The film morphology evolution and growth simulation of Cu$_2$ZnSnS$_4$ (CZTS) solar cells during electrodeposition

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Abstract — A three dimension (3D) Kinetic Monte Carlo coupled multi-body embedded-atom method (KMC-EAM) model has been developed to simulate the CZTS film growth and morphology evolution during electrodeposition. The influences of the deposition factors, including electrolyte concentration, temperature and electrode potential, on film growth were studied. The results show that the electrolyte temperature and potential have significant effects, while concentration has little effect on the film growth. The roughness show the lowest with smoother morphology under temperature (338K), concentration (0.5mol/L) and potential (-0.9V). The texture parameters, such as cluster size, was selected to describe the microstructure evolution. The film morphology has been visualized by 3D diagram, and a competing mechanism between nucleation and growth was proposed.

Key Words — Cu$_2$ZnSnS$_4$, electrodeposition, film morphology, growth evolution, KMC-EAM simulation.

I. INTRODUCTION

The kesterite quaternary compound, Cu$_2$ZnSnS$_4$ (CZTS), has attracted much attention in the last years. The CZTS thin film is a promising candidate absorber material for its naturally abundance, low cost and non-toxicity and excellent material properties for photovoltaic (PV) applications, such as suitable band gap energy of 1.4-1.5 eV and absorption coefficient over 10$^4$ cm$^{-1}$.

CZTS phase stability and control of the intrinsic defects can be identified as the two major challenges to further increase the material quality. A more critical issue to improve the material quality is the control of intrinsic defects in the absorber layer. The low open-circuit voltage $V_{oc}$ has been indeed attributed to the electron-hole pair recombination phenomena, due to the activity of detrimental defects, which can be located into the bulk [1-2] as well as at the grain boundaries [3]. Theoretical works have investigated the possible intrinsic defects, their formation energy and position energy level inside the bandgap [4]. However, further efforts are required to experimental verification which defects are produced during actual fabrication process. A deep knowledge of defect nature, their formation mechanism, location and impact on CZTS performance is indeed a very important issue to identify both the proper growth conditions and the optimal film composition. The role of the electrochemical reaction on the film growth properties and on its intrinsic defect density is still unclear. The clear understanding of these issues still remains an open problem.

Kinetic Monte Carlo (KMC) simulation have been demonstrated to be extremely useful for the study of growth process on a microscopic level. They offer a potential way to explore the growth mechanism, optimize deposition conditions and design film properties [5-6]. The embedded-atom method (EAM) has been shown to accurately characterize metal/metal interaction [7] and predict relevant dynamics for systems including hydrogen adsorption and segregation in binary alloy [8]. Gimenez et al. [9] carried out KMC calculation simulating two dimensional deposition and limited the process to the growth of a single monolayer. J. Liu et al. [10] developed a 2D cross-sectional KMC model which enables to simulate both the nucleation process at early stages and the crystal growth process at later stages (e.g. merging of nuclei and faceting).

In this work, the KMC-EAM model is employed to simulate the film growth of CZTS precursor fabricated by electrodeposition. The model is fully described, and applied to study the effects of the deposition parameters including applied electrode potential, concentration of electrolyte and deposition temperature on film morphology and microstructure. Moreover, the tentative film nucleation and growth mechanism is proposed.

II. SIMULATION METHODS

A. Event

The reaction mechanism involves the electrochemical reduction of M$^{n+}$ ions in solution and the diffusion of metal atoms (M) on the surface. Simulations were performed under conditions of low applied potential and short duration for which depletion of M$^{2+}$ due to diffusion limitation was insignificant. Therefore, a constant M$^{n+}$ concentration was used at all surface sites for all times during the simulations. Metal ions at the electrode surface were reduced on either the substrate S or previously deposited metal M atoms. There are no adsorbed metal ions; that is, metal ions in solution were
not explicitly included in the simulation, other than that they were available be reduced to metal adatoms. It was assumed that the system is sufficiently far from the equilibrium potential that anodic dissolution can be neglected.

