MULTISCALE MODELS FOR ELECTROPLATING OF THROUGH SILICON VIAS

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ABSTRACT

We present multi-scale models providing guidelines for defect free growth of filling of through silicon vias (TSV) by electroplating. Using first-principles calculations, we understand the chemistry of the electroplating process. We use density functional theory calculations to identify the reaction mechanisms and calculate the reaction energies of the different additives i.e., chloride ion, suppressor, and accelerator in the plating solution. We also present a kinetic Monte Carlo model that can incorporate the chemical and transport properties of the ions and additives during the electroplating. We demonstrate the role of aspect ratio and attachment rates on defect-free bottom-up filling. These multiscale tools can provide the inputs for a continuum phase field model to predict the microstructure during TSV filling (not reported here).

Key words: Through silicon via, multiscale modelling, DFT calculations, kinetic Monte Carlo.

INTRODUCTION

Through silicon vias (TSV) used in three-dimensional integrated circuits are means of realizing vertical interconnects of stacked silicon wafers architecture to achieve superior electrical performance at a lower cost. Nevertheless, as the package size get smaller, the aspect ratio of the TSVs increases, which can result in defects in them during their deposition. These defects, which include the voids, seams, impurities and grain boundaries, degrade the electrical and mechanical performance of the system. Apart from the aspect ratio and plating conditions, the deposition of TSVs are heavily influenced by the chemical and transport properties of the additives used in the plating solution. A full understanding of these various factors and hence the electroplating process, can be achieved through an integration of multiscale modeling and experimental characterization and tests of the process. Yang et. al coupled a nucleation model at the micro-scale along with a current distribution model to understand the multiscale behavior of electroplating [1]. They also developed a dynamically coupled kinetic Monte Carlo (KMC) model for surface reactions with a finite volume model for transport and chemical reactions and a level-set model that tracks the metal/electrolyte interface macroscopically. However, these modelling methods do not include first principle methods essential to compute the adsorption and transport properties and the reaction pathways and activation barriers of the additives. Here, we present sequential multi-scale modelling tools including first principle calculations and a kinetic Monte Carlo model to provide growth guidelines for defect-free electroplating of high aspect ratio Cu interconnects.

The electrolyte for the electroplating of copper has multiple additives, which have varying reactive, adsorption and transport properties. Apart from the chemical interactions of the additives in the electrolyte, the adsorption and transport properties of the additives determine their local concentration and gradients in the TSV. As the role of additives is to enhance metallization at the bottom of the TSV (and

suppressing metallization near the top), it is essential to optimize the concentration gradients of the additives in the TSV. Due to the different time and length scales of these processes during the electroplating, we employ multi-scale modelling tools to study the process. The chemistry of the electroplating process which includes studying the roles of the various additives is carried out using Density Functional Theory (DFT) and Molecular Dynamics (MD) simulations. The filling of the TSVs by electroplating is studied at the continuum scale using level set methods to track the growth interface. A kinetic Monte Carlo (KMC) model has been developed to bridge the scales between these two schemes of studying the electroplating of copper. These models will study the electroplating of TSV as a function of parameters including the concentrations, diffusivities, adsorption properties of ions and additives, applied current density, and temperature. In this work, we present the results of our DFT studies on the mechanisms of the additives and the KMC model to understand the transport and adsorption properties of additives during electroplating of TSVs.

DENSITY FUNCTIONAL THEORY STUDIES

We have studied the mechanism for the accelerating effect of bis-3-sulfopropyl disulfide (SPS) and suppressing effect of polyethylene-glycol (PEG), both of which are widely used additives in through silicon via (TSV) copper plating. We employ first-principles density functional theory (DFT) calculations to study the energetics of several adsorptions, dissociation and displacement reactions that have been proposed to explain the action of the additives [3,4]. In our calculations, the Cu electrode and adsorbate molecules are modeled at the DFT level and the water solvent is represented through an implicit model based on the Poisson-Boltzmann equation [5]. This model incorporates the dielectric screening due to the permittivity of the solvent and the electrostatic shielding due to the mobile ions in the electrolyte. The tuning of the electrochemical potential is achieved by charging the system and tracking the changes to the workfunction [6]. The free energy of the electron-ion pairs in electrochemical reactions are evaluated using the computational hydrogen electrode (CHE) and linear free energy relationship for electrode potentials (LFER-EP) [7]. In addition, we have also tried to include the dispersion forces using the DFT-D2 scheme to compensate for deficiencies in GGA xc-functionals [8].

