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A kinetic study of Current distribution by electrodeposition in Copper coatings

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Abstract

This model addresses the precise an analytically derived model for the current distribution on a resistive electrode subject to Butler-Volmer kinetics, with parameters typical to copper plating. The deposit thickness uniformity in copper metalized semiconductor wafers is adversely affected by the limited conductivity of the thin copper seed layer. It is noted that, as expected, the current distribution is more uniform when a less conductive electrolyte is used and when the electrode kinetics are slow down. The resistive substrate tends to cause the copper to plate primarily near the terminal contact at the wafer edge. Models for this terminal-effect have been presented for simpler electrode configurations using unrealistically simplified, linear electrode polarization. The predicted current distributions are compared to numerical simulations using electrochemical computer aided design (CAD) software program, is a freeware program written in MATLAB[4, 5].

Keywords: Deposition kinetics; Numerical modeling, electrode kinetics, electrode polarization, Galvanic electrodeposition;

1. Introduction

Electrodeposition of copper layer on semiconductor silicon wafers in order to provide high-conductivity interconnects, cannot be electrodeposited directly onto the silicon. A thin barrier layer of nitride is applied first. Since electroplated copper does not adhere to the barrier materials, a thin copper seed is deposited first on top of the barrier layer, typically, by PVD.

Economic and engineering considerations require that the thickness of this seed layer be as thin as possible over the flat surface of the wafer. Though, because the current for electroplating the copper layer must be given from electrical contacts on the wafer

circumference, the plating current must pass radically through the thin seed and barrier layers. Because of the high electrical resistance of these thin layers, the plating current responsible to concentrate near the wafer circumference, leading to a thicker deposit near the edge than at the center. As the deposition proceeds, the resistive substrate effect reduces due to copper conductive layer. The final deposit profile exhibits, the effects of the initial non-uniform deposition, as shown below. This terminal effect is a major cause for non-uniformity in the plated copper layer, and its counts and minimization is of practical importance.

The effects of resistive substrates on the current distribution have been analyzed in the literature[1-3] .Tobias and Wiejsman[1] presented an analytical solution for parallel plate electrodes under linear polarization. Uziel Landau et al[2, 6, 8] developed a solution to the more practical Tafel range, extending it also to a larger variety of electrodes.

Takahashi[3] analyzed the wafer configuration, developing a general solution, he has made the assumption that the current distribution is essentially uniform, deriving the range of parameters that support this uniform distribution. We present here the results of an analytical solution that considers linear, Tafel and linearized Tafel polarizations for the plated wafer configurations and compare those with numerical distributions simulated using commercial CAD (Computer Aided Design) software that has been developed specifically for modeling electrochemical systems[4, 5].

2. Model of the resistive electrode

This model have resistive electrode as a thin disk with radius R and thickness $h < R$, as shown schematically in Fig. 1. The current density i_c from the electrolyte into the electrode corresponds to a current density i within the seed layer or the pre-deposited copper layer on the wafer. Assume that a homogeneous distribution of current across the thin conductive layer, i.e., no current density variations exist in the z-axis direct ion within the electrode.

