Simulation of Current Density for Electroplating on Silicon Using a Hull Cell

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Abstract: Electrodeposition has a major advantage over other methods of thin film deposition. It allows deposition at atmospheric pressure and room temperature, requiring relatively inexpensive equipment [1]. However, there are several parameters which can influence a metal layer quality when electroplating. The current density distribution over the cathode is usually the one which has the biggest attention [2]. The Hull cell is a miniature electrodeposition tank with a cathode angled with respect to the anode. The resulting current density will vary along the length of the cathode surface [3]. Therefore, it is possible to obtain an optimal plating distance for certain given parameters of the system.
A semiconductor sample holder was built to allow experiments with this type of cathode in the Hull cell. The setup was tested and simulated in 2 and 3 dimensions for the Hull Cell. A modified Hull cell design is suggested for further experiments.

Keywords: Electrodeposition, semiconductor, Hull cell, current density.

1. Introduction

Working with galvanic structuring processes has been a great motivation considering costs and further development of new applications such as in IC-technology [4], fuel cells [5] and solar cells [6,7].

There are, normally, practical problems if a semiconductor is used as cathode where the deposition takes place [8]. A full back-contact has to be provided to avoid different deposition rates due to the high resistivity of a doped semiconductor (e.g. Si) substrate compared to a metal cathode. An electrical non-conductive holder is used to prevent deposition other than through the front opening where the cathode has its interface with the electrolyte. Furthermore, the native SiO_2 on Si has to be removed right before the plating process starts (e.g. etching). The sample has to be brought rapidly into the electrolyte avoiding the re-growth of native SiO_2.

1.1 Hull Cell

The Hull cell has become a very useful tool due to its cost, simplicity and special shape for electroplating. A lot of researchers have worked with it and even modified its shape to adjust for their requirements [2]. The shape and dimensions according to the German Standard can be seen in the following Fig. 1.

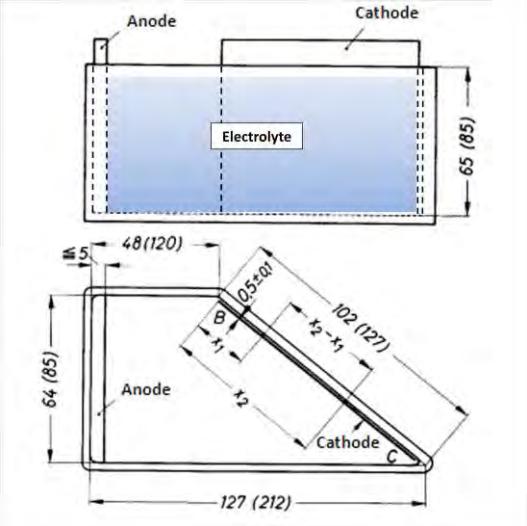

Figure 1. 250 ml Hull cell top and side view with dimensions in mm (between parentheses: 1l-Hull cell) [9]

Fig. 2 shows a top view of the current density distribution in the electrolyte. It is easily noticed that the intensity is higher closer to the anode and it decreases with increasing separation between cathode and anode.

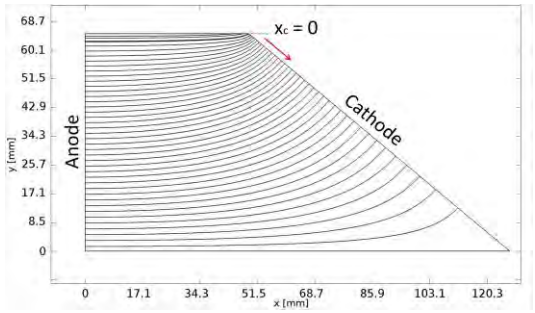

Figure 2. 250 ml Hull cell current density streamlines

The current distribution along the cathode for 250ml Hull cells [9]:

$$I_c = I(5.1 - 5.24 \log x_c) \quad (1)$$

I_c - cathode current density [A/dm^2]
I - total current in the cell [A]
x_c - coordinate along the cathode [cm]

Taking a look on Fig. 1, x is equal 0 at position B and 102 at C.
The normalized (to maximum) current density curves from the DIN 50957 and Comsol simulation for x between 1 and 8 cm can be seen in Fig. 3.

