Molecular dynamics simulation of platinum film growth based on thermal evaporation method

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Abstract. Platinum film growth using thermal evaporation method was studied using molecular dynamics simulation. This platinum film was intended as catalyst film for graphene growth. Tersoff, Eam and Lennard-Jones potential were used to describe interaction of Si-Si, Pt-Pt and Pt-Si respectively. Deposition process was performed with low incident energy to represent thermal evaporation method. Our simulation found that heating temperature at 400 K produced platinum film with higher percentage of crystal structure than other heating condition 300K, 500K & 600K. We also found transition phase from fcc to bcc at 600K.

Keywords: Platinum, film, evaporation, molecular dynamics

1. Introduction
Platinum thin film had several application, such as resistive sensor and catalyst substrate on graphene growth. Platinum film was chosen because it had relatively low solubility [1]. It is one of important factor to grow graphene. It was reported that the primary growth mechanism of graphene on platinum film were segregation or surface deposition [2,3]. Another factor is crystal structure quality of substrate catalyst. Because it affected quality and grain area of the produced graphene [4]. Therefore, it was concern to control and to get ideal metal catalyst substrate.

There are several method for deposition thin film, such as sputtering method, thermal evaporation method, molecular beam epitaxy, chemical vapor deposition. Among of its method, thermal evaporation method is interesting method because it involved relatively small energy. So, it cannot damage the substrate or film. However, there are some lack of this method, is poor quality film (amorphous structure). One of solution of this problem is give heating temperature on growth process to get better structure [5].

In this paper, we study molecular dynamics simulation of platinum film growth on silicon substrate to know basic mechanism of its process. Effects of heating temperature on platinum film catalyst substrate were investigated. Based on our knowledge, our study has not investigated yet by any researcher, in issue of growth and annealing simulation study corresponding to thermal evaporation method with incident energy 0.35 eV.
2. Simulations Method

Figure 1 shows silicon substrate system with dimension 4a x 4a x 3a (a = 5.43 Å, lattice constant of diamond structure) and consists of 416 atoms. Periodic boundary conditions were applied in the x and y directions.

![Figure 1. Dimension and region division of silicon substrate](image)

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 in constant condition. 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 $\Delta t = 1$ fs. We used Berendsen thermostat to control temperature with a damping parameter of 10 timesteps.

The simulation process was initiated by equilibration stage of silicon substrate at 300 K for 750 ps. Then the simulation was followed by deposition process of platinum atom on silicon substrate. The growth simulation was performed based on thermal evaporation method with incident energy 0.35 eV [6]. The deposition process was performed at 1 atom/3ps [7]. This proceeded until 700 atoms were deposited on the substrate. All of our molecular dynamics simulations were performed with using LAMMPS (Large-scale atomic / molecular massively parallel simulator) [8]. We used OVITO (Open Visualization Tool) to visualize the system from LAMMPS output data. By using Common Neighbour Analysis method [8], we identify the structure of Pt & Si atoms [9]. By using Visual Molecular Dynamics (VMD), we analyzed radial distribution function of platinum catalyst substrate [10].

In this study, we used very simple method for interaction between Si and Pt. Tersoff potential [11], Eam potential [12] and Lennard-Jones potential were applied to describe Si-Si, Pt-Pt and Si-Pt interaction respectively. Interaction between Pt-Si atoms was governed by equation:

$$ E_{ij} = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right] $$

where $E_{ij}$ is potential energy between two atoms, $\varepsilon$ is depth well potential, $\sigma$ is the finite distance at which the inter-particle potential of Lennard Jones is zero and $r_{ij}$ is distance between two atoms. Interaction between Pt-Pt atoms was governed by equation:
\[ E_i = F_\alpha \left( \sum_{j \neq i} \rho_\beta (r_{ij}) \right) + \frac{1}{2} \sum_{j \neq i} \phi_{\alpha \beta} (r_{ij}) \]  

where \( F_\alpha \) is the embedding energy which is a function of atomic electron density, \( \phi \) is a pair potential function, \( \alpha \) and \( \beta \) are element types of atom i & j. The parameters of potential interaction function were given by table 1. Parameter R & D are cutoff parameters. Parameter A, B, \( \lambda_1 \), \( \lambda_2 \), \( \lambda_3 \), \( \alpha \), \( \beta \), n, c, d, h are fitting parameters of Tersoff potential.

| Parameter | \( \varepsilon(eV) \) | \( \sigma(\text{Å}) \) |
|-----------|----------------|----------------|
| Si-Pt     | 0.14523        | 3.1505         |

Table 2. Lennard Jones parameter for Si-Pt interaction

3. Results and discussion

In this simulation, we deposited platinum film on Silicon substrate. Deposited platinum film, namely platinum film catalyst substrate was produced by thermal evaporation method with incident energy 0.35 eV. Figure 2 shows percentage of each crystal structure on variation of substrate temperature.

