

Numerical Simulation of Silicide Growth near an Insulator with Tin Oxide Thin Films Deposition

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Abstract

Silicide films have received much recent attention because of their practical applications for VLSI technologies. Titanium silicide is among the most common silicides employed in the semiconductor industry because it can be self-aligned, has low resistivity and is stable at temperatures consistent with device fabrication processes. However, with scaling to submicron dimensions and polycide/salicide technology development, computer simulation and models that could handle complicated geometrical movements of multi-layer materials, coupled with defects injection and impurity redistribution at the moving interfaces or inside the material layers are required for the development of improved silicide processes. Hence, this study is based on numerical simulation of silicide growth near an insulator in tin dioxide with COSMOL multiphysics software. The result showed that at constant temperature changes of 0.0513°C to 0.753°C in the time range of 0-30sec, 0-60sec, 0-240sec and 0-600sec. The electrode growth is at its minimum, at the same temperature changes of 0.0513 to 0.753 in the time range of 0-96hrs. The electrode growth reaches its maximum close to the insulator-silicide edge; this is due to the higher silicide current in the region. With these results, we have demonstrated that numerical simulation lead to a better understanding of the physical properties of deposited films devising a new tool for the deposition of film with desirable properties, related to uniformity and homogeneity. As the electrolyte potential and electrolyte current increases, the velocity magnitude at every point get closer. Therefore, getting the isolated boundaries to zero normal mesh displacement instead of using the defaulted zero normal mesh velocity improves the numerical stability of the silver. Meanwhile, the boundaries condition for moving fluid surface should be considered for better results with minimum surface assumptions.

Keywords: Silicide films, numerical simulation, COSMOL multiphysics software.

Introduction

Computer simulation has become an essential part of science and engineering. Digital analysis of components, in particular, is important when developing new products or optimizing designs. Today a broad spectrum of options for simulation is available; researchers use everything from basic programming languages to various high-level packages implementing advanced methods. When considering what makes software reliable, it's helpful to remember the goal: you want a model that accurately depicts what happens in the real world.

A Computer simulation environment is simply a translation of real-world physical laws into their virtual form. How much simplification takes place in the translation process helps to determine the accuracy of the resulting model.

COMSOL provides a simulation environment that gives you the possibility to add any physical effect to your model. It's a flexible platform that allows both the novice and advance users to model all relevant physical aspects of their designs and use their knowledge to develop customized solutions applicable to their unique circumstances. With this kind of all-inclusive modeling environment,

COMSOL gives you the confidence to build the model you want with real-world precision.

Certain characteristics of COMSOL become apparent with use, Compatibility stands out among these. COMSOL requires that every type of simulation included in the package has the ability to be combined with any other. This strict requirement actually mirrors what happens in the real world. For instance in nature, electricity is always accompanied by some thermal effect; the two are fully compatible. Enforcing compatibility guarantees consistent multiphysics models, and the knowledge that, even as the COMSOL family of products expands, you never have to worry about creating a disconnected model again. Another noticeable trait of the COMSOL platform is adaptability. As your modeling needs change, so does the software. If you find yourself in need of including another physical effect, you can just add it. If one of the inputs to your model requires a formula, you can just enter it. Using tools like parameterized geometry, interactive meshing, and custom solver sequences, you can quickly adapt to the ebbs and flows of your requirements.

COMSOL Multiphysics also has several problem-solving benefits. When starting a new project, using COMSOL helps you understand your problem. You are able to test out various geometrical and physical characteristics of your model, so you can really hone in on the important design challenges. The flexible nature of the COMSOL environment facilitates further analysis by making "what-if" cases easy to set up and run. You can take your simulation to the production

level by optimizing any aspect of your model. Parameter sweeps and target functions can be executed right in the user interface. From start to finish, COMSOL is a complete problem-solving tool.

Numerical simulation is the recreation of an appearance of reality, to produce an image which appears real. It is the process by which one or more programs are performed on one or more computers. It is widely used in many fields for research and development such as mechanics, nuclear physics, aeronautics, climatology, meteorology, theoretical physics, quantum mechanics, biology, chemistry, etc to study operations and properties of a system and to predict its evolution. Numerical simulation is cheap, fast performing and addresses economic challenges such as reactivity, anticipation and competitiveness (productivity gains). This is done by defining the numerical values of the parameters at every point for purpose of feasibility

Tin dioxide (SnO_2) thin films present high technological interest due to high quality properties such as transparency in the visible range, high reflectivity in the infra-red, fair n-type conductivity and good chemical stability. SnO_2 is an important material used in copper gallium diselenide based solar cells. Its high chemical stability makes it a suitable replacement for wide band gap semiconductors such as zinc oxide (ZnO) in order to improve the long-term device reliability. This overall picture allows the utilization of this compound in a large variety of applications such as optoelectronic

devices, solar collectors, gas sensors, transparent electrodes, and displays among others.