The simulation model represent an idealized system in order to focus on interactions between the deposition metal (M) and substrate(S) for several limiting cases of behavior involving relative rates of charge transfer and surface diffusion. The geometric details of the substrate and deposited metal were purposely kept simple, as was the chemistry reaction. The objective is to simulate the deposit morphology that arise for various combinations of the rate of deposition and surface diffusion.

In our three-dimensional model, an atom must fall on the stable position that consists of atoms shown as in Fig.1. If the position is unstable, the atom would fall on the lower one until becomes stable.

Fig.1 The diagram of structural arrangement of adatoms

The thin film growth comes down to deposited atoms diffusion until they find appropriate positions. Therefore, deposition, diffusion during the growth process need to be discussed in detail. Each of these process is independent of the other.

If the deposition process takes place, first of all, the kind of deposition atom is selected from metals, e.g. copper. Next the initial position (i, j, k) on the substrate is selected for the deposited atom, i and j mean the location in this layer, and k represents the layer number of the adatom. Both of the two steps use random numbers generated by the computer to finish the selection. If the position (i, j, k-1) is occupied, then the atom lands on the position (i, j, k). If the position is vacant, the atom fills the position (i, j, k-1), repeat this step until the atom finds the appropriate position and the deposition process is completed. The deposition rate \( R_d \) is the number of atoms deposited on the substrate per unit time. Its expression is as follows (1):

\[
R_{d_{\mu}} = k_M C_M e^{-\alpha_M q/RT} \tag{1}
\]

Where \( k_M \) is the rate constant, \( C_M \) the concentration of the metal ions, \( \alpha_M \) the charge-transfer coefficient for metal deposition on substrate, \( n \) the electron number, \( F \) the Faraday constant, \( \eta \) electrode potential, \( R \) the ideal gas constant and \( T \) the temperature.

In the diffusion event occurs, first, the grid must be marked as Fig.2 to determine neighborhoods, second, the kind of diffusion adatom is selected from metal (M) via their diffusion rate. The last step is to find the position where the adatoms diffuse to. Diffusion can happen in the same layer or in different layers. In the case of the same layer diffusion, in our simulation, the diffusion atom can only hop to the nearest neighbors marked 2, 4, 6 and 8 shown in Fig.2.

![Fig.2 Square lattice substrate and neighborhoods locations](image)

If there are no vacancies in the four nearest neighbors, the diffusion atom is dead which means it cannot diffuse. In the case of different layers, if the ending position is instable, we choose the same method of depositing to determine the target position. An adatom needs to overcome the energy barrier that comes from neighbors and substrate. So the diffusion rate of a single adatom is given by the expression as follows Arrhenius equation (2).

\[
R_{\alpha_{\mu}} = \begin{cases} \nu & \Delta E \leq 0 \\ \nu \exp \left( -\frac{\Delta E}{K_B T} \right) & \Delta E \geq 0 \end{cases} \tag{2}
\]

Where the activation energy \( \Delta E \) is the energy barrier that a metal (M) atom must overcome in order to diffuse. The higher the energy barrier is, the less it is possible for an atom to diffuse. The energy barrier utilizes the multi-body embedded-atom (EAM) potential [11] to characterize the adatoms. Its expression is as follows (3):

\[
\Delta E = E_{a_{\mu}} - E_{a_{\mu}}(S_{i} - S_{i} - S_{i}) + E_{a_{\mu}}^{S_{i} + S_{i} + S_{i} + S_{i}} \tag{3}
\]

Where \( E_{a_{\mu}} = 0.494 eV, E_{a_{\mu}} = 0.265 eV, E_{a_{\mu}} = 0.024 eV, S_{i} (i = 1~8) = 0 \) stand for the site was occupied and \( S_{i} (i = 1~8) = 1 \) stand for the site was vacant.

