Molecular Dynamics Simulation of Cu-Se Interactions for CIGS Solar Cells Growth Process

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***Abstract*— In this work, we analyzed the interactions between copper and selenium (Cu-Se) atoms in the second stage of a co-evaporation growth process of copper indium gallium diselenide (CIGS) material, through computational simulation. To achieve this conditions, we used Molecular Dynamics method (MD) via the open access code LAMMPS, reproducing the thermodynamic phenomena occurring in the deposition process. We built different models in concordance to the information found in repositories for the interatomic Morse potential between Cu and Se. As a part of results, we obtained 24 samples of interactions, with different temperatures and cutoff radius. We found that the improvement of the Cu-Se interactions occurred at values of 2.5 cutoff radius and 550 K temperature, since it was observed a more stable interaction at the interface.**

Keywords*— *Cu-Se interactions, Deposition process by co-evaporation, Molecular Dynamics Simulation.

I. Introduction

In recent years, thin film technology has demonstrated a high capacity to produce solar cells with higher efficiencies and with improved properties compared to crystalline silicon cells. This type of cells are made up of layers of different semiconductor materials that act as the active region; among the best known are those based on cadmium telluride (CdTe) and copper indium gallium diselenide [$Cu(In_{1-x}Ga_x)Se_2$] also known as CIGS. This material have become one of the most promising semiconductor compounds for the production of efficient solar cells. The discrepancy in efficiency of CIGS solar cells lies in the compound concentrations, and the thickness of the absorbent layer. Currently, CIGS cells have been produced with a record efficiency of 23.4% [1], [2]. Nonetheless, the research to optimize the properties of this material is still in progress, by the aid of computational tools that have already proven their effectiveness for other materials.

CIGS solar cells have been studied extensively, due to their significant properties, e.g. a high absorption coefficient, high temperature stability, and are low-cost compared to other semiconductor materials [3]. The CIGS solar cell structure consists of a) a Mo layer (as bottom contact), b) CIGS absorber layer as p-type film, c) CdS as window layer (facilitate the electrical transition from CIGS to top electrical contact), and d) transparent Al doped ZnO contact [4].

Otherwise, the experimental research to improve the properties of CIGS is not the unique investigation line under development, but also the computational modeling methods that are demonstrated their effectiveness in the study of other semiconductor material systems. [5], [6]. Such is the case of Molecular Dynamics, which, as its name indicates, is a type of computational simulation that allows us to analyze the dynamics of a system over the time, calculating the forces of the atoms using Newton's equations of motion.

Molecular dynamics is able to reproduce on a micro or nano scale, the structural behavior of an atomic/molecular system given by the interactions between atoms of the same or different nature, and repeat the process several timesteps to obtain the positions of the elements. A computational flow diagram process used in this investigation is described in [Fig. 1].

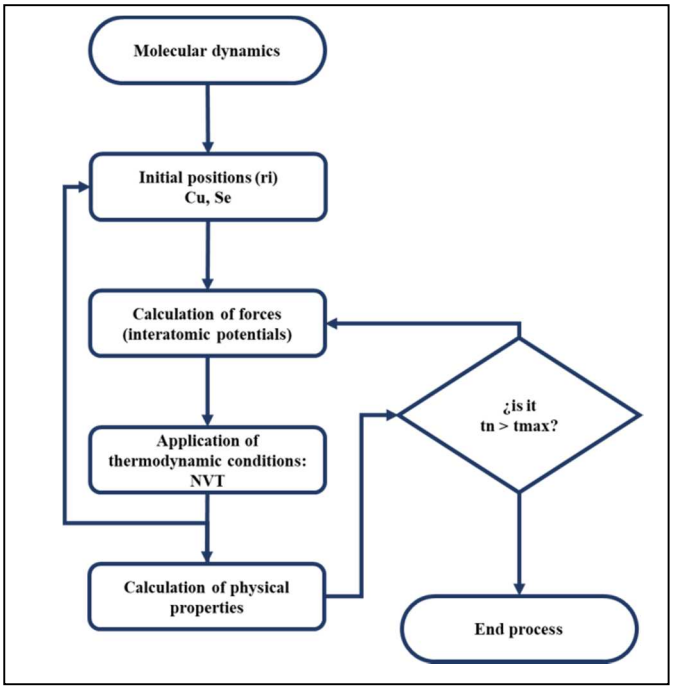

Figure 1. Computational flow diagram process.

