

SIMULATION OF COPPER DEPOSITION BY ELECTROCHEMICAL PATTERN REPLICATION

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ABSTRACT

A simulation model for copper deposition by Electrochemical Pattern Replication (ECPR) has been developed taking electrode kinetics and mass transport into account. An arbitrary Lagrangian-Eulerian method was implemented to simulate moving boundaries corresponding to the deposition and dissolution of copper on the electrode surfaces. Effects of ion concentration, current density and a protrusion on the cathode surface were studied by the model. Based on experimental measurements an adjustment of the model was made to improve correlation between simulations and experiments.

KEYWORDS

Micro cells; modelling; copper plating; microelectronics; ECPR; simulation

INTRODUCTION

The continued increasing demand for faster, smaller and cheaper microelectronics devices has led to a change in the industrial manufacturing process. The traditional aluminium circuits in microchips have been replaced by electroplated copper mainly due to better electrical and thermal properties [1]. The present manufacturing process is based on the “trough-mask”-plating technology, where copper is deposited in the cavities of a patterned photoresist onto a substrate. Creating the photoresist mask on each substrate is an expensive and time-consuming process which has led to an increasing interest in printing techniques (e.g. nanoimprint) that uses a stamp to create an electroplating mask in a polymer as an alternative to photolithography [2-5]. ECPR is a novel metallization method that utilizes a reusable patterned electrode (master) for direct metal replication. The method is more time and cost efficient than traditional lithography since a number of steps in the fabrication process can be excluded. The template (master electrode), consisting of a conducting electrode layer with a patterned insulating top-layer, is pressed against a substrate with an electrolyte applied between the two surfaces (Fig. 1). When put in contact local electrochemical micro-cells are formed according to the pattern of the master. When an external potential is applied, metal ions dissolved at the anode are transported through the electrolyte in each micro-cell and deposited on the cathode resulting in high resolution replication of the pattern defined by the master (Fig. 2) [6]. The basic idea of the ECPR concept is to reuse the master electrode for many substrates instead of defining the pattern as a polymer template on each substrate prior to metallization.

To be able to predict the result of copper deposition, the development of simulation models for through-mask-plating has been extensive in the

microelectronics industry. Since electrodeposition by ECPR is different from through-mask-plating, the traditional simulation models are not directly applicable for ECPR. The aim of this study was to develop a model for copper deposition by ECPR, which simulates the effect of ion concentration, current density and protrusions in the surface. The model was implemented using the simulation software FEMLAB 3.

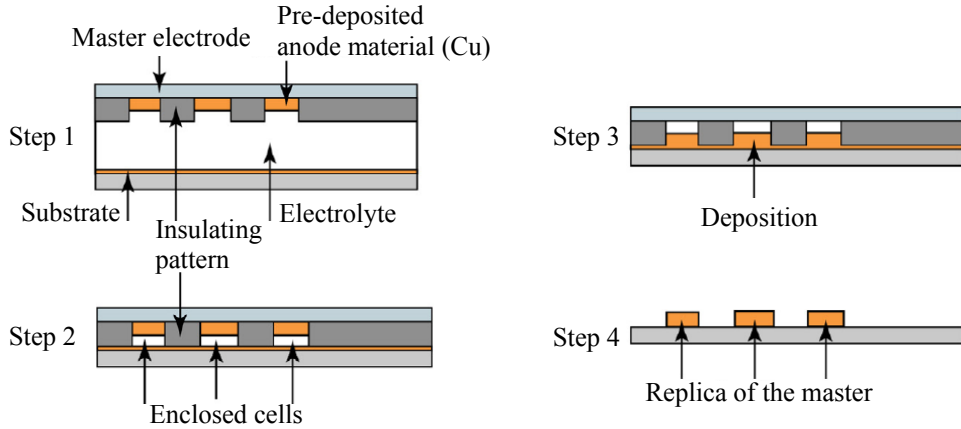


Fig. 1: The ECPR process. (1) Master with predeposited copper. (2) Master and substrate are pressed together enclosing electrolyte in the cavities of the master. (3) Electrochemical transfer of copper from the master to the substrate inside the cavities. (4) The master has been removed and the pattern has been replicated to the substrate.