**B. KMC-EAM algorithm**

There are several other KMC variants in common use today. We focus on a kinetic adaptation. At this core, the kinetic version of Monte Carlo, i.e. the KMC method, stochastically explores sequences of transitions in the state of a model system, selecting “links” in the chain of events according to the rates of the transitions. A KMC model was parameterized by at least the rates of each type of transition, and the change (usually local) that each transition induces in the model system. Matrices were used to store and organize the data, which takes advantage of the discrete periodic nature of a crystal lattice. A L*J matrix M was used to represent all the lattice sites. Each element of the matrix corresponds to a lattice site. If a site is occupied, the corresponding element is evaluated with 1, otherwise 0. The deposition rates and surface diffusion rates were also organized in two matrices of same size respectively.
The indices of the rate matrices correspond to the location of the site as the M.

The energy barrier for diffusion is a very important variable for simulation. A very effective method for simulation of the electrodeposition process, without resorting to first-principles calculations, is through the use of molecular dynamics that makes use of a suitable interaction potential. The embedded atom method (EAM) [11] was obtained to calculate the energy barriers between metal atoms and has been shown to accurately characterize metal/metal interactions. The EAM potential has been extensively validated for metallic system. This method uses semi-empirical potentials and provides a good description of the energy barriers. The EAM method was based on density functional theory. The energy barriers are calculated for all local environments, as shown in Fig.2.

III. RESULT AND DISCUSSION

The thin film growth is decided by deposition and diffusion process. During electrochemical reactions, the metal ions are transferred into the deposited adatoms. Thus, the electrodeposition parameters have affect the morphology and microstructure in the reaction process.

A. Parameters effect on morphology evolution

The Simulations were conducted with different electrodeposition parameters including concentration, temperature and applied electrode potential. The size of the crystal lattice of the substrate is 50×50.

Fig.3 shows the cross-section morphology of the concentrations varied from 0.1~1mol/L under 338K temperature and -1V potential.

Fig.3 the cross-section morphology of different concentrations (0.1mol/L (a1, a2); 0.5mol/L (b1, b2) and 1mol/L (c1, c2))

The results obviously indicate that as concentration increased, the morphology become rougher, the vacancy increased. It mainly due to that the electrochemical reaction rate increased with the arising concentration, resulting in more adatoms deposit on the substrate. The adsorption adatoms are easy to be buried by the new adatoms and difficult to diffuse enough, so the morphology become rough, vacancies increase and the isolated islands increase.

As shown in Fig.4, the temperature (318K~338K) increase results in the smooth morphology. The main reason is that as the temperature increases, adatoms obtain more diffusion ability and energy which can drive them move further. Thus, they have more opportunities to combine with other adatoms or islands and arrive in the lowest energy position, so that the system can reach the lowest free energy and the isolated island and vacancy decreased. From the thermodynamic point of view, a smoother surface is more stable having lower surface energy. Such lower-energy surface profiles must be formed and maintained through diffusion since deposition events are insensitive to the energetic state of atoms.

Fig.4 The cross-section morphology of different temperature (318K (a1, a2); 328K (b1, b2) and 338K (c1, c2))

Varying the applied electrode potential has an influence on the deposition morphology as shown in Fig. 5. From the results, it is not difficult to identify that the more negative the applied electrode potential, the faster the growth, the smaller the average grain size, and the more the variance (c1, c2). The more negative the applied electrode potential could accelerate the nucleation or growth, which can hamper the adatoms from diffusing enough. It is obvious that a crude surface profile is formed consequently.

The film surface morphology can be characterized by roughness. We probe into the roughness under influence of
temperature, applied potential and concentration. A set of parameters including the potential range (-0.85 ~ -1.2V), the concentration metal ions range (0.1 ~ 1mol/L) and the temperature range (308 ~ 348 K) were selected to show the combined effects of these deposition parameters on surface roughness, as shown in Fig.5 (a-c). The average roughness \( R \) is calculated using (4)[12]:

\[
R = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (h_i - h)^2}
\] (4)

Where, \( h_i \) the height of each surface atom, \( h \) the average height and \( n \) is the number of surface atoms.