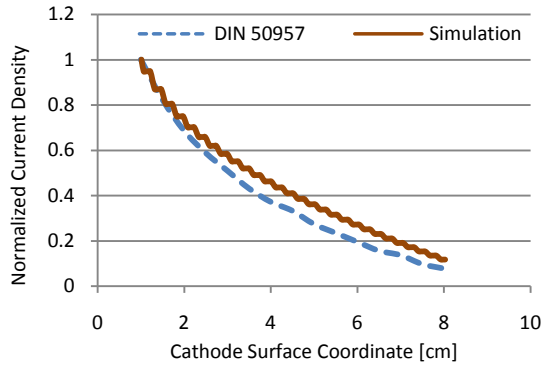

Figure 3. Normalized current density along the cathode ($1 \leq x \leq 8$ cm)

1.2 Sample Holder

Since the cathode is a silicon sample, a full back-contact can be used to minimize problems which could be caused due the low conductivity. The metal (e.g. Cu) layer growth should be as less as possible influenced by the electrical connections on the cathode. For this reason, a sample holder was built to be used in a 250 ml Hull cell like the one in Fig. 1. The holder can be seen in Fig. 4.

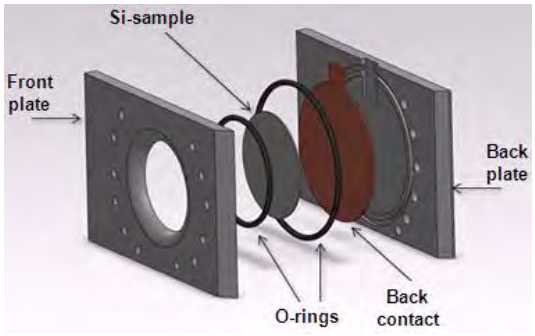

Figure 4. Sample holder and back electrical contact

It is expected that the current lines in the plating cell will be influenced by the holder. Trying to minimize that, the holder opening for the cathode was made as central and as large as possible. Some pre-requirements have limited the opening: front and side fluid leak-proof which should be circular (commercial O-rings) and the standard cathode dimensions are in a rectangular shape: 65 x 102 mm (see Fig. 1). These influences will be investigated with Comsol.

2. Model Description

The simulation considers the Hull cell standard dimensions with the sample holder as it can be seen in Fig. 5.

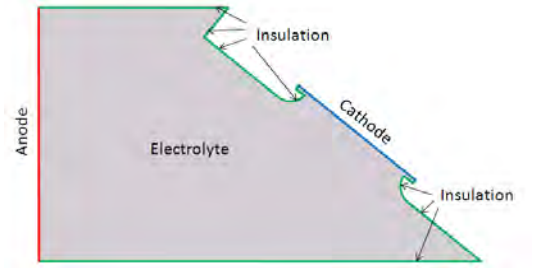

Figure 5. Model domain and its boundaries

The electrolyte used has copper (Cu^{+2}), sulfate (SO_4^{-2}) ions and no further additives were considered. The model was simulated using "tertiary Nernst-Planck" interface [10]. It describes the current and potential distribution in an electrochemical cell taking into account the ions in the electrolyte through the migration, diffusion and convection [10] as it is shown in Eq. (2). A magnetic mixer was used in the experiments, however, convection was not considered in this work.

$$N_i = -D_i \nabla c_i - z_i u_i F c_i \nabla \varphi_i \quad (2)$$

Meaning of the variables used in Eq. (2):
N_i - transport vector of species i [mol/(m^{2}s)]
D_i - diffusion coefficient [m^2/s]
c_i - concentration in the electrolyte [mol/m^3]
z_i - charge for species i [unitless]
u_i - mobility of the charged species i [m^2/(sJmol)]
F - Faraday constant [96485.3 C/mol]

The first term on the right side of Eq. 2 calculates the diffusion contribution and the second one calculates the contribution due to the ion migration (drift) in the electric field.
The model considers the electrolyte in equilibrium and with a soluble anode, for each Cu ion deposited onto the cathode, another one with the same charge will go from the anode to the electrolyte. The reaction happening on the anode is:

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^- \quad (3)$$

and on the cathode:

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \quad (4)$$

where:
(s) stands for solid and (aq) for aqueous.
The current density is given by the following Eq. (5) as a function of potential and Cu concentration [10]:

$$i_{ct} = i_0 exp\left(\frac{1.5F\eta}{RT} - \frac{c_{Cu^{2+}}}{c_{Cu^{2+},ref}} exp\left(-\frac{0.5F\eta}{RT}\right)\right) \quad (5)$$

where: i_0 - exchange current density [A/m^2]
η - overpotential
R - gas constant [8.314 J/molK]
T - temperature [K]
C_{Cu2+} - Cu^{2+} concentration [mol/m^3]
$C_{Cu2+,ref}$ - the reference C_{Cu2+} in the bulk electrolyte [mol/m^3]

3. Simulations

The simulations were realized using the domains and equations shown in the previous topic. The studies were done using "time dependent with initialization" and the mesh element size chosen was the built-in "extremely fine" option.

