



Effect of substrate temperature on quality of copper film catalyst substrate: A Molecular Dynamics Study

*Rinaldo Marimpul**

Department of Physics, Faculty of Science and Technology, Buddhi Dharma University
Jl Imam Bonjol No 41 Tangerang, Indonesia

*Correspondence: rinaldo@buddhidharma.ac.id

ABSTRACT

Copper film growth using thermal evaporation methods was studied using molecular dynamics simulations. The AISiMgCuFe modified embedded atom method potential was used to describe interaction of Cu-Cu, Si-Si and Cu-Si atoms. Our results showed that the variations of substrate temperature affected crystal structure composition and surface roughness of the produced copper film catalyst substrate. In this study, we observed intermixing phenomenon after deposition process. The increasing of substrate temperature affected the increasing of the total silicon atoms had diffusion into copper film.

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1. INTRODUCTION

Copper film has many applications such as ohmic contact and catalyst substrate as medium of graphene growth (Yamada *et al.*, 2012; Bae *et al.*, 2010; Butler *et al.*, 2013). One of criteria of catalyst substrate for graphene growth medium is good crystallinity (Kim *et al.*, 2012). Kim reported that crystallinity of metal catalyst substrate affected physical properties of the produced graphene (Kim *et al.*, 2012).

Many methods of thin film growth were used such as evaporation thermal and sputtering. Sputtering method uses high energy atom on deposition process. Meanwhile, thermal evaporation method uses relatively low energy atom. Therefore, evaporation thermal method tend to produce film with poor quality (amorphous structure). For solving this problem, annealing process is done to repair the structure of film (Rosikhin *et al.*, 2016).

A molecular dynamics simulation study of growth process and annealing of copper film was done by many researchers (Marimpul *et al.*, 2017; Zhang, 2012; Zhang, 2013; Syuhada, 2016; Hidayat *et al.*, 2016). This study is done to get spesific understanding on atomic scale, to predict and to complete experiment result. Marimpul reported that the improvement of film crystallinity at annealing process was initiated by atomic diffusion (Marimpul *et al.*, 2017). Zhang *et al.* reported that substrate temperature affected the percentage of crystal structure and surface morphology of film (Zhang, 2012; Zhang, 2013; Syuhada, 2016; Hidayat, 2016).

In this paper, we simulated growth process of copper film on silicon substrate based on thermal evaporation method to get metal catalyst substrate for medium of graphene growth. This study is improvement from previous study (Hidayat, 2016). In

previous work, the simulated study of growth process was based on general deposition and just analyzed effect of substrate temperature on percentage of amorphous structure. We simulated growth process based on thermal evaporation method and modified simulation method. We investigated the effect of substrate temperature on crystal structure and surface morphology of copper film catalyst substrate. We observed the intermixing phenomenon on atomic scale and thus the produced of copper film catalyst substrate can be used for application ohmic contact, besides graphene growth medium.

2. SIMULATION METHOD

Figure 1 shows the silicon substrate system with dimensions $4a \times 4a \times 3a$ ($a = 5.43 \text{ \AA}$, the lattice constant of a diamond structure) and consisting of 416 atoms. Periodic boundary conditions were applied in the x and y directions.

There are three regions on silicon substrate, namely fixed region, thermal region and newtonian region. Fixed region consists of three layers of atom who prevent atom moving and fix in position when deposition process. Thermal region consists of six layers of atoms who control substrate temperature to remain constant. Newtonian region consists of four layers of atoms. The motion of atoms in thermal region and newtonian region is governed by Newton's equation. For solving the equation of motion, we used Verlet Algorithm with timestep $\Delta t = 1 \text{ fs}$. We used Berendsen thermostat to control temperature with a damping parameter of 10 timesteps.

This simulation was initiated with equilibration step on silicon substrate at each temperature 300 K, 400 K, 500 K and 600 K for 1 ns. Then we simulated deposition process of copper atom on silicon substrate with incident energy 0,35 eV (Marimpul, 2017).