Amorphous SnO₂ are use in glass over layers for covering the entire device and protecting it against water permeation i.e. in applications where water penetrates into the layers under the oxide layer thereby reducing the long term reliability of the devices such as CIGS thin film solar cells.

Mixture of amorphous and nanocrystalline SnO₂ where nanocrystals are embedded in amorphous matrix without forming grain boundaries may even achieve better charge transport properties without sacrificing the barrier properties. Thus, it is important to be able to control the structure of SnO₂ films between amorphous and poly-crystalline because amorphous films have superior water permeation resistance while poly-crystalline films generally have better charge carrier transport properties. This can be achieving by an X-ray diffraction and Hall-effect measurements. SnO₂ is produced artificially as a white amorphous powder occurring naturally in the mineral cassiterite. It is use to manufacture white enamels and under the name of putty powder for polishing glass. Tin dioxide crystallizes in tetragonal cassiterite crystal structure with lattice parameters.

$$a = b = 4.737\text{\AA} \quad (1)$$

$$\text{and} \quad (2)$$
$$c = 3.185\text{\AA}.$$

Electrically, tin dioxide is a n-type semiconductor with wide band gap of (about 3.8 eV) due to oxygen vacancies and interstitial tin atoms which acts as

donors in the matrix, yielding electrical conduction even for undoped material. Doping increases the n-type conductivity, which when allied to its transparency, allows the application of this compound as transparent electrodes. It leads to high resistivity due to the acceptor-like behavior of doping, inducing high charge compensation in the matrix. These properties can be related to Liquid phase behavior during the thin film deposition because the doping incorporation, homogeneity, thickness, of the growing film, are associated with the movement of the liquid phase, which is the colloidal suspension of SnO₂. When SnO₂ is doped with E³⁺, it leads to the technological innovation leading to creation of optoelectronic devices, such as electroluminescent apparatus. E³⁺ has high technological potential due to large emission at about 1540nm; this is because it coincides with the minimum absorption of silica-based optical fibers. E³⁺ infrared emission is indicated for the construction of optical amplifiers to replace electronic converters and decrease its operation cost.

Thin films formation via dipping, spray pyrolysis, polymeric or particulate inorganic precursors are concentrated on the substrate surface by a complex process involving gravitational draining with concurrent drying and continued condensation reactions. The structure of films deposited from polymeric precursors depends on such factors as size and structure of the precursors, relative to the rate of condensation and evaporation, capillary pressure and substrate withdrawal speed.



Figure 1: Example of a tin films technology such as in photovoltaic solar panel.

SnO_2 films shows very little absorbance in the visible IR-range, are very resistant against chemical attack, have high mechanical strength, good electrical conductivity when doped, relatively high hydrogen and oxygen over voltages and can easily be prepared as thin film electrodes. Therefore, SnO_2 films meet the general requirements for dimensionally stable electrode host material.

The aim of this work is to study the electrolyte uniform deposition distribution with computer simulation and to monitor the thickness of the deposited layer (electrode) using Comsol multiphysics software.

Material and Methods

The following are the material and instruments used at the course of the project work:

- a. A laptop (64-bit operating system, 4.00GB RAM, 2.53GHz)
- b. A COMSOL MULTIPHYSICS software (version 4.2)

Methodology Flow Chart

The flowchart below presents a summary of the design methodology:

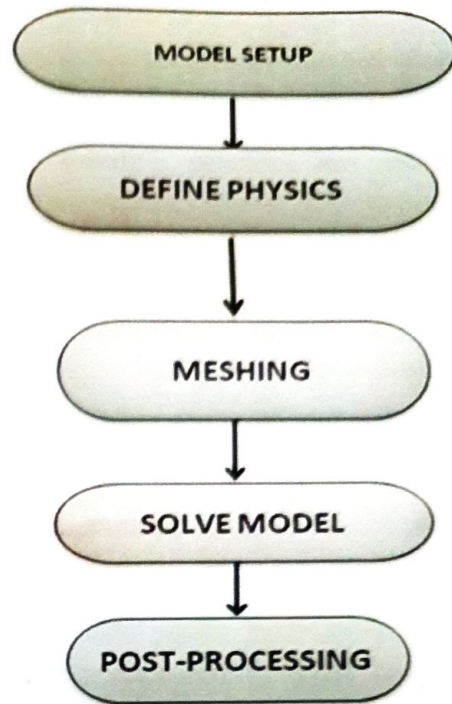


Figure 2: Methodology Flow Chart

Implementation of Simulation in COMSOL

Below are the procedures for modeling in comsol multiphysics software.