From figure 2, it was shown that the percentage of crystal structure relatively increased as the increasing of substrate temperature and the percentage of other (unidentified structure) relatively decreased. With the total percentage of crystal structure at 400K, 500K and 600K are 41.5%, 38.9% and 22%. Meanwhile the percentage of other (unidentified structure) at 400K, 500K and 600K are 58.5%, 61.0% and 78.0%. During deposition process, we gave different treatment of heating temperature. The increase of temperature also affected velocity (or kinetic energy) was possessed by Pt atoms. Then Pt atoms can move from their lattice positions. When atoms had enough energy to move from their perfect lattice positions and then diffuse in surface. And it can affect Pt atoms in disorder structure.
We identified Pt atoms in different kind of environment: hcp (hexagonal close packed), bcc (base centred cubic), fcc (face centred cubic) and other (unidentified structure). We found that different heating on substrate affected the difference of dominant structure crystal in platinum film. The dominant structure at 400K, 500K and 600K are fcc, fcc and bcc respectively. As we know that each crystal structure need different energy required for the formation of the structures. It means difference in heating temperature also affected different energy having by each atom. From figure 2, we found Pt tend to form fcc at 400 K & 500 K. Ideally the structure of Pt atoms is fcc, however at 600 K, we found that Pt atoms tend to form bcc. Based on our knowledge, this phenomenon was occurred because energetically favourable structure by Pt atoms at 600 K.

We plot radial distribution function (rdf) graphic to know the effect of temperature on density of the atoms. As we know that the radial distribution function is a measure of the probability of finding atoms from another atom at specific distance. From this graphic, we want identify the structure of system. From figure 3, we can see at short distances, where distance is less than atomic diameter, \( g(r) \) is zero because of strong repulsive forces between Pt atoms. We found that first peak formed at around \( r = 2.65-2.75 \) Å. This first peak corresponded to the nearest neighbour Pt atoms. We observe at first peak that shifting peak was occured as variation of temperature. From 300 K to 500 K, the intensity is relatively increase. It indicated atoms have moved from their lattice positions. However the intensity was drop at 600 K. Ideally, it was occurred because atoms have enough energy (or velocity) to move from their perfect lattice positions and then diffuse in surface. And it can affect Pt atoms in disorder structure. The second peak was formed at around \( r = 3.95 \) Å at 400 K & 500 K. This peak imply lattice constant of Pt atom.However the formed peak were still relatively wide that indicated the structure in short order range. As a validation, this rdf graphic had similarity with Akbarzadeh, et.al [13].

![Figure 4](image-url)

**Figure 4.** Coordination number curve of Pt after deposition process

Figure 4 shows the coordination number after deposition. The coordination number describes the number of neighbor atoms with respect to a central atom. We observed that relatively coordination number at 400 K & 500 K is higher than at 300 K. However at 600K, relatively had lowest coordination number at most interval radius. This is because Pt atoms get more energy with the temperature increase, then diffuse on surface substrate [14]. From figure 4, we observed that coordination number of Pt thin film at 400 K & 500 K is around 14. Theoretically, the coordination number is 12, because the ideal structure is fcc. The reason is Pt film still in different structure: fcp, bcc, hcp & other (unidentified structure). This phenomenon also occurred at 600 K, because Pt film in bcc & other (unidentified) structure.
4. Conclusion
From our study we concluded that:
• Heating treatment on 400 K gave best result with highest percentage of crystal structure among of other heating treatment.
• The analysis crystalline structure of platinum film catalyst substrate with Common Neighbour Analysis (CNA) method indicated that the change of crystalline structure was occured from fcc to bcc at substrate temperature 600K.

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