an external potential is applied over the master electrode/substrate surfaces, electrochemical material transfer takes place inside each local electrochemical cell. Metal ions that are dissolved at the anode are transported through the picoliter volume of electrolyte in each local micro cell and deposited on the cathode. Metal patterns can be either electrochemically etched or plated, depending on the polarity of the substrate.[5,6]

The basic idea of the ECPR concept is to enable reuse of the pattern defining insulating structures on the master electrode for many substrates instead of defining the pattern as a polymer template on each substrate prior to metallization, which is the case for traditional lithography based processes. When using the additive process scheme shown in Figure 1, predeposition of anode material has to be done prior to each plating cycle, or less frequently if thicker predeposited layers can be allowed. Correspondingly a cleaning step has to be performed where deposited material in the master electrode is removed after a certain number of cycles when using subtractive processing to pattern a thicker metal film on the substrate.



Step 1. The master electrode with the desired pattern predefined in an insulating pattern (checked) and the substrate with a metal seed layer is immersed in an electrolyte.

Step II. Master electrode and substrate are put in contact by applying pressure and local plating cells are formed in the micro cavities when excess electrolyte is forced away.

Step III. The pattern is replicated to the substrate when the external potential is applied to each closed electrochemical cell.

Step IV. Metal structures are fabricated by additive replication. The substrate and master electrode are separated and the seed layer is removed, typically by a chemical etchant. After a new predeposition cycle the master can be reused to make a new replica.

Figure 1. Additive ECPR process scheme.

The purpose of the master electrode (Fig 2.) is both to accommodate an electrode surface for the metal transfer from anode to cathode in each micro cavity and to accurately define each active electrode area on the substrate by a conformal master to substrate contact. A conformal master to substrate contact

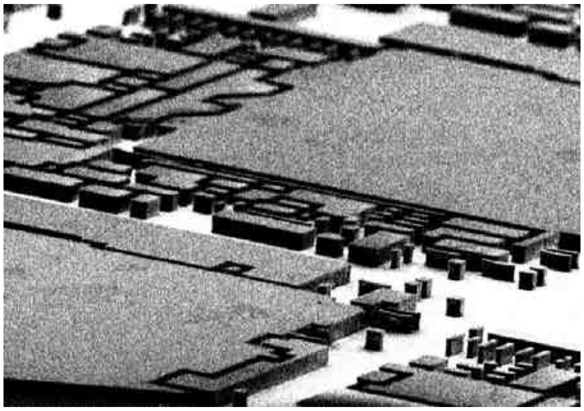


Figure 2. Master electrode surface with an electrically conducting electrode surface (white) and insulating pattern structures. (dark)

should result in an accurate contact pattern on the substrate, corresponding exactly to the pattern on the master side. With a uniform contact surface each insulating structure prevents a well defined substrate area from electrochemical reaction, resulting in high resolution replication. (Fig 3.) To enable a conformal contact over the entire surface, the insulating structures should be able to compensate for substrate roughness or small particles between the surfaces and still give a well defined contact pattern.

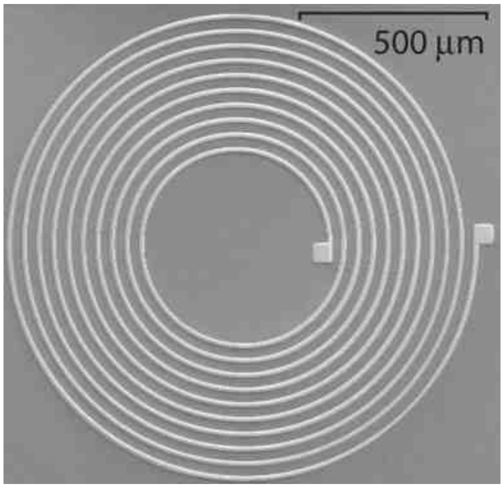


Figure 3. Copper coil fabricated on silicon substrate by additive ECPR. 10µm line width and 3µm copper thickness.

The main advantage of the proposed process is the cost and time efficiency compared to traditional lithography based metallization processes. Also compared to polymer based replication methods, a significantly more efficient production of metal structures is possible. Metallization cycles of just a few minutes per layer have been achieved, with typical material transfer rates of 1-4µm metal per minute.

In this work the surface roughness of copper structures, deposited using additive ECPR, has been investigated as a function of current density and copper seed layer grain size/roughness. Also the resistivity of deposited copper material has been studied as a function of current density.

Experimental

Two different copper seeds layers were deposited on Si/SiO_2 wafers with 10 nm of Cr as adhesion layer. Wafers with 75 nm PVD copper were prepared to serve as a standard seed with low surface roughness. Wafers with 500 nm PVD copper followed by a 60 min anneal at 200°C in N_2-atmosphere were prepared to study the effect from a seed layer with larger grain size and more surface roughness. To prevent the copper seed from air oxidation, 30 nm Ti was deposited on the copper in the PVD process. The titanium was removed by a short 1% HF etch prior to each ECPR deposition.