The current density at the beginning can be seen in the following Fig. 6.

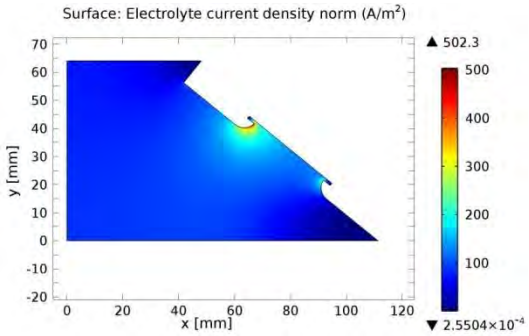

Figure 6. 250 ml Hull cell (with the holder) current density

Zooming in (see Fig. 7), one can see the first anomaly: higher current density values closer to the opening rim. The normalized (to maximum) current density values along the cathode are shown in Fig. 8.

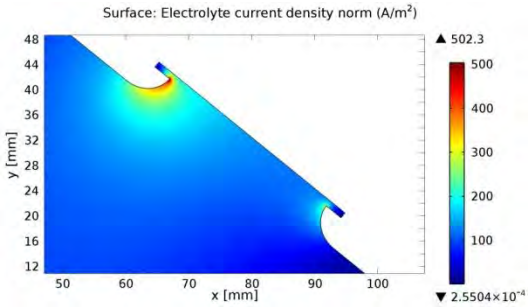

Figure 7. 250 ml Hull cell (with the holder) current density zoomed in

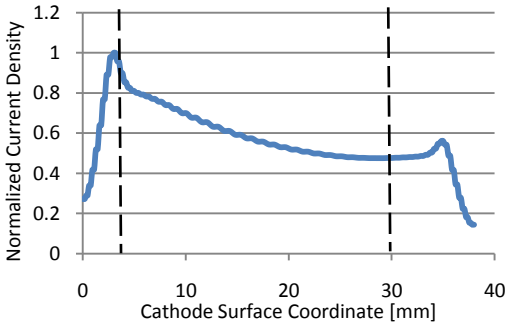

Figure 8. Current density along the cathode surface using the sample holder

In order to have a comparison with Ref. [9], both values, from the standard and simulations, were normalized as well as the cathode surface coordinates. The markers on Fig. 8 show the

range of values used in the comparison. The holder influence on the current density along the cathode is clearly seen in Fig. 9.

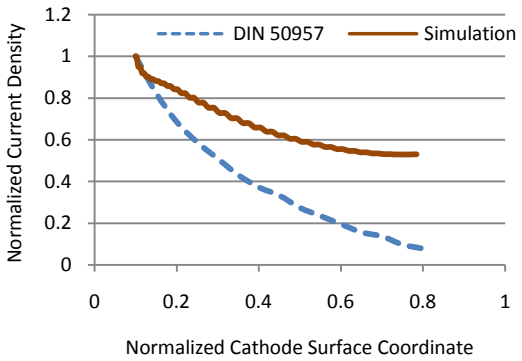

Figure 9. Comparison of the normalized current density along the cathode surface for the standard Hull cell and the one with the cathode holder

Several experiments were made with the setup. The results were usually somehow similar to the simulations, with Cu deposition happening very close to the O-ring and close to the coordinate x equals 4 where the highest current density peak occurs as it is shown in Fig. 10.

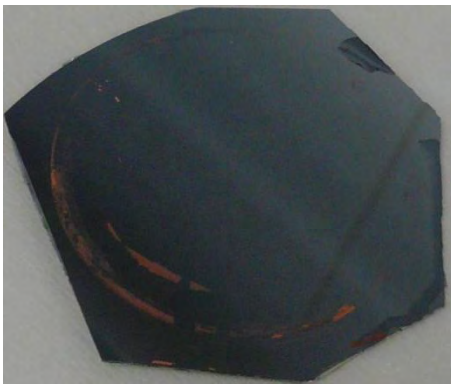

Figure 10. Copper electrodeposited onto Si-substrate

A 3-D geometry was also simulated for the same model to obtain a better view of the deposition onto the substrate as it can be seen in Fig. 11.