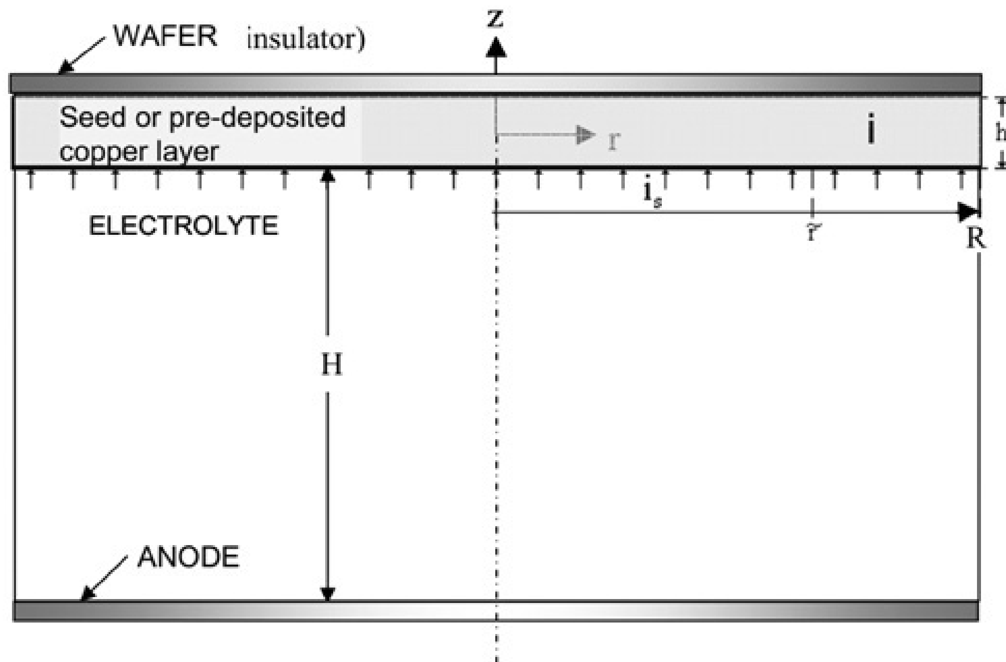

Fig.1: Schematic of configuration for the resistive electrode model

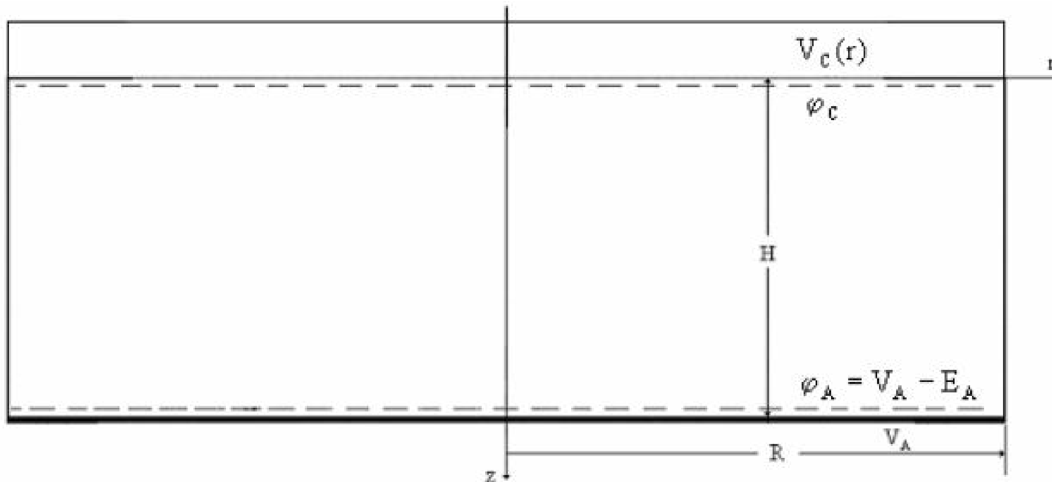

Fig.2. Schematic of the electrolyte model in the considered region

A current conservation in combination with Ohm's law provides the potential distribution along the electrode:

$$V_C(r) = V_R \int_0^R G_V(r, \acute{r}).\, i_C(\acute{r})\acute{r}\; d\acute{r} \qquad [1]$$

Here, V_R – is the voltage at the edge of the electrode and

$$G_V(r, \acute{r}) = \frac{1}{kh} ln\left(\frac{R}{n}\right), \qquad \acute{r} \le r$$
$$= \frac{1}{kh} ln\left(\frac{R}{n}\right), \quad r < \acute{r} \le R \qquad [2]$$

Is the appropriate Green function.