SIMULATION MODEL

The ECPR process is modelled by studying a 2-dimensional electrochemical micro-cell between the master electrode and the substrate. The electrolyte consist of copper (Cu^{2+}) and sulphate (SO_4^{2-}) ions. The deposition process is simulated at $\text{pH} > 4$, which implies that the proton concentration is very low compared to the copper and sulphate ion concentrations. For this reason, the assumption is made that the material balance of protons could be ignored. In Fig. 3 the top horizontal boundary represents the copper anode in the master and the bottom horizontal boundary the cathodic substrate surface. The left and right vertical boundaries represent the insulating walls of the master. In this study, a cell with dimensions of $40 \times 50 \mu\text{m}$ was chosen.

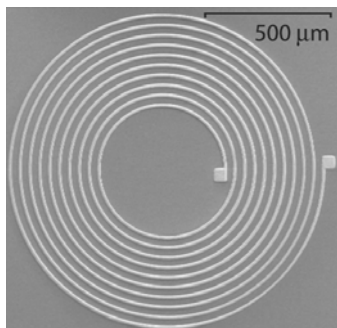


Fig. 2: Copper coil made by ECPR with $10 \mu\text{m}$ line width and $3 \mu\text{m}$ copper thickness.

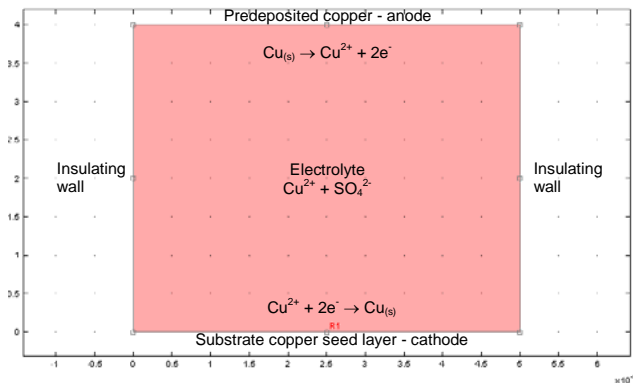


Fig. 6: The geometry of the modelled ECPR cell.

The boundary conditions of the anode and cathode are given by the Butler-Volmer equation:

$$-N_{Cu^{2+}} \cdot n = \frac{i_0}{zF} \left[\frac{C_{Cu^{2+}}}{C_{Cu^{2+},initial}} e^{-\frac{0.5F}{RT}\eta} - e^{\frac{1.5F}{RT}\eta} \right]$$

where n denotes the normal vector to the boundary and $i_0=20 \text{ A/m}^2$. Since the vertical walls are electrically insulating, the copper ion flux at these boundaries will be zero. The sulphate ion flux is zero at all the boundaries.

Electro neutrality and no convection are assumed, and the mass transport in the electrolyte is given by the time dependent Nernst-Planck equation:

$$\frac{\partial C_{Cu^{2+}}}{\partial t} = -\nabla \cdot (-D\nabla C_{Cu^{2+}} - z_{Cu^{2+}} u_{Cu^{2+}} F C_{Cu^{2+}} \nabla \phi), \quad \frac{\partial C_{SO_4^{2-}}}{\partial t} = -\nabla \cdot (-D\nabla C_{SO_4^{2-}} - z_{SO_4^{2-}} u_{SO_4^{2-}} F C_{SO_4^{2-}} \nabla \phi)$$

$$\text{where } u_{Cu^{2+}} = u_{SO_4^{2-}} = \frac{D}{RT} = \frac{1 \cdot 10^{-9} \text{ m/s}}{8,314 \text{ J/moleK} \cdot 298 \text{ K}}$$

A method called the arbitrary Lagrangian-Eulerian (ALE) formulation was applied in order to handle the moving boundaries. The method was implemented into a Finite Element (FEMLAB 3) model by introducing variables describing the mesh velocity and displacement. The method computes on the original mesh points by adjusting the equations for the mesh movements. In order to implement the ALE method in FEMLAB the equations have to be written on weak form, i.e. as integrals, instead of Partial Differential Equation (PDE) form [7].