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Moreover, it is important to note that this simulation is based on a co-evaporation growth process, in its second stage. This process is one of the most promising technique currently used to obtained CIGS layers [7]. The second stage consist in an evaporation of Cu and Se around the substrate [8]. The election of the temperature (550 K) corresponds to the computational time to execute the simulation. Ga and In were not considered because their interaction have been investigated previously [5,9]. This part of the process is of great relevance for a complete simulation due to there is not enough information about how the interactions between Cu-Se atoms influence the growth conditions.

In order to find better conditions for the growth process, several simulations have been carried out for the interactions of the selenium flux on a copper substrate. The simulations are directly affected by the interatomic potential, which vary in relation to the cut-off radius, as well as the thermodynamic conditions.

II. METODOLOGY

A. Simulation configuration

The 24 simulations were developed with the method of molecular dynamics using the open-source LAMMPS code. Furthermore, we visualized the results with the open-source software OVITO, using the "create bonds" modifier for the analysis of the interactions between Cu-Se atoms.

B. Hybrid interatomic potential

Although there is no interatomic potential for CIGS, there are some theoretical approximations [10], [11], we used the hybrid/overlay form in LAMMPS to declare all the interactions between Cu-Cu, Se-Se and Cu-Se atoms, supported by Cu-meam potential [12], Cd-Te-Zn-Se-Hg-O Stillinger-Weber potential [13], and Morse potential [14], respectively. This series of potentials, with different styles and compatibility, guarantee all the free interactions between Cu-Se atoms, benefiting their study.

C. System geometry

The system geometry consists on a Cu buffer layer with a 54.15 Å in x and y direction, and a thickness in the z direction of 10.83 Å corresponding to a group of seven monolayers (3,150 atoms). [Fig. 2]. To set all the correct simulation characteristics, the Cu buffer layer was divided into three regions: A) bottom fixed layer, which consist of two layers at the bottom substrate to avoid the incident energy of the adatoms, since these particles transfer momentum to the superficial atoms of the substrate. B) a middle thermal region represents the buffer layer'sthermal control through a Nosé-Hoover algorithm implemented by the canonical NVT ensemble, where the number of atoms, the volume, and the temperature are considered constants [15]. The temperature was set between 325K to 550 K.

This process of interaction at the surface of the Cu buffer layer can be observed in Figure 3, showing the bonds of a Cu-Se junction.The incident ratio of Se atoms was set to 3.28 Å/ps in the negative z direction, based on the range of temperatures using in the thermal control process.

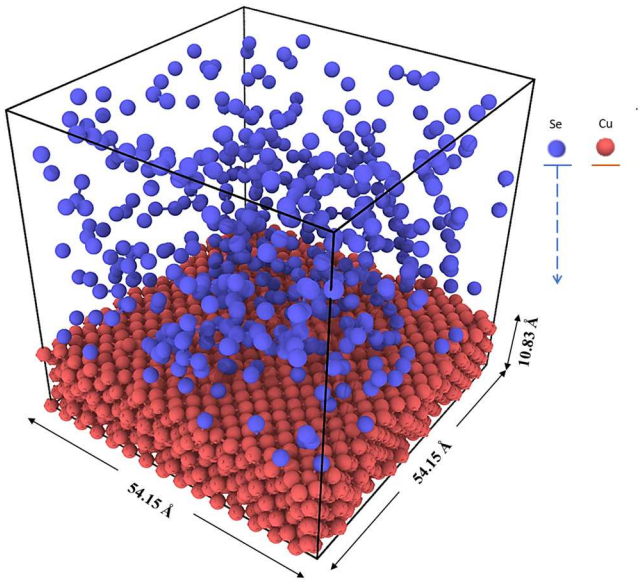

Figure 2. General process of the deposit of Se (blue) on the Cu (red) buffer layer.