Procedure for Modeling in Comsol: The simulation processes were carried out in the COMSOL multiphysics software and below are the procedures for numerical simulation of an electrode growth close to an insulator.

Model Setup: Modeling instructions has to do with all the necessary commands been taken place in the COMSOL multiphysics software for an effective model to yield an excellent result.

Below are the steps:

Model builder

Model Builder is where you find the model wizard window after clicking the root node.

The 2D button is then selected and a Next command is selected.

To add a physics, the electrochemistry

The first dialog box that appears at the very moment you launch the COMSOL MULTIPHYSICS icon from the desktop or through the command prompt is the Model Navigator. In this area you have to define the space dimension, select the actual application mode (from either the heat transfer, radiofrequency, structural mechanics, e.t.c), select the study type (steady state or transient), set the element type (it tells the software how to interpolate). For the purpose of this research, the following steps should be applied during the model setup.

Width	Height	Base: Corner (r)	Base: Corner (z)
30[cm]	10[cm]	0[cm]	0[cm]

Table 1: Geometric values

Width	Height	Base: Corner (r)	Base: Corner (z)
20[cm]	0.1[mm]	0[cm]	0[cm]

Table 2: Input numerical values.

Secondary Electrodeposition

Modeling and simulations are cost effective ways of understanding, optimizing, and controlling electrodeposition processes. The electrodeposition Module is intended for investigating the influence of different parameters, in an electrodeposition cell, on the thickness and composition of deposited

layers. Important parameters that can be studied with the module are the following:

1. Cell geometry
2. Electrolyte composition and mixing
3. Electrode kinetics
4. Operating potential and average current density
5. Temperature

A typical simulation yields the current distribution in the electrodeposition cell and at the surface of the electrodes. Faraday's law and the properties of the deposited material give then the thickness and composition of the deposited layer. The module is able to model cells both when the deposited thickness is negligible in comparison to the inter-electrode gap and where the growth and dissolution of the electrodes have to be taken into account using moving boundaries. The targeted applications for the Electrodeposition Module are the following:

- i. Copper deposition for electronics and electrical applications.
- ii. Metal deposition for protection of parts, such as corrosion protection and protection against wear.
- iii. Decoration of metals and plastic parts.
- iv. Electroforming of parts with thin and complex structure.
- v. Metal electro-winning.

Electrodeposition Interfaces

The Electrodeposition interfaces cover secondary and tertiary current distribution with and without moving boundaries. The Electrodeposition, Secondary interface assumes a perfectly mixed

electrolyte. The activation over potential for the electrochemical reactions, which is caused by the activation energy, is on the other hand taken into account in the analysis. The Electrodeposition, Tertiary Nernst-Planck interface accounts for the transport of species through diffusion, migration, and convection and is therefore able to describe the effects of variations in composition on the electrodeposition process. The kinetics expressions for the electrochemical reactions account for both activation and concentration overpotential.

The Electrodeposition, Tertiary Nernst-Planck interface applies the equations of electro neutrality to the set of equations that describe the species and current balances. This also implies that all charged species in the electrolyte have to be defined in the simulations, except those species that are present at very low concentrations and can therefore be neglected in the balance of current. In the cases where the thickness of the deposited layer at the surface of the cathode is negligible for the current distribution in the cell, the fixed geometry study may be selected both for secondary and tertiary current density distribution. Even for the fixed geometry cases, the thickness and the composition of the deposited layer may be simulated and plotted at the surface of the cathode. If the thickness of the deposited layer is of the same order of magnitude (or one order lower) compared to the geometrical details of the electrodes, then the options with moving boundaries may have to be used. The figure above shows an example from the tutorial that is included in this introduction. The solid line shows the original shape of the cathode surface and

the deformed field shows the shape of the surface after 10 s of deposition.

The colour table shows the copper ion concentration. The Electrochemistry interfaces also include the generic Primary, Secondary, and Tertiary Current Distribution interfaces. These interfaces differ from the Electrodeposition interfaces in that they do not include the ability to by default keep track of the thickness and composition of the deposited layers. However, in combination with the Surface Reactions interface found for Chemical Species Transport, these physics interfaces can be manually set up to model the deposited layers, but then only for fixed geometries.