New variables are introduced: $x(X,Y,t)$, $y(X,Y,t)$, $X,Y \in \Omega$, $x,y \in \bar{\Omega}$, $t \in R_+$, where X, Y are the mesh coordinates in the original domain Ω ; x, y are the mesh coordinates in the deformed domain $\bar{\Omega}$, and t is the time. The deformed domain can be mapped to the original domain by introducing the Jacobian inverse defined as [7]:

$$\begin{bmatrix} I_{Xx} & I_{Xy} \\ I_{Yx} & I_{Yy} \end{bmatrix} = \frac{1}{D_J} \begin{bmatrix} y_Y & -x_Y \\ -y_X & x_X \end{bmatrix} \quad \text{where } D_J = x_X y_Y - x_Y y_X$$

The Nernst-Planck equation can be formulated on the original domain as:

$$\int_{\Omega} -D_J \left((D_{Cu^{2+}} C_{Cu^{2+},x} + z_{Cu^{2+}} u_{Cu^{2+}} F \phi_x C_{Cu^{2+}}) (\hat{C}_{Cu^{2+},X} I_{Xx} + \hat{C}_{Cu^{2+},Y} I_{Yx}) \right. \\ \left. + (D_{Cu^{2+}} C_{Cu^{2+},y} + z_{Cu^{2+}} u_{Cu^{2+}} F \phi_y C_{Cu^{2+}}) (\hat{C}_{Cu^{2+},X} I_{Xy} + \hat{C}_{Cu^{2+},Y} I_{Yy}) \right) + \hat{C}_{Cu^{2+}} \frac{\partial C_{Cu^{2+}}}{\partial t} \Big) d\Omega = 0$$

and

$$\int_{\Omega} -D_J \left((z_{Cu^{2+}} u_{Cu^{2+}} - z_{SO_4^{2-}} u_{SO_4^{2-}}) F C_{Cu^{2+}} \phi_x (\hat{\phi}_X I_{Xx} + \hat{\phi}_Y I_{Yx}) + (z_{Cu^{2+}} u_{Cu^{2+}} - z_{SO_4^{2-}} u_{SO_4^{2-}}) F C_{Cu^{2+}} \phi_y (\hat{\phi}_X I_{Xy} + \hat{\phi}_Y I_{Yy}) + \hat{\phi} \frac{\partial \phi}{\partial t} \right) d\Omega = 0$$

where $\hat{\cdot}$ denotes a test function and the derivatives of the concentration $C_{Cu^{2+}}$ and voltage ϕ are denoted by

$$\left\{ \begin{array}{l} C_{Cu^{2+}x} = \frac{\partial C_{Cu^{2+}}}{\partial x} \quad C_{Cu^{2+}y} = \frac{\partial C_{Cu^{2+}}}{\partial y} \\ \phi_x = \frac{\partial \phi}{\partial x} \quad \phi_y = \frac{\partial \phi}{\partial y} \end{array} \right\}$$

in the deformed domain $\bar{\Omega}$ and the derivatives of the depending variables $C_{Cu^{2+}}$ and ϕ in the deformed domain are denoted by:

$$\left\{ \begin{array}{l} C_{Cu^{2+}X} = \frac{\partial C_{Cu^{2+}}}{\partial X} \quad C_{Cu^{2+}Y} = \frac{\partial C_{Cu^{2+}}}{\partial Y} \\ \phi_x = \frac{\partial \phi}{\partial X} \quad \phi_y = \frac{\partial \phi}{\partial Y} \end{array} \right\}$$

in the original domain Ω , deriving a set of equations that can be solved together with the equations below describing the moving mesh [7].

To model the moving boundaries, Poisson's equation can be used to solve the mesh velocity for the moving coordinate system, where $\psi = (\psi_x, \psi_y)$ denotes the mesh velocity [7]:

$$\begin{aligned} \int_{\Omega} D_J \left((\hat{\psi}_{xx} I_{xx} + \hat{\psi}_{xy} I_{yx}) \psi_{xx} + (\hat{\psi}_{xx} I_{xy} + \hat{\psi}_{xy} I_{yy}) \psi_{xy} \right) d\Omega &= 0 \quad \frac{\partial x}{\partial t} = \psi_x \\ \int_{\Omega} D_J \left((\hat{\psi}_{yx} I_{xx} + \hat{\psi}_{yy} I_{yx}) \psi_{yx} + (\hat{\psi}_{yx} I_{xy} + \hat{\psi}_{yy} I_{yy}) \psi_{yy} \right) d\Omega &= 0 \quad \frac{\partial y}{\partial t} = \psi_y \end{aligned}$$