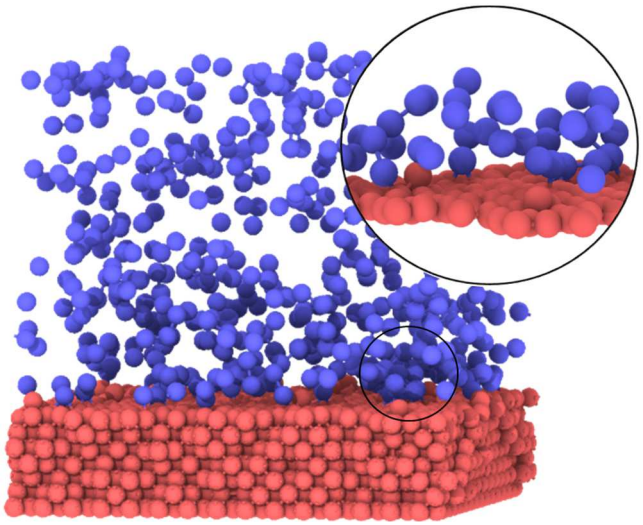

Figure 3. . Cu-Se interactions at surface. Velocity @550 K, cutoff: 2.5 Å, 20k time steps. Blue and rose spheres represent Selenium and cupper atoms respectively.

D. Boundary conditions

For the simulation conditions, periodic boundary conditions in were set in x and y directions; nevertheless, in z direction a non-periodic boundary condition was established to achieve the free interaction process between the superficial Cu atoms and the Se ejected atoms.

A. Morse interatomic potential

As we anticipated in the hybrid interatomic potential section, the computation of pairwise interactions between Cu and Se atoms follow the Morse potential style which is a classic pair potential applied as model for the potential energy of a molecule and has the same behavior as the Lennard Jones potential (LJ). Each has a pair of repulsion and attraction

potentials; two adjustable parameters and they are generally used in packed crystal structures. [16]

However, the morse potential has a higher precision in the cases of approximation of the potential energy of a diatomic molecule. In addition, it is widely used in the simulation of molecular dynamics of some metals such as copper [17,18], or in the simulation of molecular dynamics of structures joined by covalent bonds. Furthermore, we selected this form of potential to describe the Cu-Se interactions, considering that it is use for diatomic molecules and interactions between the atoms and surfaces.

The Morse potential [14] is described by the equation below:

$$E = D_0[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}]\ ;\ r < r_c$$

Where D_0 is the dissociation energy,α is a control factor to modify the "width" of the potential, r is the internuclear distance between atoms, and r_0 is the equilibrium bond distance.

Finally, the cutoff radio r_c will be considered as one of the variables to study in this work in order to clarify whether the cutting distance is the necessary to calculate the total interaction of the Morse potential selected. In addition, the cutting distances have been seen as an influence on the interfacial properties (since the boundary conditions must lead to obtaining a finite potential energy in a range of $r < r_c$) [19]

III. Results

Several simulations were performed for the interactions of a selenium flux on a copper buffer layer according to experimental studies about these phenomena [20], [21], [22], as is described in Table 1. The simulations varied in relation to the cutoff radius for the calculation of the interactions, as well as some variations in the simulation were considered as a function of the energy (temperature) of the atoms [Fig 4].

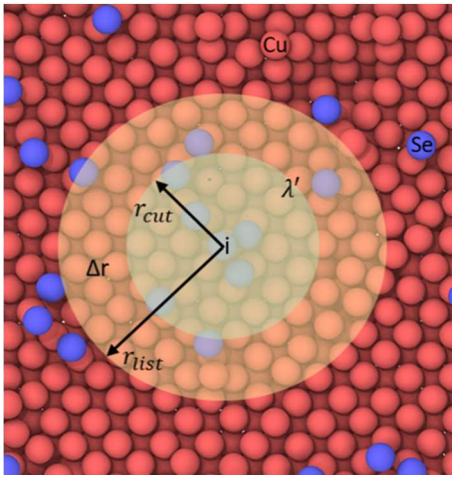

Figure 4. Representation of the cut off radius for Se atoms.

Table 1. Conditions for the simulation of the interaction process

Sample	Cutoff (Å)	Temperature(K)
1	1.0	325
2		550
3	1.3	325
4		550
5	1.6	325
6		550
7	1.9	325
8		550
9	2.1	325
10		550
11	2.3	325
12		550
13	2.5	325
14		550
15	2.8	325
16		550
17	3.1	325
18		550
19	3.4	325
20		550
21	3.7	325
22		550
23	4.0	325
24		550

Improvement results were expected with a cutoff radius (r_{cut}) close to 2.5 Å since it is considered the standard for LJ interactions. We worked around this data to obtain several results, with variations of 0.3 Å, and to visualize the effect that these produced in the simulations. The results indicate that, at asmaller cut-off radius, in the range of 1 to 2.2 Å, the selenium atoms come into contact with deeper layers in the copper substrate, which deforms the structure of the copper substrate [Fig. 5].