PEG Suppressor

In copper deposition from a Cu^{2+} solution, the basic plating reaction proceeds via two steps, from Cu^{2+} to Cu^{+} which is the rate determining step, and Cu^{+} to Cu which is much faster. The plating in the presence of additives occurs through a large number of possible interconnected reactions that happen between the Cu surface, additives and various ions [3]. The first reaction is the adsorption of the suppressor PEG at the outer surface of the via, as PEG diffuses slowly and adsorbs quickly. In a Cl^- containing solution, it was proposed that PEG grasps the positive Cu ions to form a complex which then binds to the negatively charged Cl^- ions on the Cu surface [9]. This results in the formations of a PEG-Cu^+-Cl^- complex on the copper surface that has been verified by surface enhanced Raman spectroscopy measurements [10], and this inert layer prevents further plating on the surface thus achieving a suppressing effect. To study this process, we have performed calculations of a PEG complex adsorbed on a chloride covered Cu (110) surface with 0.25 coverage. To make the calculations feasible, we have represented PEG with a segment of three monomers $HO(C_2H_4O)_3H$ due to size constraints. Also, we found that chloride ions prefer the bridge site at 0.25 coverage.

By performing total energy calculations on isolated PEG-Cu-Cl complexes in the presence of our model dielectric solvent, we have identified that the Cu ion prefers to bind to the side oxygen of PEG. Next lowest in energy is for the Cu to bind to one of the middle O atoms, and the configuration with Cu bound to two middle oxygen atoms on PEG is least stable (Figure 1a). This might be due to the electrostatic repulsion between the O atoms in this configuration. Since the real PEG polymer in experiment contains many more middle than side oxygen atoms, we only consider binding to middle O atoms when studying PEG-Cu-Cl complexes adsorbed on the electrode surface (Figure 1b). We find again that the energy of a PEG-Cu-Cl complex with its Cu binding to one middle O atom is preferred to that where it binds to two.

Using this result, we focus on geometries where the Cu in the complex is bound to a middle O atom on PEG and investigate different modes of decay for the complex adsorbed on Cu (110). We computed the dissociation energy of the PEG complex through breaking the (a) Cu(slab)-Cl bond, (b) Cl-Cu(complex) bond and (c) Cu(complex)-O bond as shown in Figure 2. These calculations are performed on neutral systems in the presence of our model solvent. As can be seen, the system is stable to decay for all three modes with the lowest energy mode being breaking the Cu(slab)-Cl bond. Next, we specialize to this mode and investigate the dependence of the binding energy of the PEG-Cu-Cl complex on the applied bias (Figure 2d). It can be seen that the adsorption energy of PEG-Cu-Cl varies from ~ -0.6 to -1 eV over a range of +/- 0.5 V vs SHE. The adsorption gets weaker for more negative voltages and this might be due to the repulsion between Cl- and the negative charge on Cu. Also, this is consistent with the experimental observation that the suppression effect of PEG in a chloride solution disappears for negative enough voltages as the PEG complex gets desorbed [11].

SPS/MPS Accelerator

For the accelerator, SPS diffuses faster than PEG due to its smaller mass and quickly descends into the via, thus promoting plating in the via. Outside the via, PEG dominates initially as it adsorbs much faster than SPS, and plating is slowed. One of the proposed accelerating mechanisms is shown in Figure 3 [4]. SPS is first physisorbed on Cl^- covered Cu and diffuses to areas of exposed Cu. The Cu then catalyses

the decomposition of SPS into two adsorbed mercapto-1-propanesulfonate (MPS) molecules by breaking the S-S bond, and there is partial desorption of these molecules into the solution. One of the acceleration mechanisms is that the adsorbed SPS and MPS competes for space with the suppressor, thus allowing plating where PEG is absent or replaced by the accelerator. Another possible reaction is the conversion of MPS to SPS accompanied by the reduction of Cu^{2+} to Cu^{+} ions, an important precursor for copper plating. Finally, the desorbed MPS can also dissociate the PEG-Cu-Cl complex by attacking the Cu-O bond, resulting in the release of PEG and adsorption of MPS on copper. In addition to the above reactions, we have also studied two MPS formation reactions where Cu^{+} is oxidized to Cu^{2+} and SPS is converted to MPS [3].
To study the above reactions, we first compute the adsorption energies of SPS and MPS on Cu (110) with 0.25 Cl^{-} coverage. As before, we study the adsorption energies over a range of applied biases using the charging method and model dielectric solvent [5-7], and the results are plotted in Figure 4. Both SPS and MPS are known to adsorb on the thiol end [11] and MPS preferentially adsorbs on a Cu bridge site while SPS approximately adsorbs with S atoms sitting on the top sites of Cu. These energies show some dependence on applied bias with adsorption decreasing for more negative biases. Importantly, E_{ads} is larger for both MPS and SPS than for the PEG complex. This is in good agreement with the fact that SPS and MPS are good accelerators that can block out or replace the PEG complex on the Cu surface, and lends support to our primary accelerating mechanism.