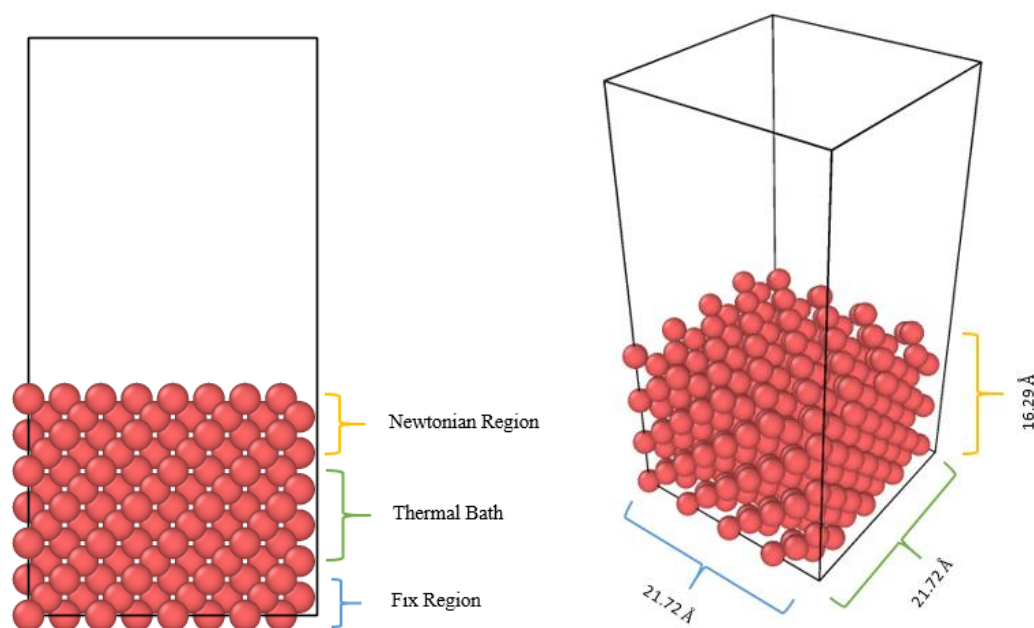


Figure 1. Dimensions and region division of the silicon substrate.

In this process, each copper atom was deposited on silicon substrate every 2000 timesteps. Therefore, deposition rate, in this simulation, is 1 atom/2 ps (Hou *et al.*, 2000). This proceeded until 390 atoms were deposited on the substrate and then system was equilibrated at each temperature 300 K, 400 K, 500 K and 600 K for 1 ns. It was intended to make system in relax condition. All of our simulations were performed using LAMMPS (Large-scale atomic/molecular massively parallel simulator) (Plimpton, 1995). The visualization of system from LAMMPS output data was used by OVITO (Open visualization tool) (Stukowski, 2010). We used common neighbour analysis (CNA) method with OVITO software to calculate and to analyze crystal structure and to calculate surface roughness of catalyst substrate.

The interactions between Si-Si, Cu-Cu and Cu-Si are described by the AlSiMgCuFe modified embedded atom method (MEAM) potential (Jelinek *et al.*, 2012). These interactions are governed by the equation:

$$E = F_i(\rho_i) + \frac{1}{2} \sum_{j \neq i} \phi_{ij}(r_{ij}) \quad (1)$$

where F_i is the electron density function and ϕ_{ij} is the interaction of a pair of atoms, limited by a certain cut-off radius. The parameters of the potential interaction function are given in **Table 1**.