2µm copper was ECPR deposited using current densities between 4 and 14 A/dm^2 under galvanostatic control at room temperature. An electrolyte containing $CuSO_4 \cdot 5H_2O$, DI water and a proprietary wetting agent was used for the experiments.
After analyzing the surface roughness of copper deposited on 75 nm seed, deposition of 2µm copper on the wafers with 500 nm annealed seed was performed using the current density that gave the lowest surface roughness on 75 nm seed. Analysis of surface roughness and grain size of both the seed layers and deposited copper structures were done using AFM (tapping mode), SEM and optical microscope.

To measure the resistivity of deposited copper from the current density series on 75 nm seed, the copper seed and chromium layers were removed by a wet etch, leaving only the deposited copper circuitry on SiO_2. A 4-point probe station was used for Kelvin measurements of ECPR deposited resistivity chains, shown in Figure 4.

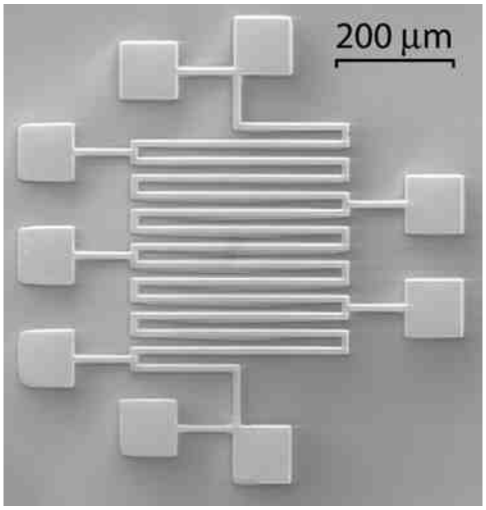


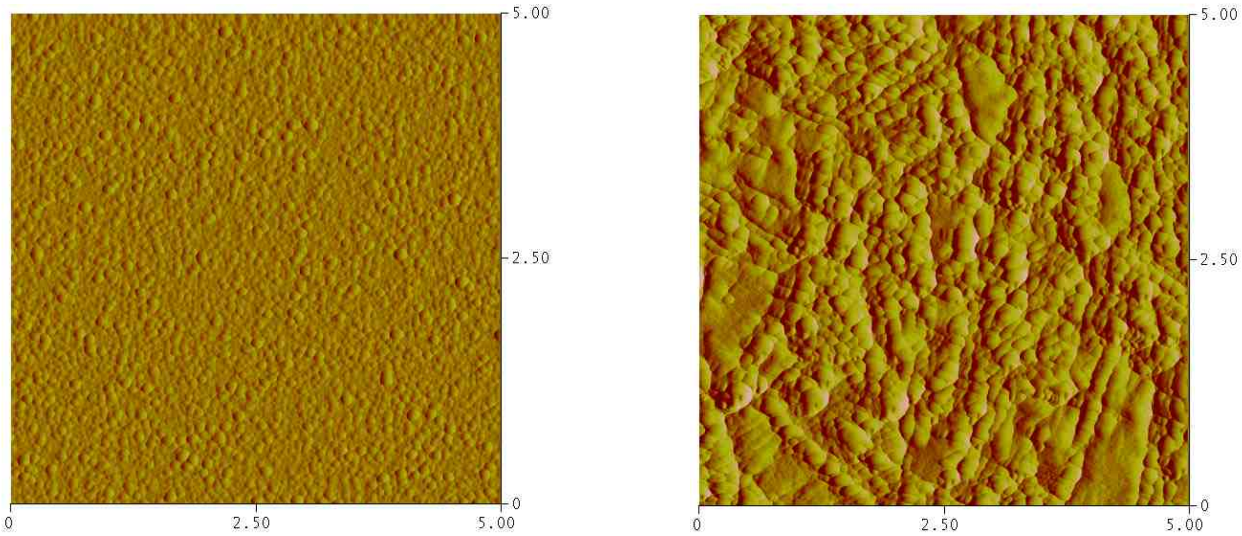
Figure 4. Replicated resitivity chain with 10µm line width.