Next we assess the previously proposed MPS formation reactions and these are depicted in Figure 5a with the reaction energies plotted in Figure 5b [3,4]. As can be seen, all the reaction energies are negative, and they are all feasible reaction routes. Between reactions (1) and (2) that both oxidize Cu^{+} to Cu^{2+} and convert SPS to MPS, the first reaction that results in MPS adsorbed on Cu is energetically much more favorable than the one with solvated MPS, mostly because an additional Cu^{+} ion is captured onto the surface and binds to MPS relative to the second reaction. For reaction (3) where SPS is deposited and decomposed into two adsorbed MPS molecules, the reaction is also energetically very favorable, with the adsorption of SPS accounting for half of the reaction energy and dissociation of adsorbed SPS to two adsorbed MPS giving rise to the other half. We also see that the second reaction, which does not involve the substrate or change in number of electrons does not have a bias dependence, while reactions (1) and (3) are more favorable for positive biases around 0V vs SHE.

It was also proposed that the MPS in solution may dissociate the PEG-Cu-Cl complex by attacking it at the Cu-O bond, replacing it with MPS-Cu-Cl and releasing PEG in the process [3,4]. In our calculations, we consider two possible geometries for the final MPS-Cu-Cl complex. One is with the complex adsorbed on the surface, with its Cu binding to both surface Cu and Cl (reaction 1) and another is that the complex is solvated (reaction 2). With this set up, we computed the reaction energies as shown in Figure 6, and the case with MPS-Cu-Cl solvated is energetically unfavorable, while the case with the complex adsorbed on the surface is much more favorable. This is due to the strong slab-complex bond that needs to be broken for the case where MPS-Cu-Cl is solvated. Finally, we have also studied the reaction where MPS reduces Cu^{2+} to Cu^{+} and gets converted back to SPS (reaction 3), and it was found to be energetically favored. Finally, it can also be seen from the Figure 6b that the reaction energies are slightly more favorable at positive biases but only weakly dependent on bias.

In summary, using our DFT calculations we have verified that the PEG-Cu+-Cl^{-} complex formation is the essential step in the fast adsorption of the suppressor. For the accelerator mechanism, we show that the dissociation of SPS to MPS is the intermediate that can replace the suppressor and also enable the reduction of Cu2+ to Cu^{+}.

Kinetic Monte Carlo Model

In the following we present a kinetic Monte Carlo (KMC) model developed to understand the role of the reaction and transport kinetics of the ions and various additives during the electrodeposition of the TSVs. The KMC model has been developed as a bridge between the first principle DFT calculations and the continuum phase field models. A solid-by-solid (SBS) KMC model for the surface reactions which also includes migration of ions in the electrolyte as random walk developed by Kaneko et. al [12] could show the formation of voids and their influence on bottom-up filling. A two dimensional model including the role of additives has been developed by Fukiage *et al.*[13] applying different waveforms of applied current. In our KMC model, the various reactive and transport processes are executed with probabilities proportional to their rates. These rates will be calculated from the activation barriers obtained by DFT and molecular dynamics simulations. The results from the KMC simulations can aid in identifying the relevant parameter space for detailed continuum models like phase-field simulation models.
In this model, apart from the Cu^{2+} metal ions and the copper electrode, we consider the roles of the accelerators and suppressors in the reaction kinetics. The features of these additives are as follows:

1. accelerator(A) diffuses faster than suppressor(S)
2. $D_{Cu^{2+}} > D_A > D_S$
3. presence of suppressor decreases the rate of attachment of metal ion to the electrode
4. presence of accelerator increases the rate of attachment of the metal ion to the electrode by

altering energy of affinity (bond) of metal ion to electrode.