3. Models of electrode kinetics

We apply and compare three simplified models for the deposition kinetics on the resistive electrode:

1) Linear kinetics

$$i_C = -\gamma\eta_C \qquad [3]$$

2) Linearized kinetics about the point((i_S^*, η^*) ,

$$i_C = i_S^* - \gamma^* (\eta_C - \eta_C^*) \qquad [4]$$

3) Tafel kinetics

$$i_C = i_O \exp\{\frac{\alpha_C.F}{R_g.T}.\eta_C\} \qquad [5]$$

η_C –the overpotential on the resistive electrode (the cathode):

$$\eta_C = V_C - E_C - \varphi_C \qquad [6]$$

On the anode we assume the primary electrode kinetics, i.e., we neglect any polarization effects:

$$V_A - E_A - \varphi_A = 0 \qquad [7]$$

When the anode is relatively far away from the cathode, this is a good approximation.

4. Modeling the electric field within the electrolyte

Fig. 2. Shows schematically a plating cell with radius R and height H.

The anode is assumed with a radius R (equal to the cell), positioned at the bottom of the cell. The cathode with radius R, positioned on top of the cell, as shown schematically in Fig. 2. If the distance, H, between the cathode and the anode is small compared the radius of the resistive electrode, R (Fig. 2).So that electric field in the electrolyte is homogeneous.

The solution of Laplace's equation for the potential within the cell gives the relationship between the potential and the current density on the resistive electrode

$$\varphi_C(r) = V_A - E_A - \int_0^R G_\varphi(r, \acute{r}) . i_C(\acute{r})\acute{r}\ d\acute{r} \qquad [8]$$

Where $G_\varphi(r, \acute{r}) = \frac{2}{k,R}[\frac{H}{R} + \sum_{n=1}^{\infty} \frac{th\{\omega_n \frac{H}{R}\} \cdot J_o\{\omega_n \frac{r}{R}\} \cdot J_o\{\omega_n \frac{\acute{r}}{R}\}}{\omega_n \cdot J_o^2 \cdot (\omega_n)}]$ [9]

Is the Green function of Laplace's problem. $\omega_n -$ represents the roots of the equation: $J_o(\omega_n) = 0$, $J_o(x)$ and $J_1(x)$ are the Bessel functions of orders 0 and 1, respectively. If H << R, the potential is distributed linearly in the cell:

$$\varphi_C(r) = V_A - E_A - \frac{H}{k_S} i_C(r) \qquad [10]$$

5. Current distribution on the resistive electrode

5.1. Non-uniformity of the current distribution on a resistive electrode as a function of the anode to cathode distance H.

The non-uniformity of the current density was computed as a function of the distance H, using the electrochemical CAD program[4, 5]. Fig. 3 indicates that the non-uniformity in the current density decreases when the gap is increased, because the electrolyte resistance increases. However, as H exceeds the regime (~ 30cm) an asymptotic value for the non-uniformity is reached and the current distribution is no longer affected by increase in the anode to cathode gap. This numerically determined value of about 30 cm is in good agreement with the analytically indicated value of 25 cm (Eqn. 13).Combining eqns.(1), (6) and (8), provide a non-linear integral equation for the current density i_C on the resistive electrode:

$$\eta_C(i_C) = V_R - V_A + E_A - E_C + \int_0^R G_C(r, \acute{r}) + G_V(r, \acute{r}) . i_C(\acute{r})\acute{r}\ d\acute{r} \qquad [11]$$

Where the overpotential on the resistive electrode is represented as:

$$\eta_C(i_C) = \eta^* - \frac{1}{\gamma} i_C \quad \text{Linear kinetics,}$$

$$= \eta^* - \frac{1}{\gamma^*}(i_C - i_C^*) \quad \text{Linear kinetics,} \qquad [12]$$

$$= \eta^* - \frac{R_g.T}{\alpha_C F} . ln\,(\frac{i_C}{i_O}) \quad \text{Linear kinetics,}$$

According to Eqn. (9), the non-uniformity associated with the solution of Eqn. (11) depends on H, the distance between cathode and anode within the region

$$H < \frac{R}{\omega_1} \qquad [13]$$

Where ω_1 is the first non-zero root of the equation $J_1(\omega_n) = 0$.