The Electrodeposition Module also includes the Chemical Species Transport interfaces. The Transport of Diluted Species interface in combination with the Electrodeposition, Secondary interface can be used to model systems with supporting electrolyte. In these systems, the ions that give the largest contribution to the conduction of current are assumed to be present in uniform concentrations. The fluid flow interfaces can be combined with the Electrodeposition interfaces to model free and forced convection in the electrolytic cell.

The Heat Transfer interfaces have ready-made formulations for the contribution of Joule heating, and other electrochemical losses, to the thermal balance in the cell. The detailed equations and assumptions that are defined by the physics interfaces in the Electrodeposition Module are

formulated in the Electrodepositing Module User's Guide (COMSOL multiphysics, 2010).

Meshing

Here, Zero Normal Mesh Displacement boundary condition is used to improve the numerical stability of the mesh displacement.

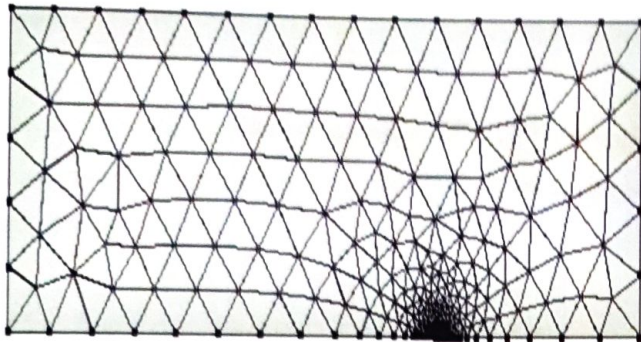


Figure 3: Meshing of the deposited electrode.

Solving Model

For the purpose of this study, the solver is set to perform simulations for time intervals of 30sec, 60sec, 240sec, 600sec and 96hr.

Post Processing

This is the second to the last stage in the modeling process. In this stage, you can create different plots such as line plots, surface plots, contour plots, slice plots and isosurface plots. In other words, pre-processing determines how the results are presented.

Results

In this section, all defined physics and equations are presented either in values, pictorial graphical or plot form by COMSOL Multiphysics solver. This section contains the results obtained during the

modeling and simulation of the problem and also the discussion of the results.

Electrolyte Potential (V) and Electrolyte Current Vector (2D Spatial) For Time Interval 0 – 600sec

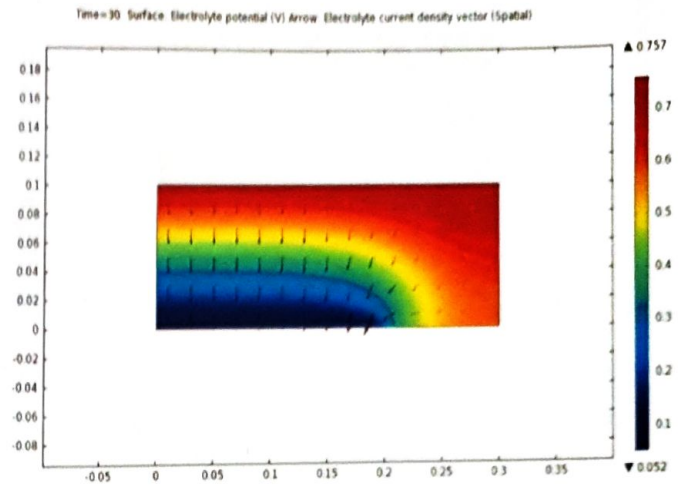


Figure 4: 2D Electrolyte potential (surface) and electrolyte current direction (arrows) at time range: 0-30sec.

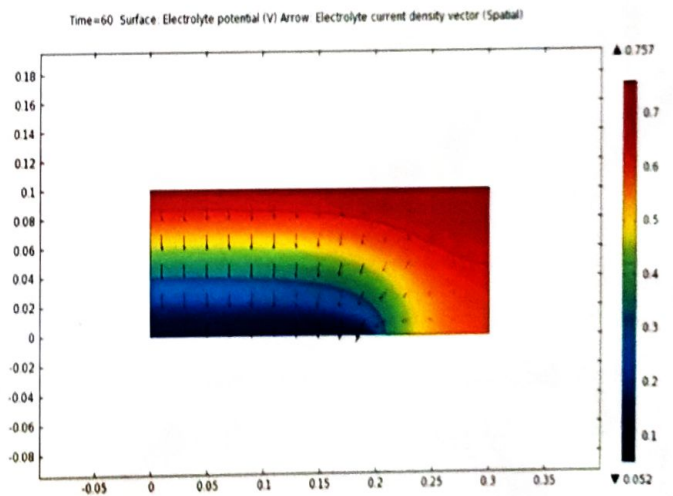


Figure 5: 2D Electrolyte potential (surface) and electrolyte current direction (arrows) at time range: 0-60sec.