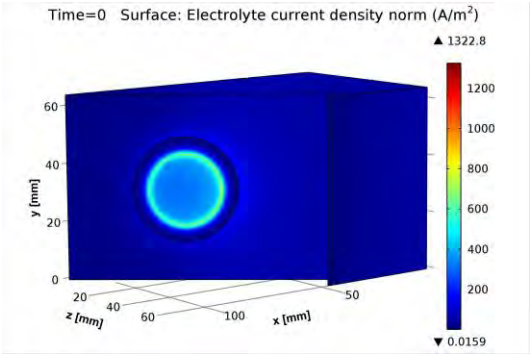

Figure 11. 250 ml Hull cell (with the holder) current density, 3D simulation

3.1 Discussion, Suggestions and Improvement

The usage of a sample holder in a Hull cell has been shown as a partial solution. It will attend some cases. However, it is difficult to make a deeper characterization on the samples electroplated this way. Furthermore, the setup does not follow the standard geometry and neither its results. Therefore, some considerations can be made for the construction of a modified Hull cell. The first point, and probably the most important, is that the current lines should flow as parallel as possible inside the electrolyte tank from the anode to the cathode. The cathode can be set vertically or horizontally: facing up or down. An O-ring could only be eliminated for the last option. An optimal design would consider the tank connecting the anode to cathode with a cylindrical shape with the same diameter as the anode. However, using an O-ring, a second cylinder with a larger diameter is necessary. It is located between the cathode and the first cylinder (see Fig. 12). Once the cathode size was defined, the other dimensions have to be reduced in the same proportion in relation to the standard Hull cell.

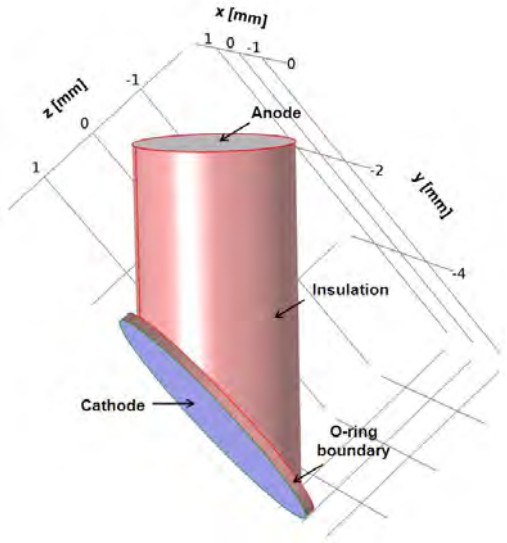

Figure 12. Modified cell 1 model domain and its boundaries

The cathode dimension was chosen starting from a sample metal disc with a 15 mm diameter. A conductive tape, with a diameter of 12 mm, is used to fix the Si-sample on the metal disc and the O-ring to make the holder leak-proof. These parts can be seen in Fig. 13.

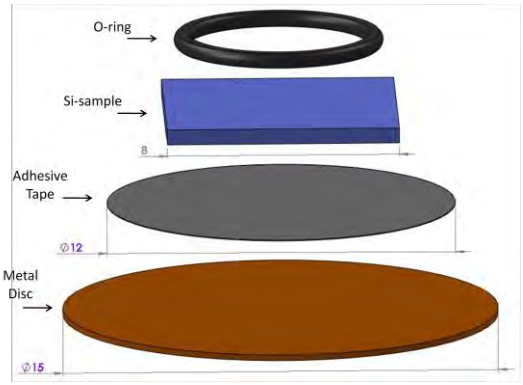

Figure 13. Sample and O-ring limiting the opening dimension to the electrolyte

So, the dimensions used for the modified cell were the ones seen in Table 1.

Table 1. Hull cell and modified cell dimensions

DIN 50957 [mm]	Modified [mm]
102	5.4
48	2.54
64	3.39
127	6.72

Table 1 shows a reduction of about 18.89 from the standard Hull cell to design the modified version.

The setup, however, does not fulfill the requirement to have the current density decreasing with increase of distance between cathode and anode as it is shown in Fig. 14.