On the boundaries where copper is deposited, the following constraints are formulated:

$$n_x (\psi_x - u) = 0 \quad \text{and} \quad n_y (\psi_y - v) = 0$$

where n_x and n_y denotes the x- and y-components respectively of the normal vector to the deposition surface and

$$u = \frac{M_{Cu}}{\rho_{Cu}} N_{Cu^{2+}x} \quad \text{and} \quad v = \frac{M_{Cu}}{\rho_{Cu}} N_{Cu^{2+}y}$$

where $N_{Cu^{2+}x}$ and $N_{Cu^{2+}y}$ are the x and y components, respectively, of the copper ion molar flux, M_{Cu} is the molar mass and ρ_{Cu} is the density of solid copper. The equations for the moving boundaries are solved on the fixed mesh with the initial conditions $x=X$ and $y=Y$.

SIMULATION RESULTS

Initially, the model was used to simulate copper deposition in a 2D symmetric 50 μm wide and 40 μm high cell. Then the effect of a protrusion on the cathode was studied. The current densities simulated in the first case were compared to experimental results. The initial CuSO_4 concentration was 0.5 M. The voltage

over the electrochemical cell was 0.28 V. Fig. 4 shows simulated concentration profiles along the cell at the initial state, after 0.05 and 1 s, respectively. After 1 s steady state condition is achieved and the concentration profile will be a straight line from 0.554 M at the anode to 0.446 M at the cathode. The current density is about 10 A/dm² and evenly distributed along the electrodes. Fig. 5 shows how the mesh elements have moved by the ALE method, simulating deposition and etching after 120 seconds. It is predicted that 5.4 μm copper has been deposited on the cathode and an equal amount has been dissolved from the anode. Due to the small distance between the anode and cathode, a high limiting current is obtained. With an initial concentration of 0.5 M, the simulation predicts the limiting current density to be 48 A/dm².

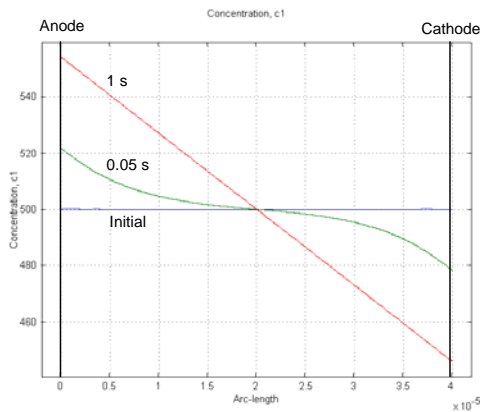


Fig. 4: Copper concentration (moles/m³) profile along the cell initially, after 0.05 and 1 s, respectively.

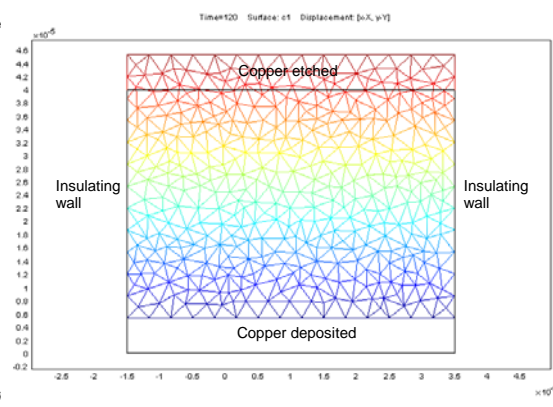


Fig. 5: Simulation of copper deposition and etch using the ALE-method to model the movement of the mesh element.

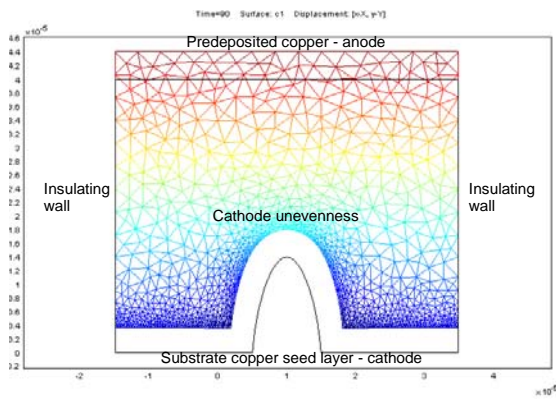


Fig. 6: Simulation of copper deposition with an elliptic protrusion on the cathode after 90 s.