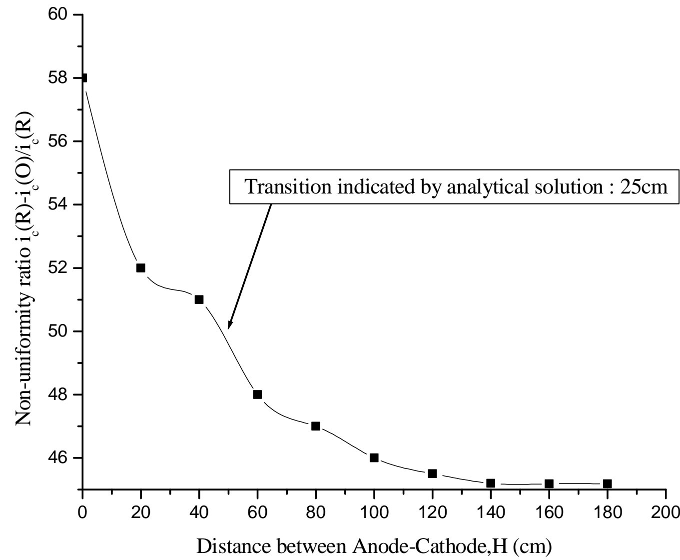

Fig.3. Non-uniformity of the current distribution on a resistive electrode as a function of the anode to cathode distance H.

The potential is linearly distributed in the cell and eqn. (11) takes the form in the reverse case, where $H < \frac{R}{\omega_1}$,

$$\eta_C(i_C) = V_R - V_A + E_A - E_C + \frac{H}{k_S}\, i_C(r) + \int_0^R G_C\,(r\,,\acute{r}\,).\,i_C(\,\acute{r}\,)\acute{r}\;d\acute{r} \qquad [14]$$

In the case of linear kinetics, eqn. (14) has a valid solution:

$$i_C = \frac{V_R - V_R + V_R - V_R}{\frac{H}{k_S}+\frac{1}{\gamma}} \cdot \frac{I_o[r/\sqrt{kh(\frac{H}{k_S}+\frac{1}{\gamma})}]}{I_o[R/\sqrt{kh(\frac{H}{k_S}+\frac{1}{\gamma})}]} \qquad [15]$$

Where $I_o(x)$ is the modified Bessel function of zero order.

5.2 Non-uniformity of the current distribution on a resistive electrode as a function of the electrolyte conductivity and exchange current density.

By using less conductive electrolyte is used, the current distribution on the cathode is more uniform and when the electrode kinetics is inhibited[6-8]]. It can be seen in Eqn. (15) that this holds for any anode to cathode gap and for nonlinear kinetics. Fig.5 and 6 represent the relative variation of the current density along the resistive electrode as a function of the electrolyte conductivity, (k_S) and the exchange current density, (i_o)respectively. The linearized kinetics constant (in Eqn. 12), was taken.