For the cutoff radius of 2.5 and the velocity depending of the 550 K temperature given by the thermal control, we observed an optimized Cu-Se interaction, analyzed through thebonds OVITO modifier. This reciprocal influence between these two different species of atoms was more stable during the time evolution at the interface, and this was possible because around this cutoff value exist a stronger covalent interaction. Opposite to this state, a radius value less than r_0, could mean a weak covalent representation and a disruption into the Cu structure.

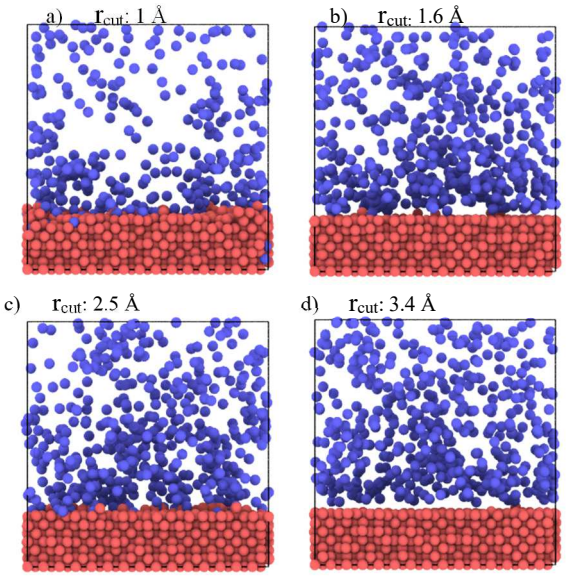

Figure 5. Se evaporation on Cu buffer layer at different r_{cut}, a) 1 Å, b) 1.6 Å, c) 2.5 Å and d) 3.4 Å. With 20 k time steps.

IV. CONCLUSIONS

We developed a series of simulation of Cu-Se interactions process using Molecular Dynamics methods. As a first approximation, we used the hybrid/overlay configuration to make possible the combination of interatomic potentials for the Cu-Cu and Se-Se interactions. Additionally, we specified conditions for the Cu-Se interatomic description through Morse potential. Moreover, we varied the velocity (depending on the control temperature) and the cutoff radius. We observed that better results were achieved when the temperature was set at 550 K and the cutoff was around 2.5 Å. These results are according with other theoretical results and experimental Cu-Se interactions studies.

V. ACKNOWLEDGMENTS

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REFERENCES

[1] "Best research-cell efficiency chart," NREL.gov. [Online]. Available: https://www.nrel.gov/pv/cell-efficiency.html. [Accessed: 10-Sep-2021].

[2] S. Sinha, D. K. Nandi, P. S. Pawar and S.H. Kim, J. Heo, "A review on atomic layer deposited buffer layers for Cu(In,Ga)Se_2 (CIGS) thin film solar cells: Past, present, and future", *Solar Energy*, vol. 209, pp. 515-537, September 2020.

[3] S.Y. Kuo, M.Y. Hsieh, D. H. Hsieh, H. C. Kuo, C. H. Chen and F. I. Lai, "Device Modeling of the Performance of Cu(In,Ga)Se_2 Solar Cells with V-Shaped Bandgap Profiles", *International Journal of Photoenergy*, vol. 2014 , pp. 6, July 2014.

[4] D. Valencia, J. Conde, A. Ashok, C.A. Meza-Avendaño, H. Vilchis and S. Velumani, "Optimization of Cu(In, Ga)Se_2 (CIGSe) thin film solar cells parameters through numerical simulation and experimental study", *Solar Energy*, Vol. 224, pp. 298-308, June 2021.

[5] C. Camas, J.E. Conde, M.A. Vidal and H. Vilchis, "Molecular dynamics simulation of cubic $In_xGa_{(1-x)}N$ layers growth by molecular beam epitaxy", *Computational Materials Science*, Vol. 193, pp. 110387, March 2021.