5. Dependence of metallization on curvature – the corners have lesser attachment barrier compared to the side walls.

6. activation barriers for the attachment of Cu^{2+} ions to the TSV substrate Cu with and without the additives

$$E_{att}^{Cu-Cu^{2+}}(A) < E_{att}^{Cu-Cu^{2+}} < E_{att}^{Cu-Cu^{2+}}(S)$$

7. accelerator replaces suppressor in the growth front

$$E_{att}^{Cu-Cu^{2+}} < E_{att}^{Cu-A} < E_{att}^{Cu-S}$$

8. concentration of accelerator is 1-2 order less than that of suppressor

$$c_S \sim (5 * c_A, 100 * c_A)$$

9. concentration of suppressor is 1-2 orders less than that of metal ion

$$c_{Cu^{2+}} \sim (5 * c_S, 100 * c_S)$$

10. $E_{nuc}^{Cu-Cu^{2+}}$: Barrier for nucleation of new metal layer on the substrate proportional to the number of metal adatom-substrate bond

11. different barriers of for nucleation on flat surfaces and on corners, with a ratio

$$r_{nuc} = E_{nuc}^{Cu-Cu^{2+}}(corners) \Big/ E_{nuc}^{Cu-Cu^{2+}}(flat\ surface)$$

12. details of levelers, different types of metal ions, actual bond energies, concentration and electric field dependence are not included

In our model, we consider the following events:

- deposition of Cu ions on the electrode (substrate)
- migration of copper ions and additives
- decay of additives
- attachment of additives to substrate
- enhancement or reduction of attachment barrier for Cu to substrate in the presence of additives

The top of the TSV is open to the electrolytic bath which acts a source of Cu ions and additives.

The KMC model with above mentioned features has been developed and the simulations results can guide the phase-field simulations by identifying the relative parameter space for the different players in the electroplating process. In all the results presented below, we have used the following parameters$c_S = 0.05; c_A = 0.01;\ c_{Cu^{2+}} = 0.3; T = 0.1;\ E_{diff}(Cu^{2+}) = 0.1;\ E_{diff}(A) = 0.05;\ E_{diff}(S) = 0.09;$

In Figure 7 a we show the simulation results with different nucleation barriers for the side wall relative to that at the corners. For a ratio $r_{nuc} = 0.1$ shown in Figure7(a-c), the metallization on the side walls is enhanced compared to the bottom (Figure 7a and 7b). In Figure 7c, a void can be seen clearly at the bottom as result of the closing of the via at the top. In Figure 7(d-f), the results of the simulations for a ratio $r_{nuc} = 0.01$ is shown. In this case, metallization starts from the two corners in the bottom (Figure 7d) which results in bottom up growth (Figure 7e) and hence, void-free filling of the TSV (Figure 7f). A lower attachment on the walls could be caused by increase in suppressor species which is a slowly diffusing additive. The higher attachment at the corner is due to the corner effect (enhancement by curvature) in addition to the increase in accelerator species as it is a faster diffusing additive and can reach the bottom faster than suppressor. As suppressor is a slowly diffusing additive, it is mainly effective in the top of the via and hence reduces the growth and pinching off the void. Figure 8 shows the KMC model results for two different aspect ratios. Figure 8a shows the bottom up filling for an aspect ratio of 1.5 and Figure 8b shows formation of void for aspect ratio of 2. As the aspect ratio increases, it takes longer for the Cu^{2+} ions and accelerator to reach the bottom of the via than the growth time at the walls. This results in faster growth at the top of via resulting in a void. These results are consistent with the results obtained in experiments [14].

CONCLUSIONS

The various energies and barriers for the different species in the system that is required for the KMC model for the different species in the system will be obtained from the first principle calculations described in this article. The results of the KMC model can identify the parameter space of efficacy for the continuum phase field model. The objective of the continuum phase field model is to simulate the electroplating process and predict the microstructure in the TSV. In summary, we have developed first principle calculations to understand the reaction mechanisms and chemistry and a kinetic Monte Carlo model to incorporate these data to obtain the rate kinetics of the electroplating process. These tools in addition to the continuum models being developed (level set and phase field models) will form a single platform to model and optimize the electroplating of through silicon via of different aspect ratios.