Results and discussion

Seed layers

Analysis of the two different seed layers used in this work showed a significant difference in grain size and surface roughness. The AFM plots and SEM images of 75 nm copper seed compared to 500 nm copper seed annealed at 200°C for 60 minutes can be seed in Figure 5. The standard 75 nm seed has an average roughness of 3.7 nm compared to the annealed 500 nm seed with an average roughness of 13.7nm. Prior to anneal the

difference in grain size and roughness was negligible, but during the anneal step the 50-80 nm large grains recrystallised to large grains, up to 500-750 nm in size. Since a SEM with a modest resolution capability was used, the grains of the 75 nm seed could not really be resolved, but the surface topography and the grains of the 500 nm seed are clearly seen.



a) 75nm Cu seed layer, Ra=3,7nm, AFM

b) 500 nm Cu seed, annealed, Ra=13,7nm, AFM

c) 75nm Cu seed layer, SEM

d) 500 nm Cu seed, annealed, SEM

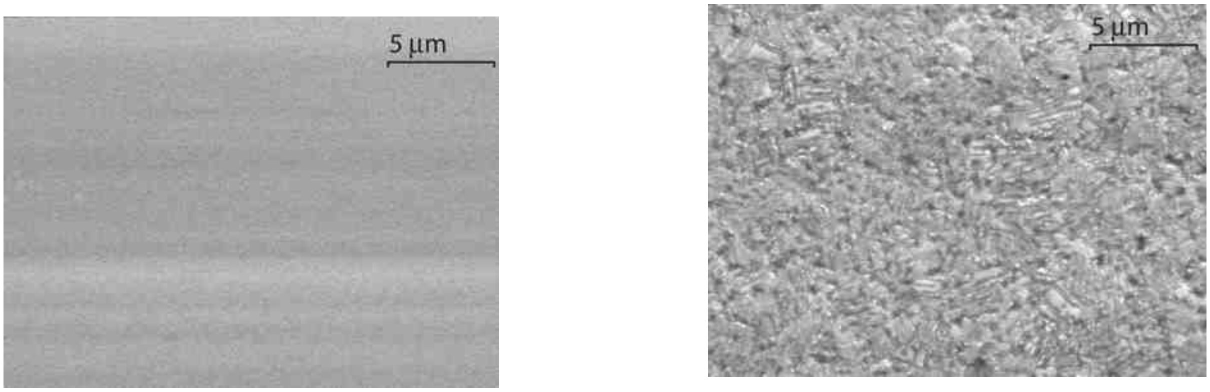


Figure 5. AFM and SEM of 75 nm vs. 500 nm copper seed layers deposited on Si/SiO2/Cr. The AFM pictures have been generated using a 5x5 µm scan.

Surface roughness and resistivity as functions of current density and seed layer

The results from depositing 2 µm copper on 75 nm seed using ECPR with three different current densities are summarized in Figure 6. A significant drop in both resistivity and average roughness could be seen when increasing the current density from 4A/dm^2 to 8 A/dm^2. Further increasing the current to 14 A/dm^2 lead to another significant drop in resistivity and a more moderate improvement in surface roughness. The average surface roughness of the deposited copper ranged from 47 to 22 nm, compared to 3,7 nm for the copper seed. Since copper is known to self anneal at room temperature, having major effects on resistivity and internal stress during the first 10-20 hours after plating[7, 8, 9], resistivity measurements were started 20 hours after completed deposition at the earliest. It should be mentioned that annealing of the deposited structures probably could reduce the resistivity further. Typically a 10-20% reduction in resistivity can be obtained by annealing after plating.

The trend with decreasing surface roughness with increasing current density can also be seed in Figure 8 and Figure 9, visualized by AFM surface plots and SEM-pictures from the current density analysis. Since 14 A/dm^2 gave the lowest surface roughness on 75 nm seed, the deposition of 2 µm copper on 500 nm seed was performed using ECPR with the same replication rate. Somewhat surprising, the surface of the 2 µm copper patterns had an average roughness of 19.5 nm, slightly lower than the copper deposited on the smooth 75 nm seed. Similar results have been shown in previous copper deposition studies[10, 11], where S. Wong et. al. explain the findings by the fact that a rough seed layer has more nucleation sites and are less oriented, and hence the grains of deposited copper are smaller and less oriented compared to a smooth seed with fewer nucleation sites. Both the resistivity and surface roughness values for the copper patterns deposited in this study are well in range with similar studies of copper plating using fountain or paddle agitation cells[8,13,14,15].