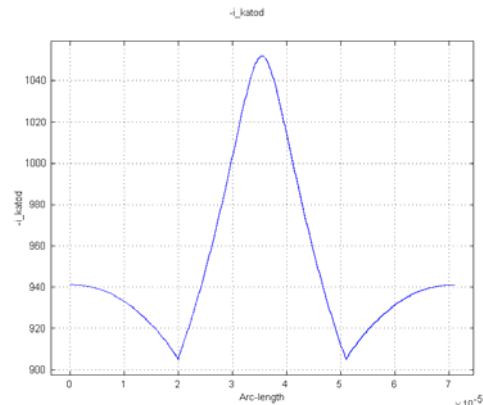


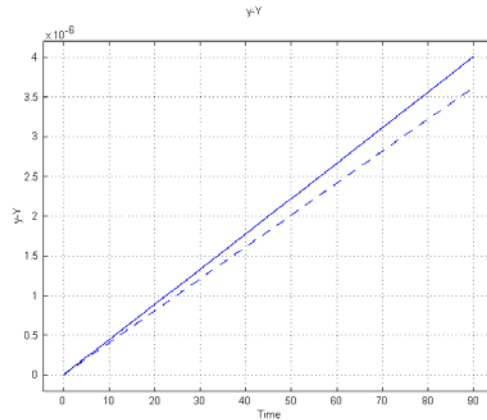
Fig. 7: Current density (A/m³) distribution after 90 s along the cathode surface with a protrusion.

In the second case, the effect of a protrusion on the cathode surface was assumed to have the shape of an elliptic half circle with dimensions of 10 μm in width and 14 μm in height. Fig. 6 shows the simulated deposition and dissolution after 90 s. Since the tip of the protrusion is located closer to the anode, the deposition rate is higher in this point. Fig. 7 shows that the

deposition rate after 90 s will be 12% higher at the tip as compared to a point located in the right or left corner on the cathode. Looking more closely at the tip of the elliptic protrusion and comparing the deposition thickness to a point in the left corner of the cathode, a difference of 0.4 μm copper thickness can be seen after 90 s (Fig. 8). When the process continues, the copper growth on the tip will accelerate.

The conclusion from this simulation is that a protrusion, that can be considered large, have some effect on the copper deposition on the substrate and very little effect on the copper dissolution from the master. The 0.4 μm difference in deposition height after 90 seconds corresponds to a 10% variation along the cathode. This is a small variation considering the large dimensions of the protrusion. Usually, the cathode surface varies less than 0.5 μm . The reason for the relatively small variations in deposition speed is the small concentration and potential variations along the cathode in spite of the protrusion, which leads to small variations in current density, i.e. deposition rate.

Fig. 8: Copper thickness (m) as a function of time (s). The solid line represents a point at the tip of a 14 μm high protrusion on the cathode. The dashed line represents a point located in the left corner of the cathode surface. After 90 seconds, the copper is 0.4 μm thicker at the tip of the protrusion.



To evaluate the reliability of the model, simulated values of current density for the base case of a symmetric ECPR cell was compared to experimental observations. The experiments were performed with a 0.5 M copper sulphate electrolyte solution with three different values of applied DC. The logarithmic values of the simulated and measured current densities were compared in a Tafel slope diagram [8] (Fig. 9). The comparisons of experimental and simulated current densities show that the slopes of the logarithmic current densities differ. Using the regressions from the plot, the model was adjusted to the experimental values by adapting the transfer coefficients and the exchange current density. With $\alpha_A=1.3884$, $\alpha_C=0.6116$ and $i_0=12.7 \text{ A/m}^2$ the model simulations fit the experimental values. The experimental and simulated values after adjusting the model inputs are presented in a second Tafel slope diagram (Fig. 10). Even if it was possible to adjust the model to fit the experimental values, there are still uncertainties concerning the reliability of the simulations. The dominating uncertainty factor is the measurements of the applied voltage. Due to the exponential relationship between the voltage and the current density, small errors of the applied voltage used in the model will have large effects on the simulated current densities.