References

1. L. Yang, A. Radisic, M. Nagar, J. Deconinck, P.M. Vereecken, A.C. West, *Electrochim. Acta*, **78,** 524 (2012).

2. L. Yang, A. Radisic, J. Deconinck and P.M. Vereecken, *J. Electrochem. Soc*. **160**, D3051 (2013).
3. N. T.M. Hai *et al.*, Electrochimica Acta **83**, 367 (2012).
4. P. M. Vereecken, R. A. Binstead, H. Deligianni and P. C. Andricacos, IBM J. Res Dev. **49**, 1 (2005).
5. K. Matthew and R. G. Hennig, arXiv: 1601.03346v1 (2016).
6. S. N. Steinmann, C. Michel, R. Schwiedernoch and P. Sautet, Phys.Chem.Chem.Phys. **17**, 13949 (2015).
7. J. K. Norskov et al., J. Chem. Phys. B **108**, 17886 (2004).
8. J. Harl, L. Schimka and G. Kresse, Phys. Rev. B **81**, 115126 (2010).
9. M. Yokoi, S. Konishi and T. Hayashi, Denki Kagaku **52**, 218 (1984).
10. Z. V. Feng, X. Li and A. A. Gewirth, J Phys Chem B **107**, 9415 (2003).
11. K. R. Hebert, Journal of The Electrochemical Society **152**, C283 (2005).
12. Y. Kanekoa, Y. Hiwatari, K. Ohara, F. Asa, *Electrochim. Acta,* **100**, 321, (2013).
13. Y. Fukiage, Y. Kaneko, T. Hayashi, K. Kondo, K. Ohara, and F. Asa, *ECS Trans.* **50**, 41 (2013).
14. D. Wheeler, D. Joseph and T. P. Moffat, *J. Electrochem. Soc.*, **150**, C302 (2003).

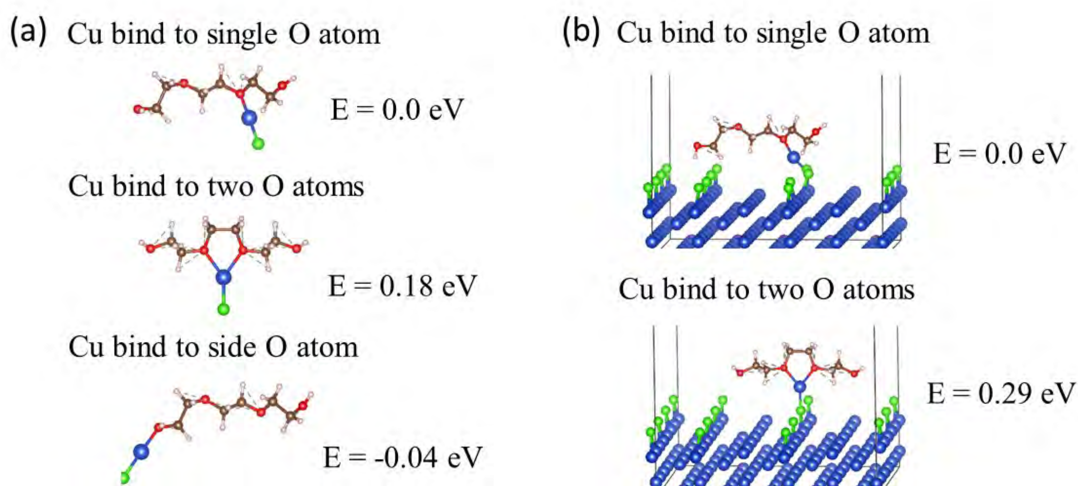


Figure 1 Formation of PEG-Cu-Cl complex. Total energy for (a) Cu atom binding to O atom in different positions and (b) binding of PEG-Cu-Cl complex to the Cu electrode