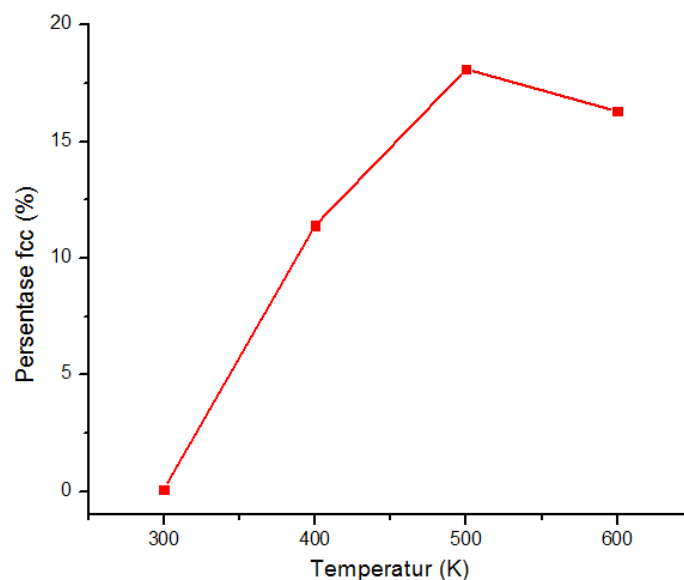
3. RESULTS AND DISCUSSION

3.1. Crystalline structure

In this simulation, we deposited copper film on silicon substrate. Therefore, the result is copper film catalyst substrate with the expectation of structure crystal was fcc (face centered cubic). **Figure 2** shows graphic of percentage of fcc structure at variation of substrate temperature. From **Figure 2** was shown that the increasing of percentage of fcc structure was occurred with the increasing of substrate temperature. The increasing of percentage of crystal structure indicated that film had more neat arrangement of atoms. It was occurred because the increasing of substrate temperature affected copper atom gained more thermal energy to overcome barrier energy from the surrounding atoms.

Tabel 1. Parameter potensial AlSiMgCuFe meam (Jelinek, 2012)

elem.	Al	Si	Mg	Cu	Fe
E_c (eV)	3.353	4.63	1.51	3.54	4.28
a_0 (Å)	4.05	5.431	3.194	3.62	2.851
A	1.07	1.00	0.8	1.07	0.555
α	4.64	4.87	5.52	5.11	5.027
$\beta^{(0)}$	2.04	4.4	4.0	3.634	3.5
$\beta^{(1)}$	3.0	5.5	3.0	2.2	2.0
$\beta^{(2)}$	6.0	5.5	0.2	6.0	1.0
$\beta^{(3)}$	1.5	5.5	1.2	2.2	1.0
$t^{(0)}$	1.0	1.0	1.0	1.0	1.0
$t^{(1)}$	4.50	2.05	10.04	4.91	-1.6
$t^{(2)}$	-2.30	4.47	9.49	2.49	12.5
t^3	8.01	-1.80	-4.3	2.95	-1.4
C_{min}	0.8	2.0	0.8	0.8	0.68
C_{max}	2.8	2.8	2.8	2.8	1.9
ρ_0	1.0	2.2	0.63	1.1	1.0

**Figure 2.** Percentage of Cu atoms with fcc structure at variations substrate temperature.

Thus, copper atom had diffusion on substrate surface and had diffusion toward other copper atoms to form the crystal structure. This result was agreed with Arrhenius Law.

The increases in percentage of FCC structure indicated that there was an improvement of crystallinity on copper film catalyst substrate. This result was expected because good crystallinity is one of criteria of catalyst substrate for graphene growth medium. Furthermore, quality of crystallinity of catalyst substrate will affect physical

properties and quality of the produced graphene (Kim *et al.*, 2012).

The interesting phenomenon was a decreased of percentage of fcc structure, from 500 to 600 K. In this condition, the total percentage of crystal structure was increased. However, copper atoms not only formed fcc structure, but also hcp and bcc structure at 600 K as shown in **Table 1**.