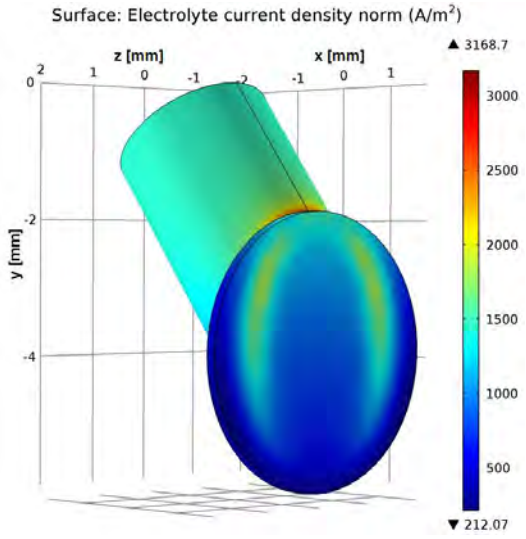

Figure 14. Modified cell 1 (with O-ring) current density

The thickness of the extra cylinder designed to allocate the O-ring was varied but no big changes on the current density profile has been noticed.

The simulation shows that the possibility of using a holder with an O-ring, for similar setups, is eliminated. A further idea is to lay the cathode facing down over a block where a Hull cell full of electrolyte is located (see Fig. 15). The full contact between the cathode and electrolyte is guaranteed by the convex meniscus of the electrolyte on the cell rim. It happens when the molecules of the electrolyte have stronger attraction between themselves than to the ones of the material which the cell is made of.

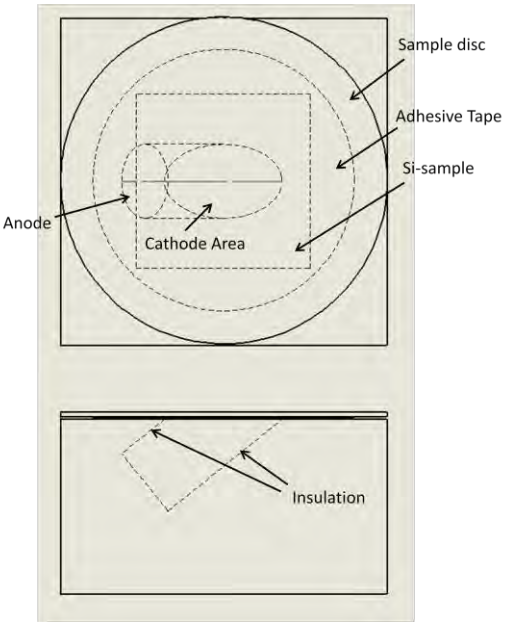

Figure 15. Modified cell 2 and sample

This design should not be used when there is formation of gases during the electroplating process. Otherwise, these bubbles would get stuck on the cathode surface and disturb the process.

A 2-D simulation was realized and the results obtained were normalized. They were very similar to the ones in Fig. 2. However, the current density is a lot larger. The same is observed in the DIN 50957, if the dimensions are reduced and the other variables are kept fixed.

The same model was simulated in 3-D and the results can be seen in the following Fig. 16.

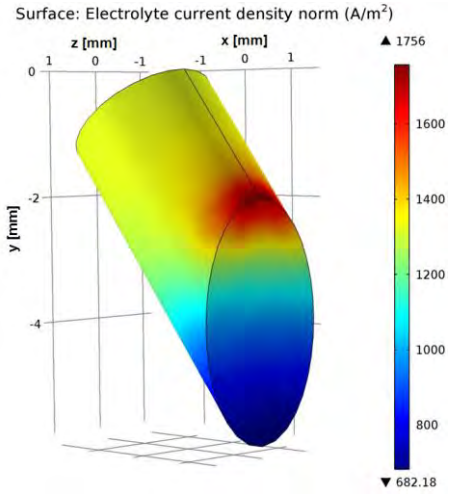

Figure 16. Modified cell 2 current density

The results are as expected from a Hull cell according to the DIN 50957. However, for a circular anode, Eq. 1 could not be used. Another equation for the current density calculation would have to be applied for this setup.

4. Conclusions

The Hull cells can be used in a huge number of experiments. They are also suitable for tests with semiconductors. However, as it has been shown in this paper, modifications have to be made.

A miniaturized Hull cell sketch is presented and simulated in Comsol. The results are satisfying but a current density profile equation still has to be defined. The design shown considers a circular anode. It would also work for rectangular shaped anodes in the same way. The design presented works if there is no production of gases during the electroplating process. If this is the case, another solution or a modification has to be made to fulfill this necessity.

5. References

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6. Acknowledgements

Many thanks to Institut für angewandte Forschung (IAF) Furtwangen and to the Ministerium für Wissenschaft Forschung und Kunst in Baden-Württemberg which has financed this project as "Kooperatives Promotionskolleg Generierungsmechanismen von Mikrostrukturen" (GenMik).