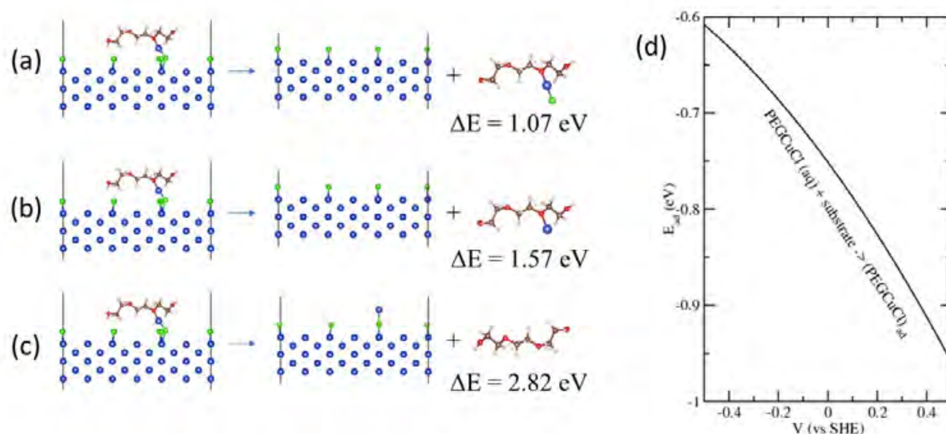


Figure 2 Dissociation energies computed for (a) Cu(sub)-Cl bond, (b) Cl-Cu(complex) bond and (c) Cu(complex)-O bond shown in (d) as a function of applied bias.

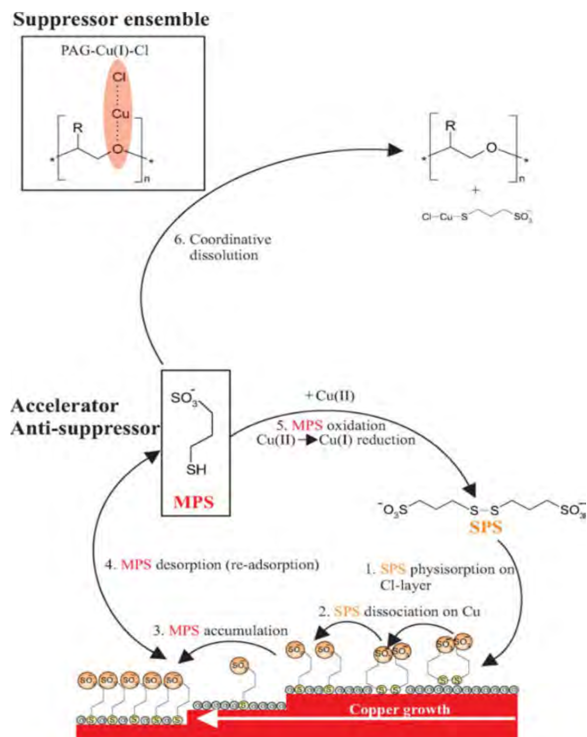
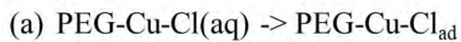
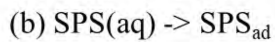
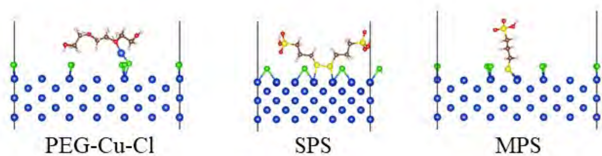


Figure 3 One of the proposed mechanisms of the accelerator.







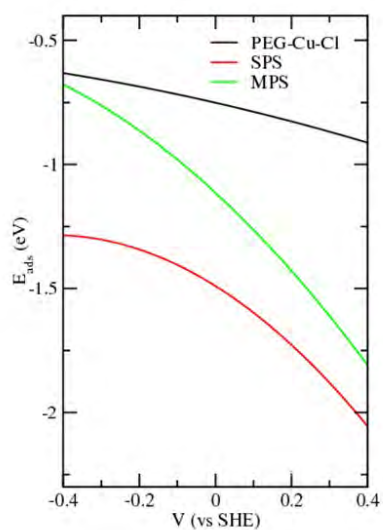
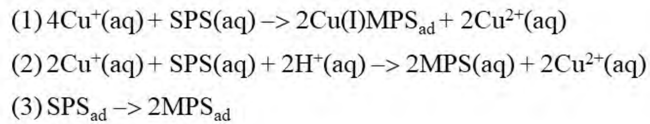
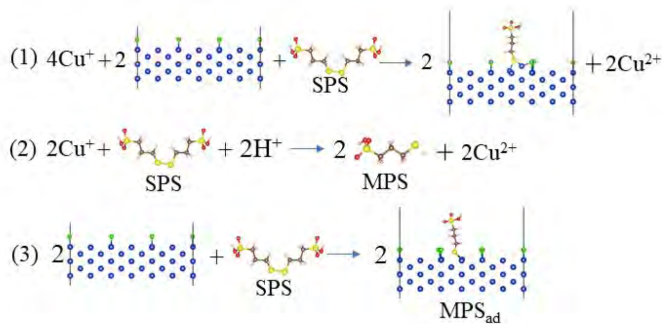


Figure 4 Adsorption energy of PEG-Cu-Cl complex, SPS and MPS on the electrode surface.