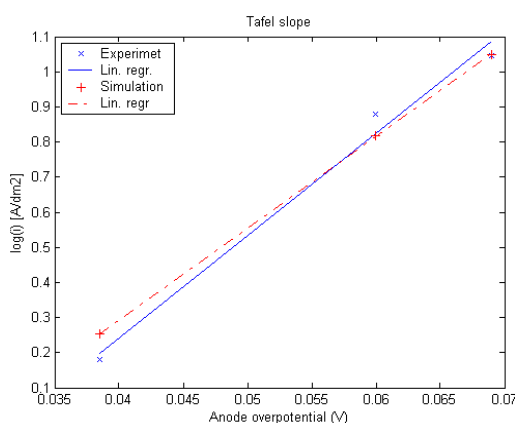


Fig. 9: Experimental and simulated anodic Tafel slopes.

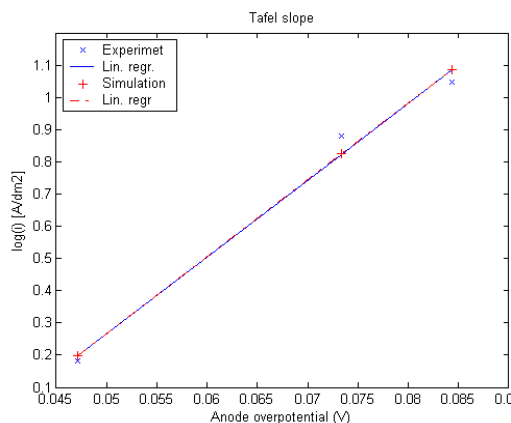


Fig. 10: Tafel slope after adjusting the model to fit experimental values.

Discussion and Conclusions

A model for simulation of copper deposition with the ECPR method has been presented. The model takes electrode kinetics and mass transport into account. An arbitrary Lagrangian-Eulerian method was implemented in order to simulate moving boundaries corresponding to the deposition and etching of copper on the electrode surfaces.

The simulations of the base case of a symmetric ECPR cell with dimensions of 40 μm in height and 50 μm in width predict that the concentration gradient will be higher closer to the electrodes during a short period of time and that steady state conditions occur after about 1 second. With an initial copper concentration of 0.5 M and no convection, the simulations predict a high limiting current of 48 A/dm^2 , due to the small distance between the electrodes.

Simulations of an uneven cathode surface predicted that the deposition rate would be highest at the point located at the smallest distance to the anode. The rate is expected to accelerate at this point as it gets closer to the anode during the deposition process. Even if a deposition height difference of 0.4 μm (10%) was predicted after 90 s, the variation is small compared normal electroplating equipment.

In order to evaluate the model reliability, simulations of current density were compared to experimental observations. The comparison of the modeled and measured current densities showed that a considerable difference was obtained. The transfer coefficients and exchange current density of the model were adjusted in order to get a good correlation between the simulations and experimental observations. However, small variations of the measured voltages may have significant impact on the results and the absolute values calculated from the simulations should only be trusted to some extent. Due to the nature of the ECPR setup, measurements that normally can be performed for electrochemical processes are limited. For instance, the closed cavities between the master and electrode make it impossible to have a reference electrode in the electrolyte. This limits the possibility to measure potentials and concentrations during the process which normally can be done with high accuracy. To

increase the model reliability, measurements of the electrolytic properties could be performed without the ECPR setup, for instance using a conductance cell.

There are a number of parameters, known to effect copper deposition, which the model does not take into account. For instance, studies have shown that the current density can have a considerable effect on the surface roughness of the deposited copper [9]. Higher current densities give less rough surface since a higher overpotential increases the density of active nucleation sites [10]. The latter study also demonstrates how the nucleation is affected by pH and copper ion concentration. For most copper deposition processes it is also common to use chloride ions and organic additives that minimize the deposition roughness. The present ECPR simulation model does not take the described factors into account but there is no reason why the model cannot be further extended to include the parameters mentioned above. The model would then have to be able to simulate several electrolyte components, how they react together and how they affect diffusion and migration. The effect of organic additives may be described using models for surface adsorption. Existing models also describe the nuclei population density as a function of the peak current and copper ion concentration [10], which may be implemented in the ECPR simulation model.

To conclude, even if the absolute values from the simulations only correlate with the experiments to some extent and that there are several parameters not taken into account, the ECPR simulation model can still be used for studying, explaining and predicting trends and effects that are practically not possible to measure or hard to anticipate without simulations. Therefore, the model may be very useful when evaluating the effect of various parameters. However the simulations should be done in combinations with experimental studies in order to confirm or discard the observed effects and to be able to suggest further model development.

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