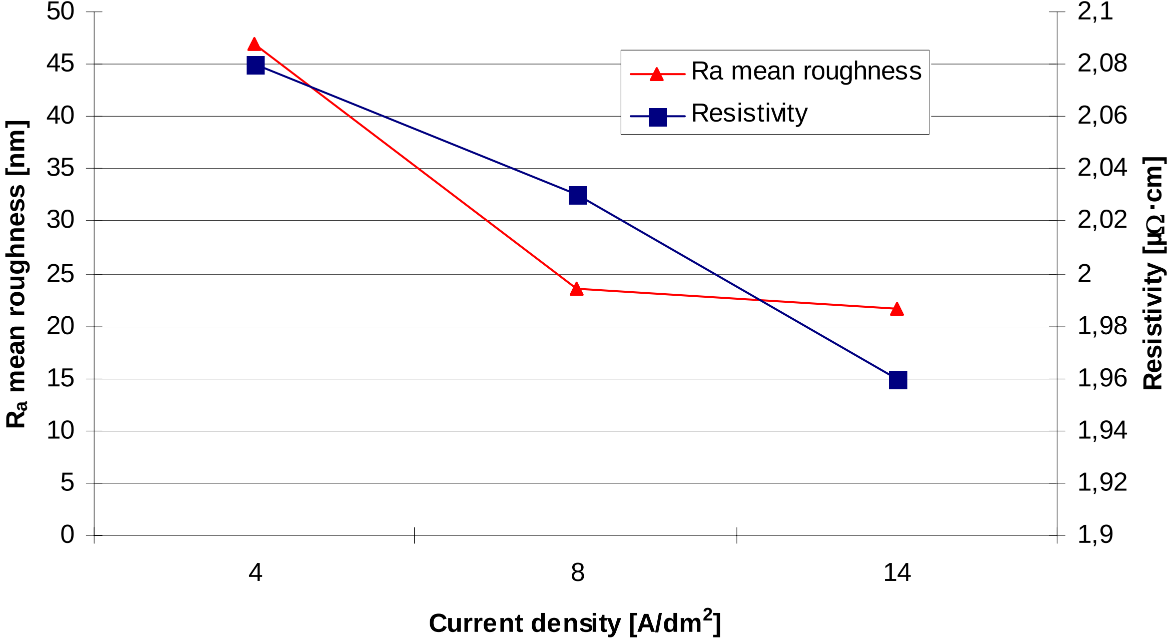
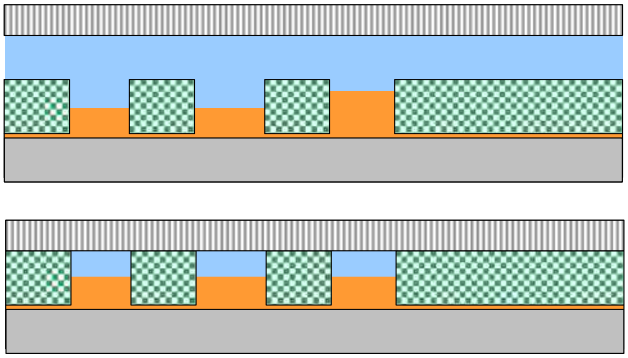


Figure 6. Average surface roughness and resistivity as a function of current density.

No process optimization to minimize average roughness and resistivity by modifying the electrolyte composition or replication parameters has been investigated in this study, the only purpose has been to demonstrate the basic capabilities of this novel deposition technique.

It is well known that an increase in current density during electrochemical deposition leads to an increased polarization and more available nucleation sites for ions at the cathode surface, giving rise to dense deposits with small grains.[8,12,13] The electroplating process can be divided into two regions with different reaction rate controlling mechanisms. At low current densities, where the concentration gradient of electroactive species at the electrode interface is negligible, the crystallization process is charge-transfer controlled. As higher current densities and hence higher bias is applied, mass transfer of electro active species to the electrode surface becomes more and more rate determining on the electro-crystallization until the limiting current is reached, where the reaction is entirely mass transfer controlled. To achieve a dense deposit with small grain size and low resistivity one wants to perform the electrochemical deposition with a high polarization and hence a high energy of the reduction species, which implies many available nucleation sites, without going to close to the region where mass transfer limitations creates a concentration gradient that gives rise to copper aggregation and accelerating dendrite formation. If a high deposition rate is desired, different means to increase the mass transfer of electroactive species exist. Forced convection created by different agitation methods is a common way. Also modification of the copper ion and acid concentration in the electrolyte are viable ways to obtain desired deposition rates without copper aggregation and dendrite growth. In this study using ECPR high deposition rates have been demonstrated without dendrite growth tendencies. The possibility to replicate metal structures using high deposition rates may be explained by the very thin diffusion layers existing inside each confined local microcell. For conventional electrochemical cells with large anode to cathode distance the diffusion layer thickness for a given electrolyte composition and current density is determined by the degree of convection. For ECPR, the thickness of the diffusion layers in the stagnant picoliter electrolyte volumes are determined by the electrode distance, i.e. the thickness of the dielectric layers in the master electrode. Mass transfer is exerted by diffusion and migration mechanisms only. Experimental studies and simulations have shown that deposition rates significantly higher than the ones demonstrated in this work are possible without the undesired effects of dendrite formation.