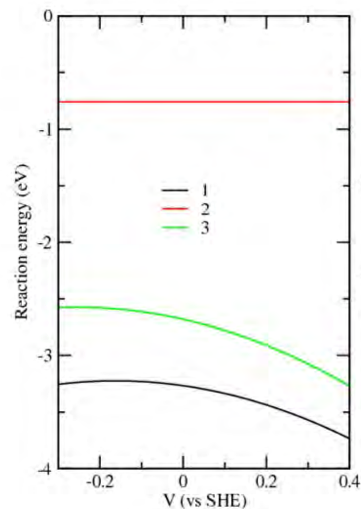
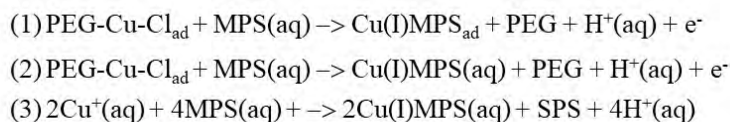
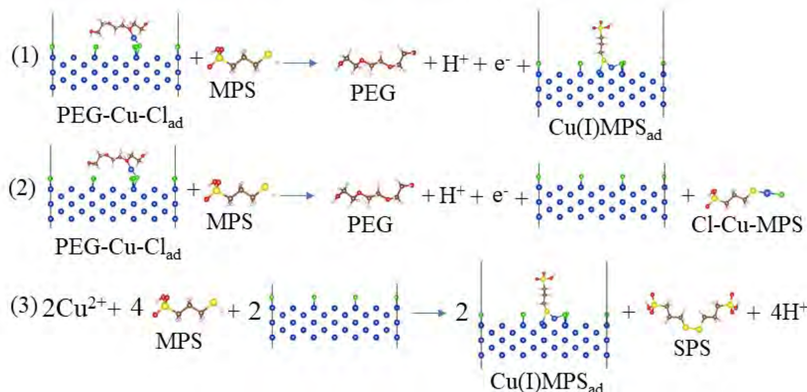


Figure 5 Reaction energies as a function of applied bias for proposed mechanisms for formation of MPS.





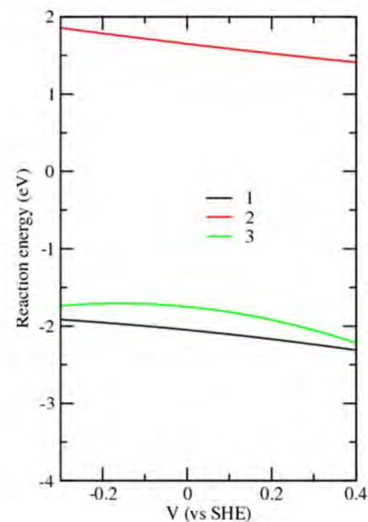


Figure 6 Reaction energies of proposed acceleration mechanism of MPS by dissociation of PEG-Cu-Cl comples.