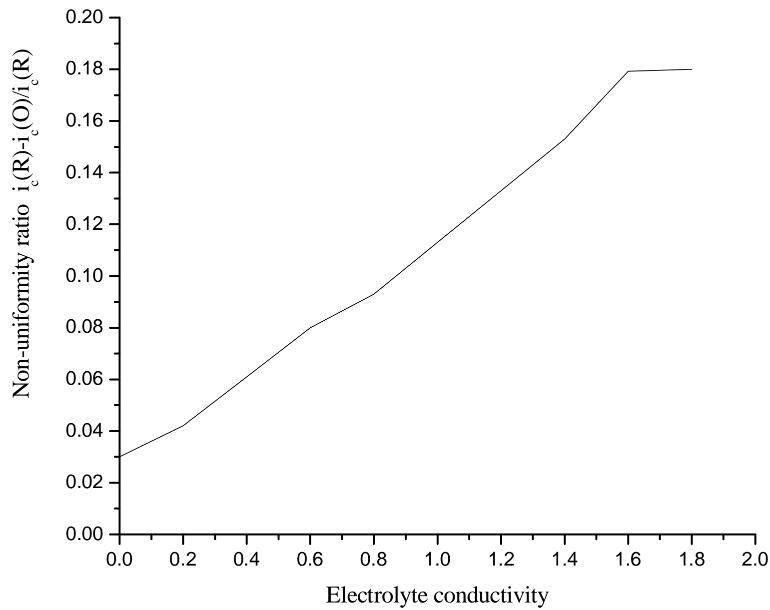

Fig.4. Non-uniformity of the current distribution on a resistive electrode as a function of the electrolyte conductivity.

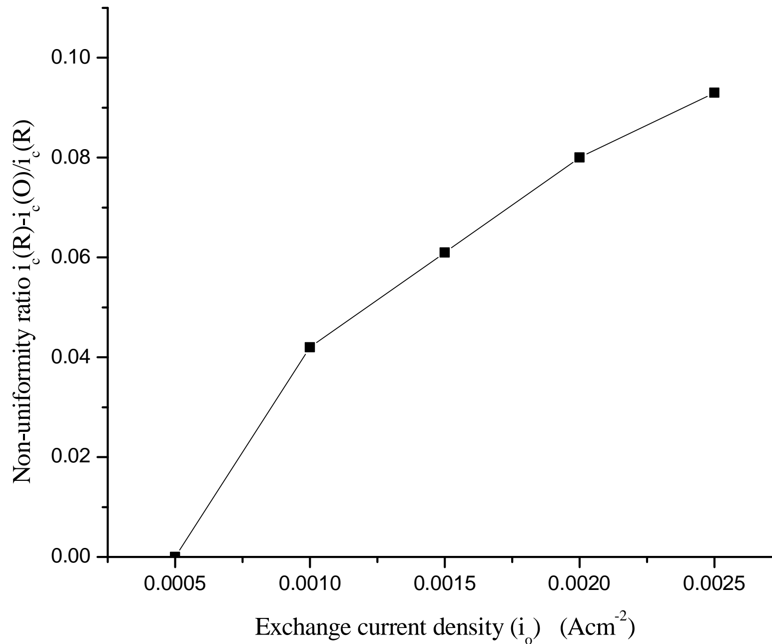

Fig.5. Non-uniformity of the current distribution on the resistive electrode as a function of the exchange current density.

It is noted that all simulations are in good agreement with the different analytical models, indicating the validity of the theoretical approach. The current density at the center of the resistive layer of electrode as computed by CAD software[11, 12] and by the analytically

derived eqn (11), for linear, linearized, and Tafel kinetics as a function of the applied voltage between the anode and the edge of the resistive electrode (cathode), is also referred to as the terminal voltage or contact voltage. The kinetics model applied to the numerical simulations is the complete Butler-Volmer model, with parameters typical to copper deposition. The differences between the models become noticeable only at fairly high applied voltages corresponding to unrealistically high current densities. The linear kinetics point out rather lower current densities at higher applied voltages; a region where deviations from the Butler-Volmer kinetics are noticeable as in Fig. 6.