A major advantage of ECPR is the uniform reaction rates over a wafer surface, nondependent of the pattern being replicated, arising from the fact that the corresponding cathode to anode area of each microcell always has a 1:1 ratio, see Figure 7. Non uniform current density distribution depending on the pattern being plated is a major problem for the entire industry and a great deal of effort is being put into minimizing the problems by different shielding concepts, dummy patterns and mathematical approaches to cope with the problem already in the design phase.[16,17,18]



Conventional plating cell with large cathode-to-anode distance giving rise to non uniform current density distribution depending on the pattern on the substrate

ECPR closed thin-film electrochemical micro-cells with 1:1 cathode to anode area ratio non depending on the pattern.

Figure 7. Non uniform current density and material distribution in a conventional plating cell compared to the 1:1 anode to cathode area ratio in ECPR giving a perfectly uniform current density distribution.

Nevertheless, because of the geometry of conventional plating cells, one can rarely solve all the problems and differences in deposition rates, depending on the pattern, do normally exist. Especially for alloy plating, the uniform deposition rate of ECPR is an important advantage over conventional methods, since the composition of an electroplated alloy depends on the current density distribution and thus the anode to cathode area ratios for each micropattern.

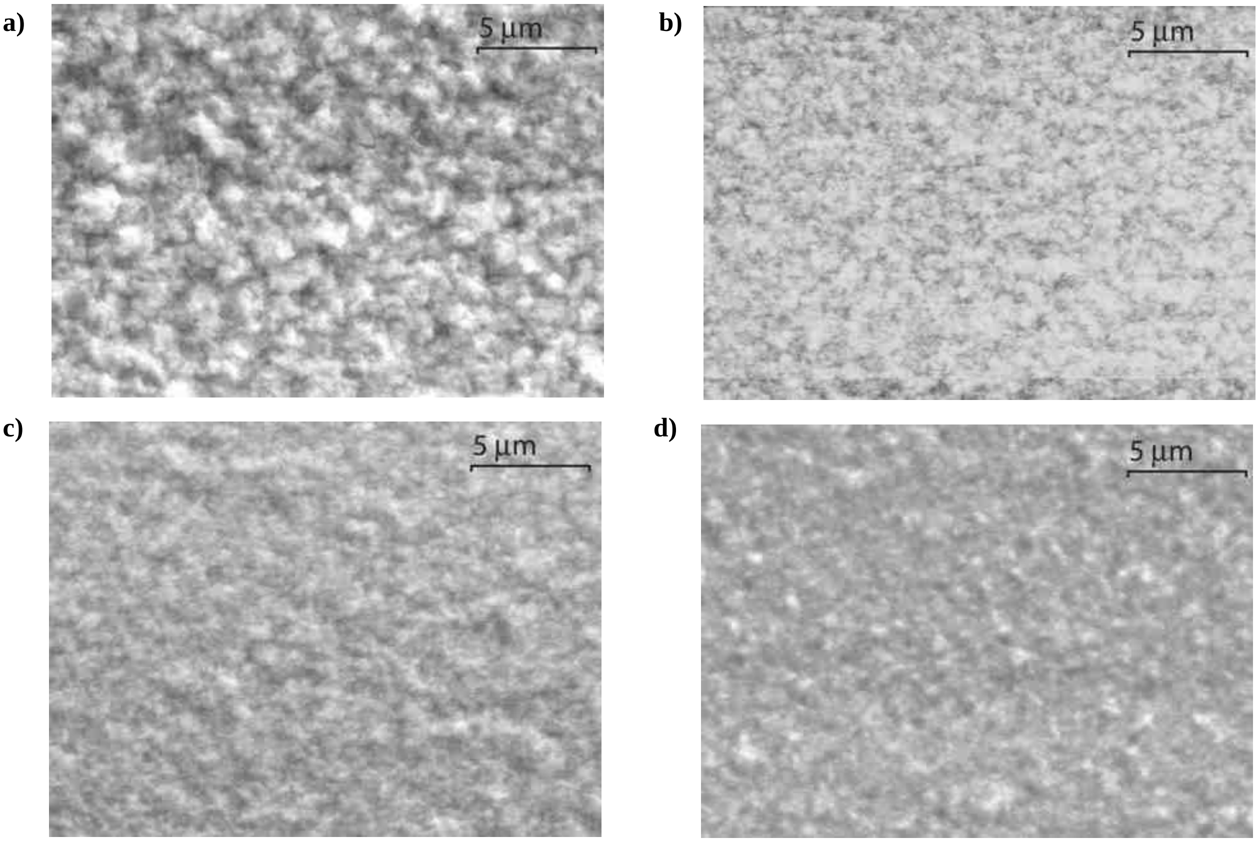
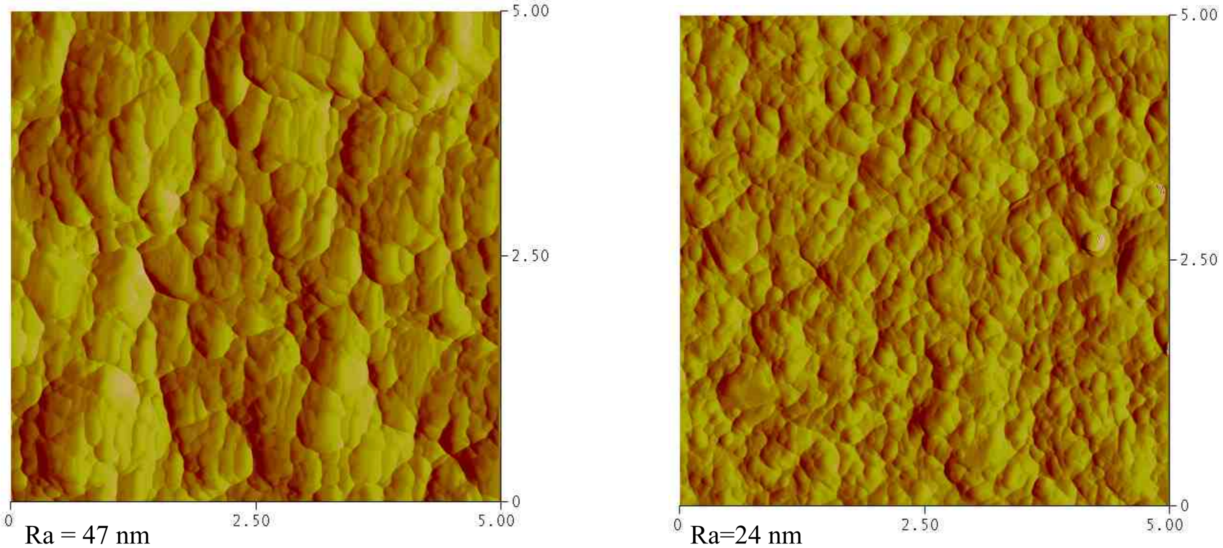