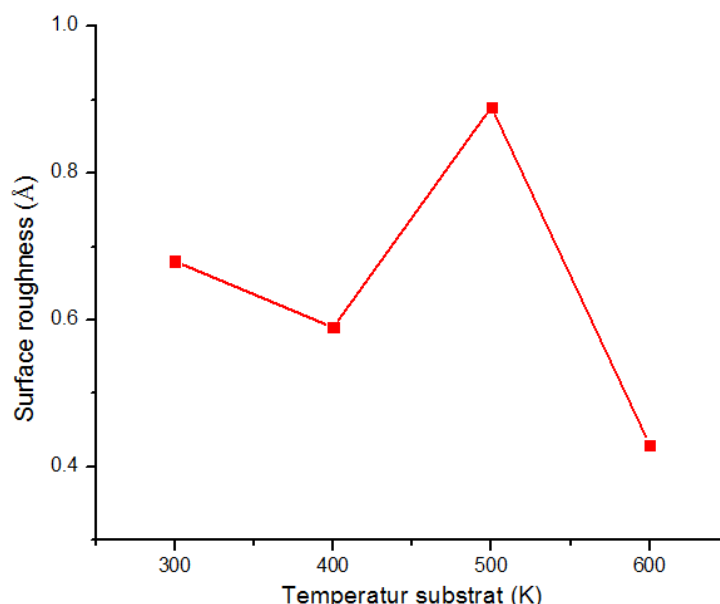


Figure 3. Surface roughness of copper film catalyst substrate versus substrate temperature.

Tabel 2. Percentage of crystal structure Cu atoms at variations substrate

Substrate temperature (K)	Percentage of crystal structure (%)			
	fcc	hcp	bcc	amorf
300	$(1/806) \times 100 = 0,1$	0	0	$(805/806) \times 100 = 99,9$
400	$(92/806) \times 100 = 11,4$	$(47/806) \times 100 = 5,8$	$(1/806) \times 100 = 0,1$	$(666/806) \times 100 = 82,6$
500	$(146/806) \times 100 = 18,1$	0	0	$(660/806) \times 100 = 81,9$
600	$(131/806) \times 100 = 16,3$	$(22/806) \times 100 = 2,7$	$(1/806) \times 100 = 0,1$	$(652/806) \times 100 = 80,9$

3.2. Surface morphology

Surface morphology is one of criteria that related to quality of film. In here, we analyzed effect of substrate temperature to surface roughness of catalyst substrate. Surface morphology affected electrical conductivity of copper film (Timoshevskii, 2008). Timoshevskii reported that surface roughness (1-3 atoms) can decrease 30 – 40 % electrical conductance of copper film. In this study, surface roughness of copper film catalyst substrate was measured quantitatively using equation of root-mean-

square roughness with OVITO (Stukowski, 2010; Zhang, 2012):

$$R_s = \sqrt{\frac{\sum_{i=1}^n (z_i - \bar{z})^2}{n}} \quad (2)$$

where z_i represents the height of the exposed atoms on catalyst substrate surface. **Figure 3** shows that the surface roughness decreased as the increasing of substrate temperature, as we observed at 400 K and 600 K. This result was agreed with Zhang and Syuhada (Zhang, 2013; Syuhada, 2016).

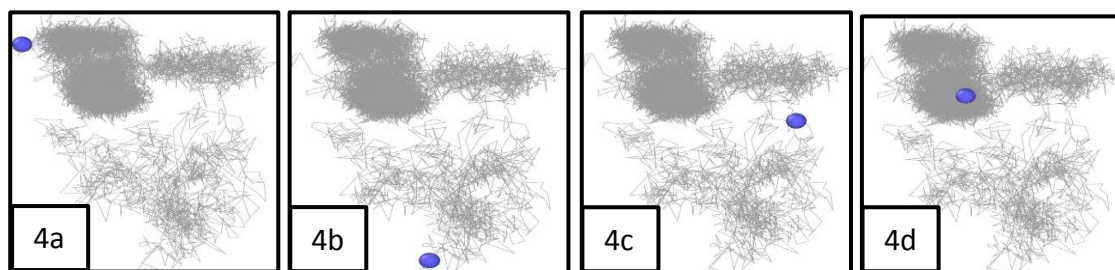


Figure 4. Trajectory of atom diffusion at 600 K (a) Timestep 0 (b) Timetep 78000 (c) Timestep 133900 d) Timestep 1000000.