Compared to concentration, the temperature have a more essential effect on roughness as shown in Fig.5 (a). The reason may be that the temperature affect the diffusion rate, and as temperature increases the diffusion rate increases. Under this potential (-1V) and concentration (0.1 ~ 1mol/L), the diffusion event have more effect on morphology.

The Fig.5 (b) shows the potential and temperature combined effect on roughness. Under a certain potential, the roughness almost maintain the same value despite temperature vary. While the temperature shows opposite result, which means that the applied potential is a significantly essential determinant on roughness compared to temperature.

The effects of potential and concentration on roughness are shown in Fig.5 (c). The results show the similar trend as Fig.5 (b), the roughness changed little as the concentration vary. Fig.5 (b) and (c) prove that the potential plays an essential role in roughness, which indicates that the potential controls the electrochemical rate under this condition.

An optimized combined parameters (temperature 338K, potential -0.9V and concentration 0.5mol/) is obtained with a smoother film morphology and lower roughness. Thus, the growth mechanism is simulated at the optimal parameters.

B. Nucleation and growth mechanism

The evolution of the film microstructure has been simulated. The individual cluster size vary due to its behaviors, and the whole island shape evolve owing to the competitive growth.

![Fig.6 The variation of cluster size with the adatoms number](image)

The cluster size vary from deposition adatoms under optimized combined parameters discussed above, as shown in Fig.6.

The one-atom cluster \( (N_1) \) and two-atom cluster \( (N_2) \) emerge at the initial deposition stage and they increased as deposition adatoms increased. However, they begin to decrease when deposition adatoms reach 500 until they disappear.

The 3-atom to 17-atom clusters \( (N_3, N_4, N_5, N_6, N_7, N_8, N_9, N_{10}, N_{11}, N_{12}, N_{13}, N_{14}, N_{15}, N_{16}, N_{17}, N_{18}, N_{19}, N_{20}) \) begin to emerge at range of 200~500 adatoms, and increase with
adatoms increasing. When adatoms rise up to 1000, the clusters gradually decrease until eliminate.

The larger clusters (N17,31, N32) emerge at the scope 500 to 1000, and increase as adatoms increase. While, the cluster reduce when adatoms arrive 1500 until vanish.

When adatoms reach 2000, only the N1 and N32 left, and adatoms reach 2800, only N32 left.

During the electrodeposition, the small clusters are formed initially, then transfer into the larger clusters with the adatoms increase, and merge into one large crystal finally.

Fig.7 The 3D diagram of the film morphology
As shown in Fig.7, the 3D diagram morphology of the film at optimal electrodeposition parameters. The morphology is similar with the observation by SEM characterization [13]. The morphology of metal film shows that the upper layers contain more vacancy, small islands, and even several isolating atoms. The lower layer, however, incudes larger islands and less voids. Based on the results from Fig.6 and Fig.7, the growth morphology evolution illuminates a competition mechanism between nucleation and growth.

IV. CONCLUSION

By using a KMC-EMA, a more realistic and efficient model has been constructed to simulate the electrochemical deposition process.

The electrolyte temperature and the potential have significant effects, while concentration has slight effect on the film growth. The higher temperature, the morphology show a smoother film, but the potential have the contrary result. The parameters has an optimal combination on roughness.

The cluster variation shows the change from small cluster size to big cluster size during the film growth. The evolution shows a competition mechanism between nucleation and growth.

From the cross-section and 3D morphology, it is evident that the bottom layers with larger islands and less vacancies (mainly Frank-vander Merwe) and the upper layers with more small islands, even isolating atoms (mainly Volume-Weber.)

The model has been proven to be able to capture the character of morphology evolution of film. This tentative mechanism investigation could give a theoretical support to illuminate the film growth, and improve photovoltaic performance.

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