[6] A. Hosseini and M. N. Nasrabadi, "Investigation of vacancy defects and temperature effects on the GaN bombarding with argon atoms: Molecular dynamics simulation" *Materials Chemistry and Physics*, Vol. 271, pp. 124854, June 2021.

[7] Y. Y. Jseng, C. J. Chao, H. H. Sung and T. C. Chen, "CIGS thin film and device performance produced through a variation Ga concentration during three-stage growth process", *Materials Science in Semiconductor Processing*, Volume 87, pp. 162-166, November 2018.

[8] C. H. Huang, W. J. Chuang, C. P. Lin, Y. L. Jan, and Y. C. Shih, "Deposition Technologies of High-Efficiency CIGS Solar Cells: Development of Two-Step and Co-Evaporation Processes" *Crystals*, vol. 8, no. 7, pp. 296, July 2018.

[9] X.W. Zhou, R.E. Jones and K. Chu,"Polymorphic improvement of Stillinger-Weber potential for InGaN" J. Appl. Phys., vol. 122, no. 23, pp. 235703, December 2017.

[10] S. Namsani, B. Gahtori, S. Auluck, and J. K. Singh, "An interaction potential to study the thermal structure evolution of a thermoelectric material: β - Cu_2Se," *Journal of computational chemistry*, vol. 38, no. 25, pp. 2161-2170, June 2017.

[11] Y. You, H. Hu, & J. H. Choi, "Atomic adsorption on monolayer Cu_2Se: a first-principles study," Physical Chemistry Chemical Physics, 2021, vol. 23, no 16, p. 9814-9821.

[12] S.A. Etesami, and E. Asadi, "Molecular dynamics for near melting temperatures simulations of metals using modified embedded-atom method", *Journal of Physics and Chemistry of Solids*, vol. 112, pp. 61-72, January 2018.

[13] X.W. Zhou, D.K. Ward, J.E. Martin, F.B. van Swol, J.L. Cruz-Campa, and D. Zubia, "Stillinger-Weber potential for the II-VI elements Zn-Cd-Hg-S-Se-Te", *Physical Review B*, vol. 88 no. 8, pp. 085309, August 2013.

[14] P. M. Morse, "Diatomic molecules according to the wave mechanics. II. Vibrational levels," *Physical review*, , vol. 34, no 1, pp. 57, July 1929.

[15] R. Chetrite and H. Touchette, "Nonequilibrium microcanonical and canonical ensembles and their equivalence" *Physical review letters*, vol. 111, no 12, pp. 120601, September 2013.

[16] L. Piela, *Ideas of quantum chemistry*. 2nd ed. Amsterdam: Elsevier, 2006.

[17] S. F. Hwang, Y. H. Li and Z. H. Hong, "Molecular dynamic simulation for Cu cluster deposition on Si substrate" *Computational Materials Science*, vol. 56, pp. 85-94, April 2012.

[18] J. Wei, et al., "Molecular dynamics simulations of the lattice thermal conductivity of thermoelectric material $CuInTe_2$" *Physics Letter A*, vol. 381, no. 18, pp. 1611-1614, May 2017.

[19] U. F. Galicia-Pimentel, D. Osorio-González and J. López-Lemus, "On the morse potential in liquid phase and at liquid-vapor interface" *Revista mexicana de física*, vol. 52, no 5, pp. 422-428, October 2006.

[20] J. Gwak, M. Lee, J. H. Yun, S. Ahn, A. Cho, S. Ahn and K. H. Yoon, "Selenium Flux Effect on Cu (In, Ga) Se_2 Thin Films Grown by a 3-stage Co-evaporation Process," *Israel Journal of Chemistry*, vol. 55, no. 10, pp. 1115-1122, August 2015.

[21] P. I. Reyes Figueroa, "Deposition and characterization of Cu ($In_{1-x}Ga_x$) Se_2 films by multiple deposition techniques" Ph.D. Dissertation, Instituto Politécnico Nacional, Mexico city, Mexico, 2016.

[22] S. U. Park, R. Sharma, K. Ashok, S. Kang, J. K. Sim and C. R. Lee, "A study on composition, structure and optical properties of copper-poor CIGS thin film deposited by sequential sputtering of CuGa/In and In/(CuGa+ In) precursors," *Journal of Crystal Growth*, vol. 359, pp. 1-10, November 2012.