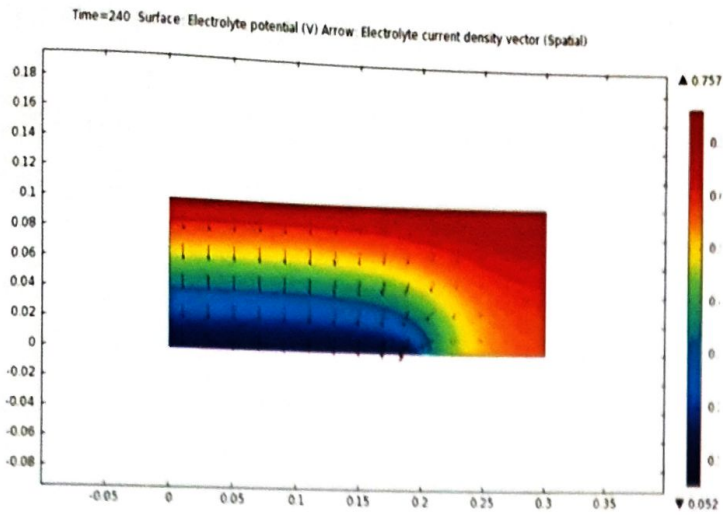


Figure 6: 2D Electrolyte potential (surface) and electrolyte current direction (arrows) at time range: 0-240sec.

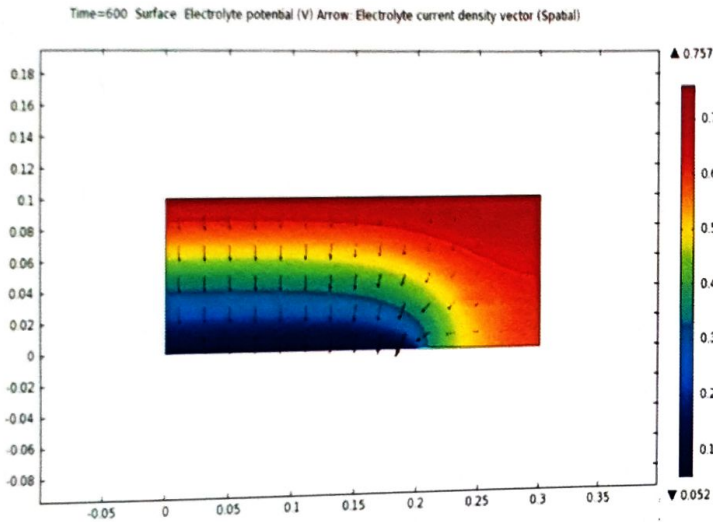


Figure 7: 2D Electrolyte potential (surface) and electrolyte current direction (arrows) at time range: 0-60sec.

Discussions

In this section, all defined physics and equations are presented either in values, pictorial graphical or plot form by COMSOL Multiphysics solver. This section contains the results obtained during the modeling and simulation of the problem and also the discussion of the results.

Electrolyte Potential (V) and Electrolyte Current Vector (2D Spatial) for Time Interval 0 – 600sec

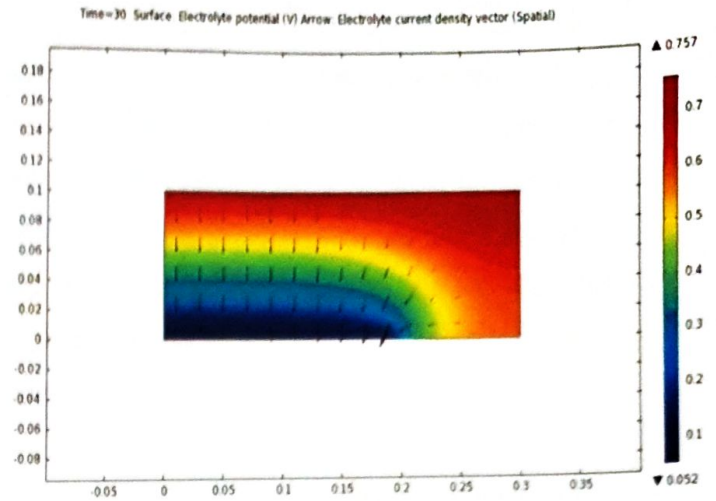


Figure 8: 2D Electrolyte potential (surface) and electrolyte current direction (arrows) at time range: 0-30sec.