The phenomenon of Cu atom diffusion on substrate, in this study, was agreed with Fick's Law that stated there was a dependence of temperature on diffusion coefficient as shown in equation:

$$D = D_0 \cdot \exp\left(\frac{-Q_d}{RT}\right) \quad (3)$$

where Q_d is activation energy and T is temperature. From this equation, we can see an empirical relationship that temperature is proportional to diffusion coefficient. The increasing of temperature affected the increasing of diffusion coefficient for D_0 and Q_d were constant. Therefore the surface of copper film catalyst substrate became smoother. However, the interesting phenomenon was occurred at 500 K. The increasing of surface roughness, in this condition, opposed with the results at 400 K

and 600 K. This was occurred because catalyst substrate at 500 K had only fcc structure. Meanwhile, the composition of crystal structure of catalyst substrate at 400 K and 600 K consists of fcc, hcp and bcc. The difference of this composition affected the arrangement of atoms became not uniform (homogeneous) and thus affected catalyst substrate surface.

3.3. Intermixing phenomenon

In this study, we also observed intermixing phenomenon. **Figure 5** shows intermixing phenomenon on copper film catalyst substrate after deposition process.

Figure 5 shows that Cu (blue colour) and Si atoms (red colour) at the interface. We also can see copper atom had diffusion to

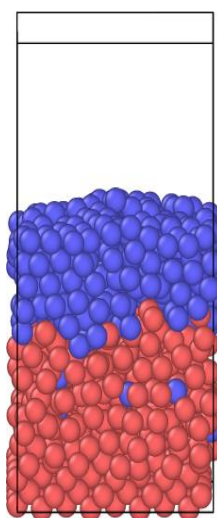


Figure 5. Intermixing phenomenon of Cu and Si atoms.

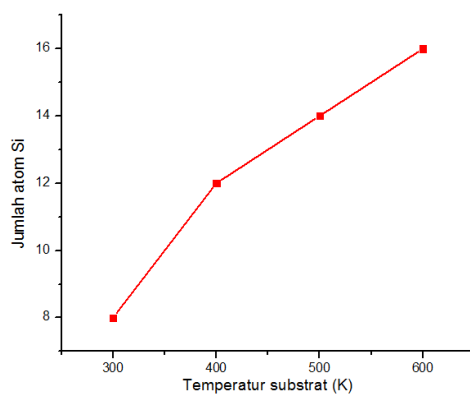


Figure 6. Number of Si atoms had diffusion into deposited copper film versus substrate temperature.

silicon substrate region. This phenomenon was observed by Echigoya. Echigoya reported that the forming amorphous of copper silicide, Cu_3Si and $\text{Cu}_{15}\text{Si}_4$, was caused by the reaction of copper and silicon at interface (Echigoya *et al.*, 1993). The forming of amorphous layer of copper silicide, Cu_3Si and $\text{Cu}_{15}\text{Si}_4$, was expected for application of microelectronic device and ohmic contact.

4. CONCLUSION

Study of molecular dynamics simulations variation of substrate temperature on growth process of copper film on silicon substrate concluded that:

Parameter of substrate temperature affected the composition of crystal structure. The produced of copper film catalyst substrate at 500 K generated the highest percentage of fcc structure.

The compositions of crystal structure affected surface roughness of copper film catalyst substrate.

Our results also indicated that there was silicon atoms had diffusion into deposited copper film. Likewise copper atoms had diffusion to silicon substrate region. **Figure 6** shows the increasing of substrate temperature affected the increasing of the total of Si atoms had diffusion into deposited copper film. This results lead to the forming of copper silicide (Echigoya *et al.*, 1993).

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6. AUTHORS' NOTE

The author(s) declare(s) that there is no conflict of interest regarding the publication of this article. Authors confirmed that the data and the paper are free of plagiarism.

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