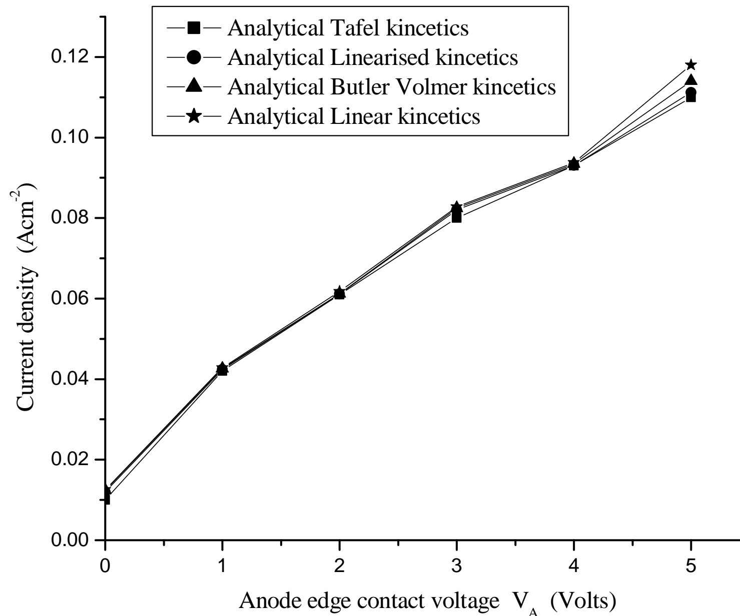

Fig.6. Current density in the center of the resistive electrode as computed by software for electrochemical cell design by using equation (11) for linear, linearized and Tafel kinetics as a function of the voltage applied between the electrode edge and the anode.

The distribution becomes significantly less uniform at higher voltages and correspondingly, at higher average current densities. The distributions were derived using two approaches: simulations by software (shown as open points) and by applying the analytical solution (solid lines). Excellent agreement is noted between the two methods. Fig. 7 shows that the radial distribution of the local current density across the resistive electrode.

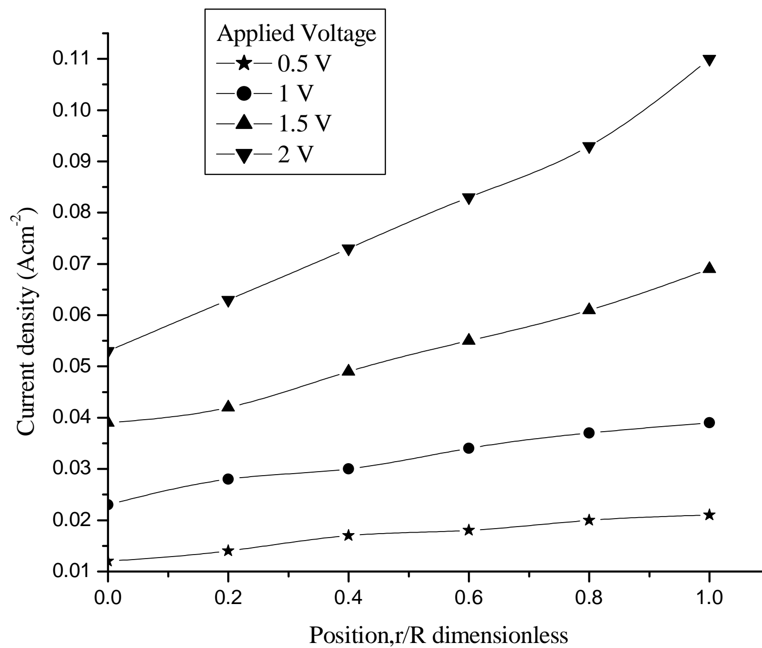

Fig.7. Current density across a resistive electrode computed by using equation 11 at different applied voltages

6. Conclusions

Excellent agreement was noted between the analytical model and the software simulations, with the linear kinetics model exhibiting slight deviation at the higher current densities. Different models for the deposition kinetics were compared: Tafel linearized Butler-Volmer equation about a point, and linear kinetics. A methodical model has been derived for the current distribution on a resistive electrode. The systematic results were also compared to an electrochemical CAD software[9, 10] that utilize the complete Butler-Volmer Kinetics. The solutions indicate as increased current distribution non-uniformity at higher electrolyte conductivity and at a higher exchange current density (more reversible kinetics). At small gaps between the anode and the cathode ($H < 30$ cm), a larger gap corresponds to a more uniform distribution due to the increased resistance of the electrolyte phase.

there is no further improvement in the current distribution when the gap is increased beyond about 30 cm in both the theoretical analysis and the computer simulations, It should be noted that all the current distributions in typical plating applications, a conductive deposit builds up on top of the substrate, in this manner reducing its resistance, leading to a more uniform current and deposit thickness distributions. It is difficult to model analytically this time-dependent effect CAD software simulation.

7. References

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