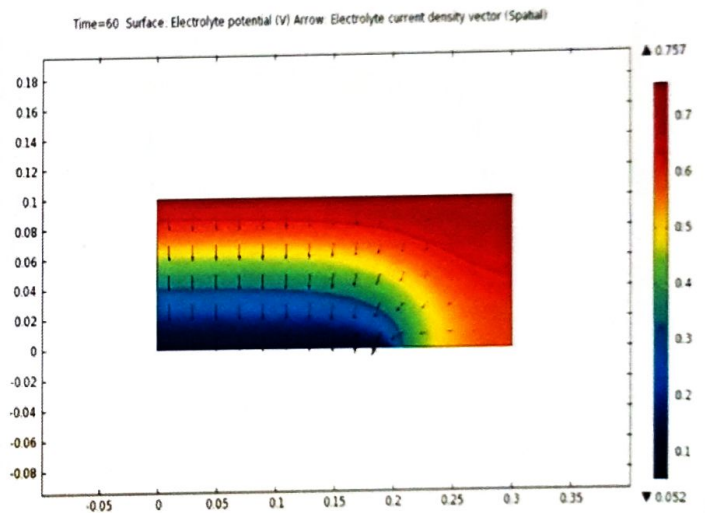


Figure 9: 2D Electrolyte potential (surface) and electrolyte current direction (arrows) at time range: 0-60sec.

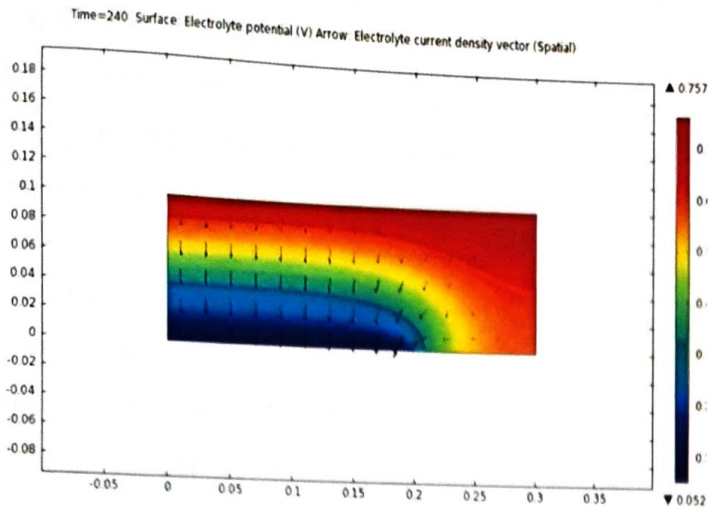


Figure 10: 2D Electrolyte potential (surface) and electrolyte current direction (arrows) at time range: 0-240sec.

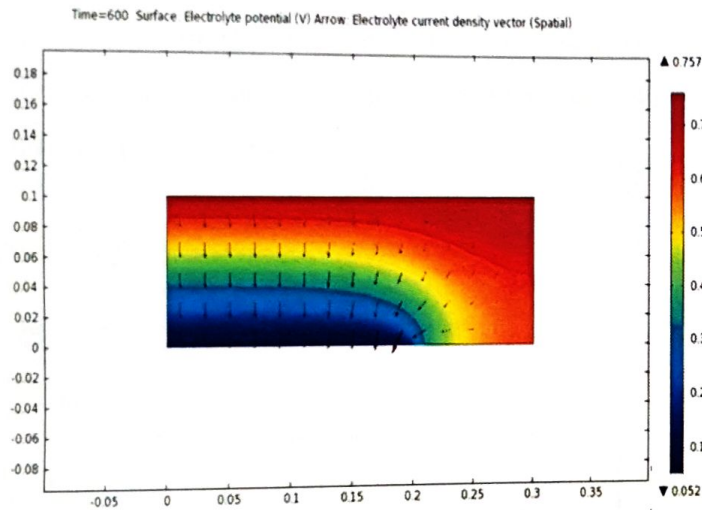


Figure 11: 2D Electrolyte potential (surface) and electrolyte current direction (arrows) at time range: 0-60sec.