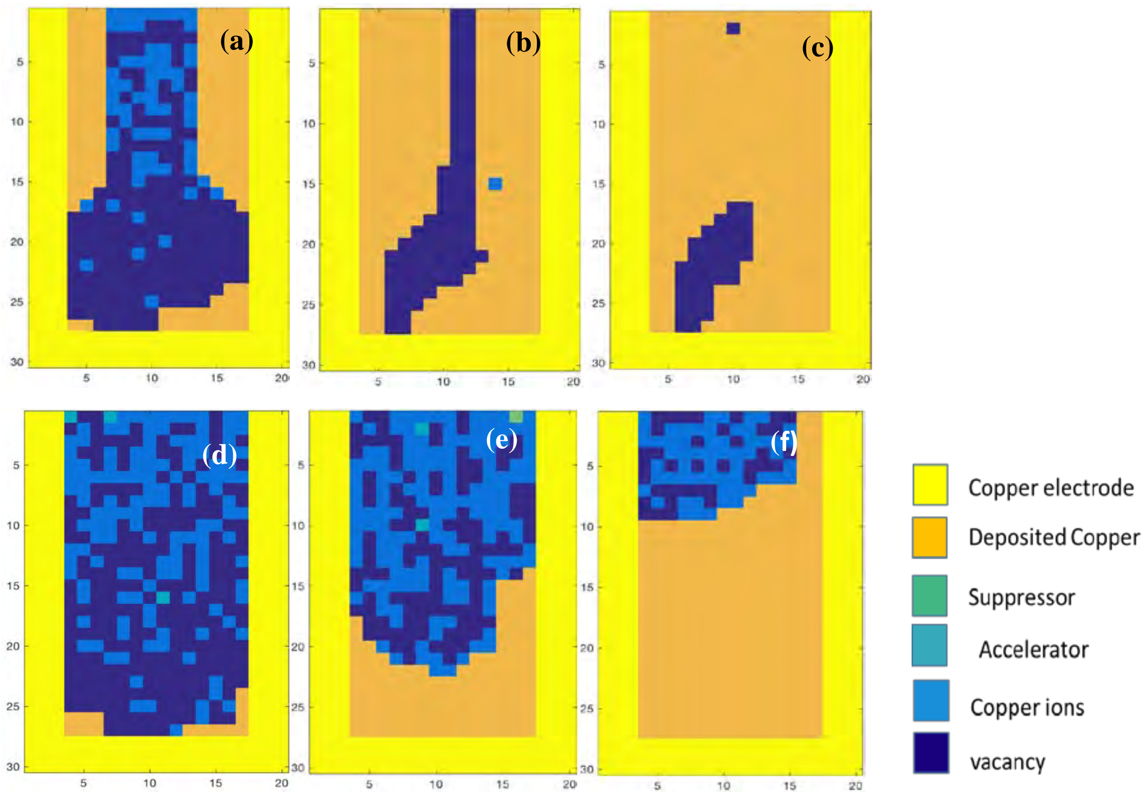


Figure 7 Formation of void in TSV filling for different ratio of nucleation barrier (r_{nuc}) for side walls to corners. (a-c) $r_{nuc} = 0.1$ (d-f) $r_{nuc} = 0.01$

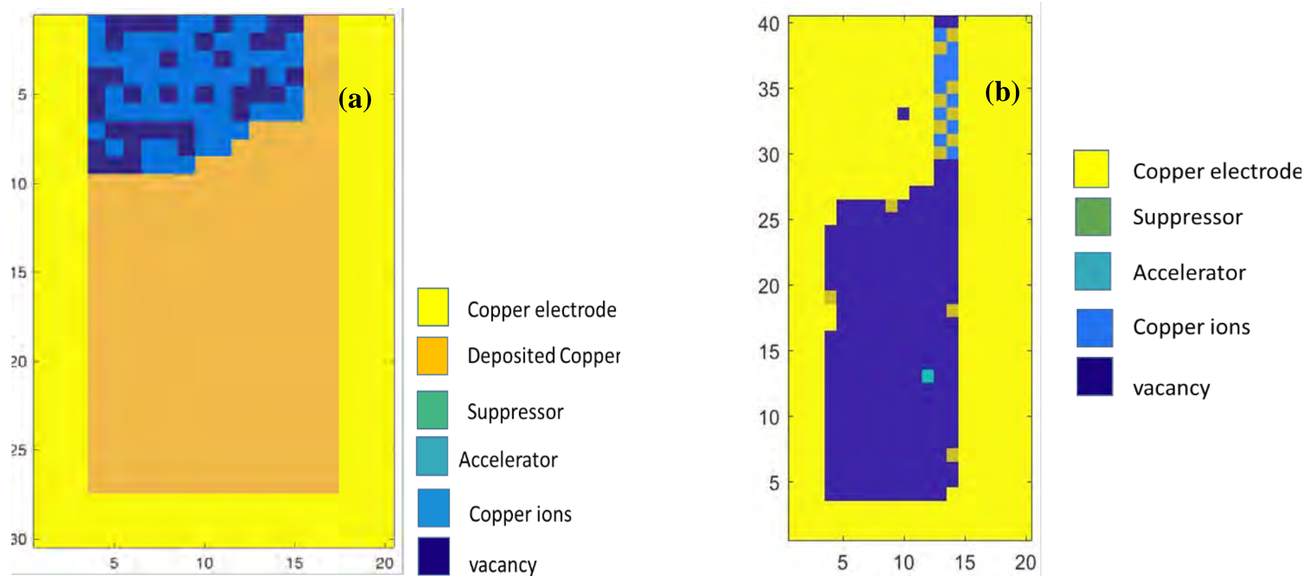


Figure 8 Role of Aspect ratio in TSV filling. (a) Bottom up filling for aspect ratio of 1.5. (b) Void formation for aspect ratio of 2.