Figure 8. a) SEM image of 2µm ECPR copper deposited on 75 nm seed at 4 A/dm^2. Ra = 47nm
b) SEM image of 2µm ECPR copper deposited on 75 nm seed at 8 A/dm^2. Ra = 24 nm
c) SEM image of 2µm ECPR copper deposited on 75 nm seed at 14 A/dm^2. Ra = 22 nm
d) SEM image of 2µm ECPR copper deposited on 500 nm seed at 14 A/dm^2. Ra = 20 nm

a) 2µm Cu deposited on 75 nm seed at 4A/dm^2.

b) 2µm Cu deposited on 75 nm seed at 9 A/dm^2.

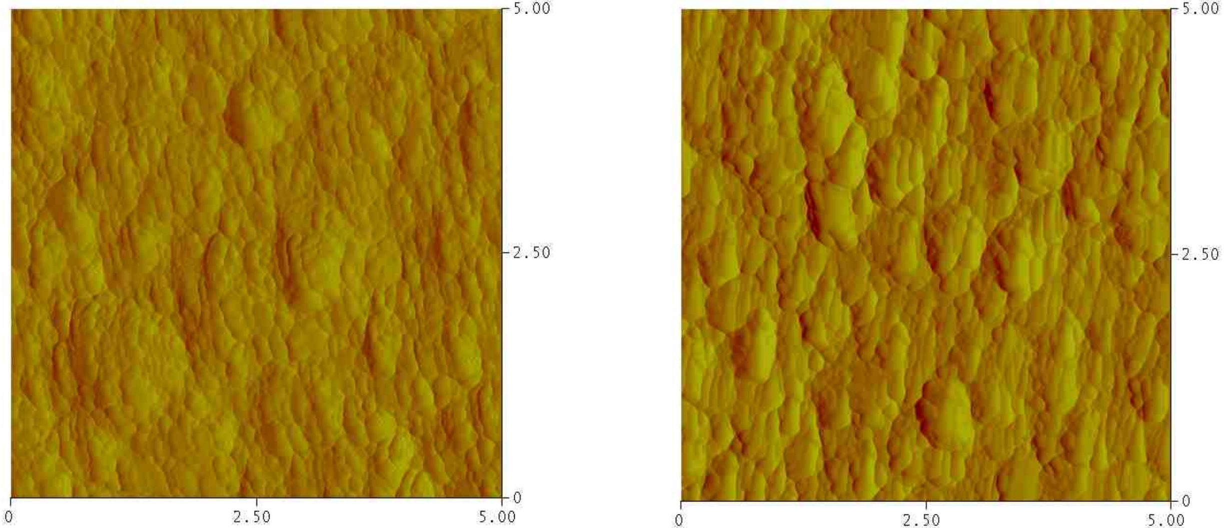


Ra = 47 nm

Ra=24 nm

c) 2µm Cu deposited on 75 nm seed at 14 A/dm^2

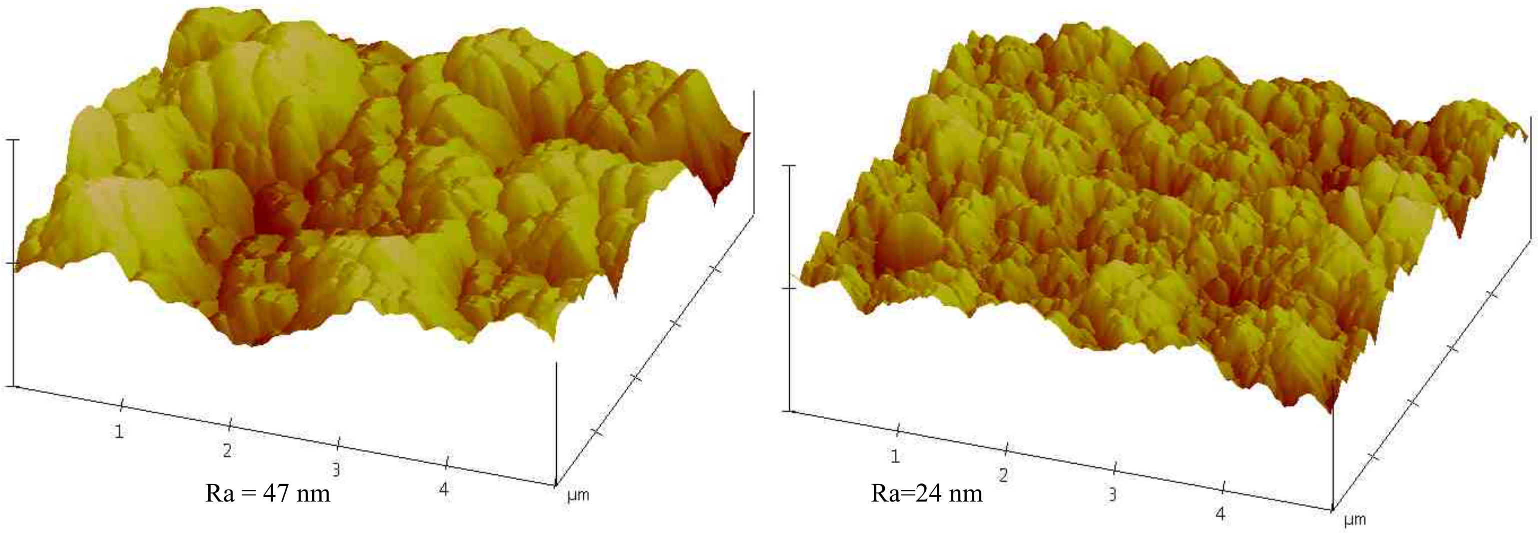
d) 2µm Cu deposited on 500 nm seed at 14 A/dm^2