Electrolyte Potential (V) and Electrolyte Current Vector (Spatial) (2d) For Time Interval 0 – 600sec

Figures 8, 9, 10 and 11 above show the spatial electrolyte distribution and electrolyte current vector in an oven of depositing electrode with temperature rise from 0.0513°C to 0.753°C for lower time ranges 0-30sec, 0-60sec, 0-240sec and 0-600sec respectively. The temperature in the oven

continues to increase rapidly until it reaches a steady state temperature on the meter calibrator. We can see that the electrolyte current distribution is uniform. At the steady state temperature, it looks like nothing is happening, but as temperature continues to decrease down close to the initial state level due to the contact with the electrode. Also it will be observed that there is no any significant change in the deposition deformation of the electrodes for these time ranges.

Electrolyte Potential (V) and Electrolyte Current Vector (2D Spatial) for Time Interval 0 – 96hrs

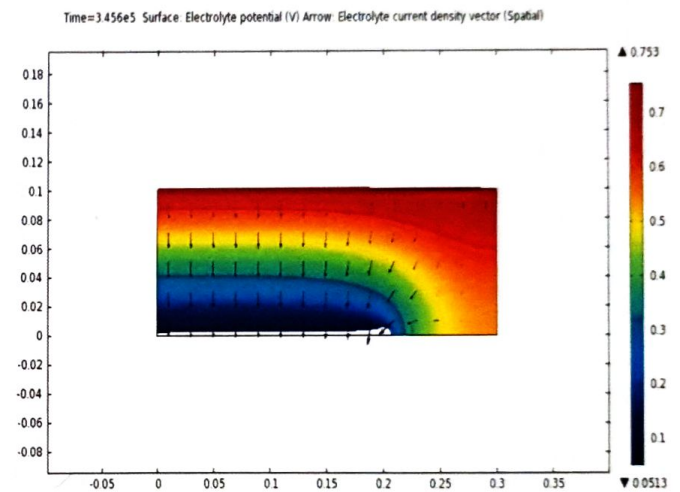


Figure 12: 2D Electrolyte potential (surface) and electrolyte current direction (arrows) at t=96 hours.

Electrolyte Potential (V) and Electrolyte Current Vector (2D Spatial) for Time Interval 0 – 96hrs

Figures 12 shows the surface electrolyte potential, spatial electrolyte distribution and electrolyte current vector of the deposited and dissolving electrode in an oven of depositing electrode with a temperature increase from 0.0513°C to 0.753°C. A time dependent study is used to simulate the electrode growth and dissolution for a period of 96

hours. The temperature continues to increase rapidly until it reaches a steady state temperature on the thermometer calibration indicator. We have that the maximum current density indicated as 'reddish brown color' (higher temperature) and the minimum current density is indicated by the 'Dark blue' (lower temperature). We can see that the electrolyte current distribution is uniform. At the steady state temperature, it looks like nothing is happening, but as temperature continues to decrease down close to the initial state level due to the contact with the electrode. Also it will be observed that there is a visible change in the deposition deformation of the electrode as the electrode growth reaches its maximum close to the insulator-electrode edge, this is due to the higher electrode currents in the region.

Profile of Depositing Electrode (1D)

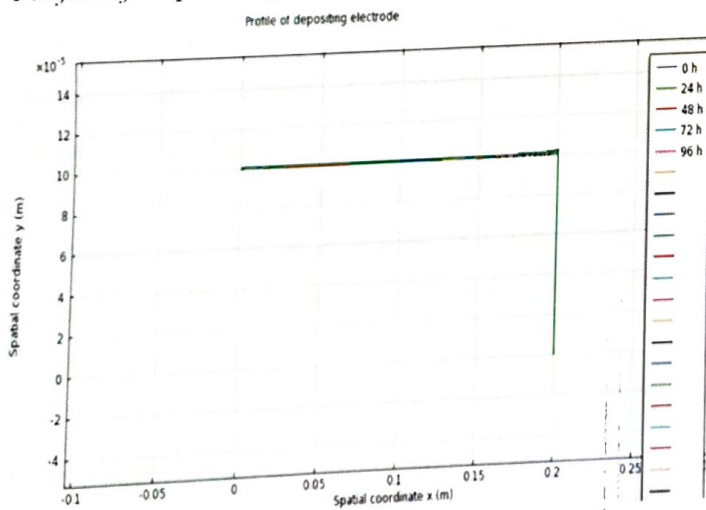


Figure 13: Profile of deposited electrode during the simulation at time range: 0-120sec.

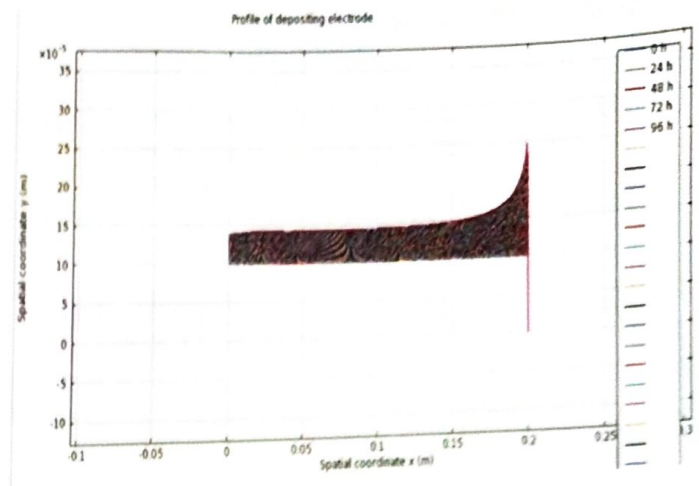


Figure 14: Profile of deposited electrode during the simulation at time range: 0-120min.

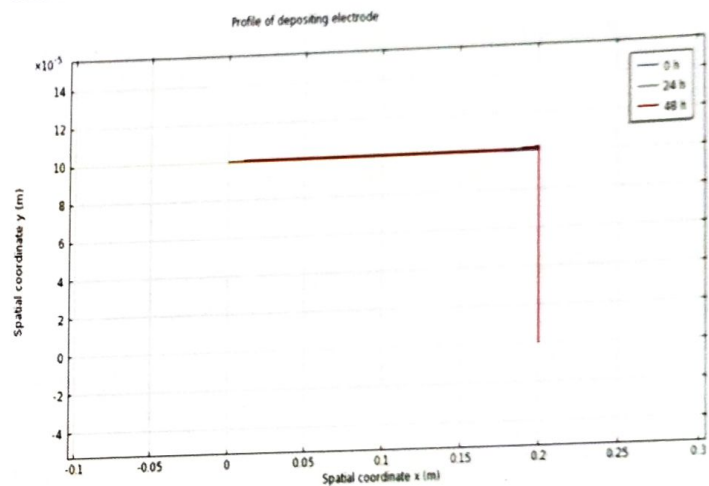


Figure 15: Profile of deposited electrode during the simulation at time range: 0.14-0.40hr.

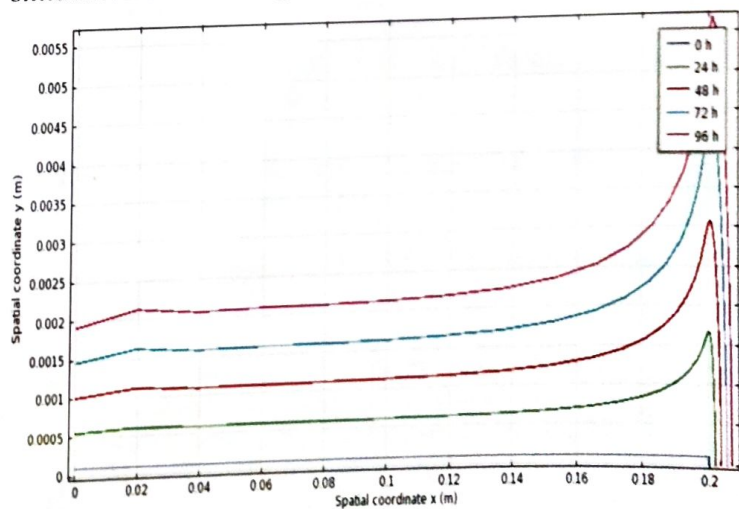


Figure 16: Profile of deposited electrode at various times during the simulation at time range: 0-96hour.

Figure 10 shows the profile change of the depositing electrode during the simulation. A plot of spatial coordinate y (meter) was plotted against spatial coordinate x (meter). The time indicator box on the right side of figure 10 shows the rise in time per hour during the simulation. This holds quite well for figures 11 to 16.

Conclusion

The numerical simulation technique leads to a better understanding of the physical properties of deposited films devising a new tool for the deposition of films with desirable properties, related to the uniformity and homogeneity. The results of the application of this technique for the deposition of SnO_2 shows the behavior of the electrolyte potential, electrolyte current and time taken for the electrode to be deposited.

The numerical simulation also provides information that close to the electrode, as the electrolyte potential and electrolyte current increases, the velocity magnitude at every point get closer. This leads to a better and more uniform material distribution all over the electrode. It is confirmed by a better crystallinity, such as in the inferred from X-ray diffraction results.

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