Ra=22 nm

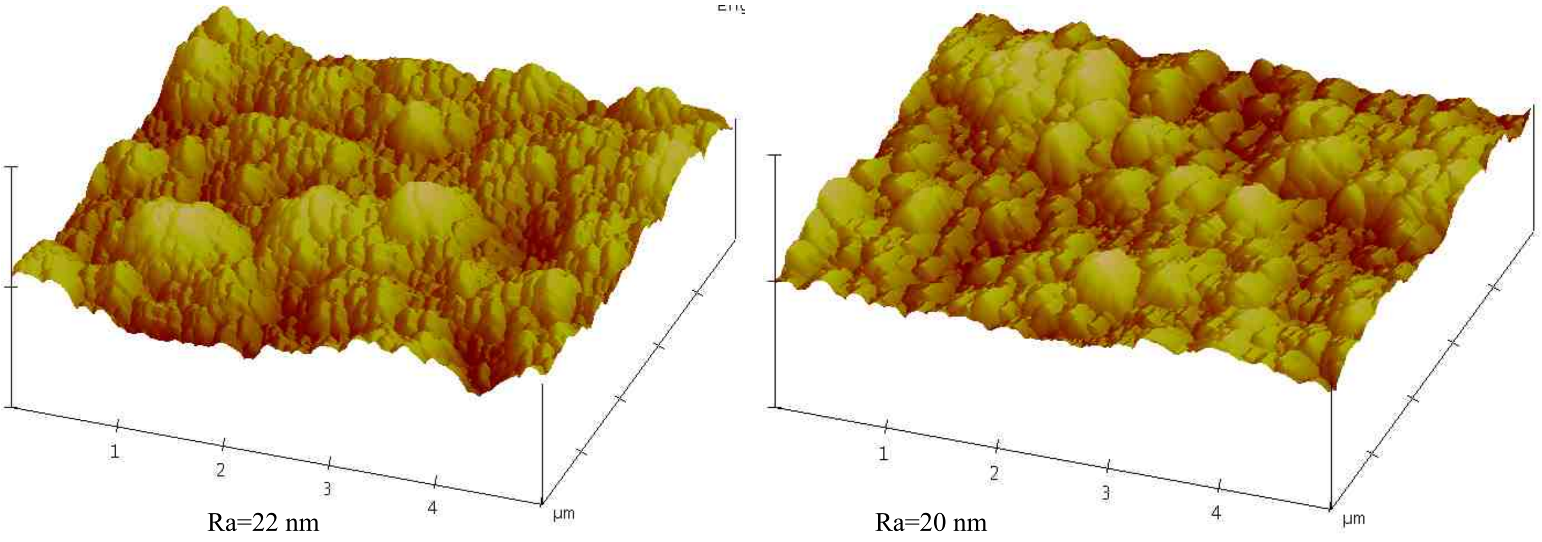
Ra=20 nm

Figure 9. a)-d). AFM images of 2µm ECPR copper deposited on different seed layers at different current densities. 5x5 µm scan size.



e) 2µm Cu deposited on 75 nm seed at 4A/dm^2.

f) 2µm Cu deposited on 75 nm seed at 9 A/dm^2.



g) 2µm Cu deposited on 75 nm seed at 14 A/dm^2

h) 2µm Cu deposited on 500 nm seed at 14 A/dm^2

Figure 9. e)-h). AFM surface plots of 2µm ECPR copper deposited on different seed layers at different current densities. 5x5 µm scan size. Z-scale = 300 nm for all plots.

Conclusions

The capabilities of depositing copper structures at high rates using a novel replication technique (ECPR) has been demonstrated and the average surface roughness and resistivity of deposited material has been studied as a function of current density and seed layer roughness. The average roughness decreased from 47 to 22 nm when increasing the current density from 4 to 14 A/dm^2. At the same time the resistivity of deposited copper decreased from 2.07 to 1.96 $\mu\Omega\cdot$cm with the increase in current density. The values for both surface roughness and resistivity are well in range with the results from similar studies using conventional electroplating processes.

Considerable savings in process costs and cycle time is possible by using this electrochemical replication principle instead of lithography based metallization where a polymer template is fabricated on each wafer prior to electroplating. In addition to the cost and time savings, processing advantages also exist because of the uniform current density distribution arising from a perfect 1:1 cathode to anode area ratio. This is a major advantage when plating alloys, since not only the material distribution but also the alloy composition is dependent on the current density distribution.

Acknoledgements

We would like to thank Dr. Erdal Suvar at SSD, Royal Institute of Technology, Stockholm, for assistance in the generation of AFM-images and Dr. Carl-Mikael Zetterling for assistance during the electrical measurements.

References

1. Whitesides G.M., Younan X., 1998, Ann. Rev. Mater. Sci. 28:153-84
2. Chou S.Y., Krauss P.R., Renstorm P.J., 1995, Appl. Phys. Lett. 67, 3114
3. Scherer A., Quake S.R., 2000, Science vol 288 7 April
4. Datta M., 1998, IBM Journal of R&D, vol 42, no 5. p563.
5. Möller P., Wiwen-Nilsson P., 2002, Diploma project Solid State Physics, LTH, Sweden.
6. Patent SE0102144-3 and PCT patent application PCT/SE02/01179
7. Volinsky A.A., Hauschildt M., 2002, Mat. Res. Symp. Proc. Vol. 695.
8. Chang S., Shieh J-M., 2002, J. Electrochem. Soc., 149 G535-G538
9. Walter D., Gross M.E., 2000, Mat. Res. Symp. Proc. Vol. 612
10. Lee H., Lopatin S.D., 1998, Mat. Res. Fall meeting, Symp. A, Paper A1.9
11. Wong S.S., Ryu C., 1998, Int. Interconnect Tech. Conf., June 3.
12. Grujicic D., Pesic B., 2002, Elecectrochimica Acta 2901-2912
13. Jensen J.A.D., 2002, PhD dissertation no. 784, Linköping University, Sweden.
14. Seah C.H., Mridha S., 1998, , Int. Interconnect Tech. Conf., June 3.
15. Kang M., Gewirth A.A., 2003, J. Electrochem. Soc., 150, C426-C434
16. Mehdizadeh S., Andriacacos P.C., Romankiw L.T., 1993, J. Electrochem. Soc. Vol 140, No. 12
17. Landolt D., 2002, J. Electrochem. Soc., Vol 149, S9-S20.
18. Park T.H., Tugbawa T.E., 2001, Int. Interconnects Tech. Conf.