CVD Graphene Growth Mechanism on Nickel Thin Films

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Abstract: Graphene is one of the most recent carbon nanomaterials that have attracted widespread attention because of its superior properties and enormous potential for various applications. Currently, Chemical vapor deposition is considered a promising method for synthesis of graphene films on different types of substrate utilizing transition metals, such as, Ni. However, synthesizing a single-layer graphene and controlling the quality of the CVD graphene film on Ni are very challenging due to the multiplicity of the CVD growth conditions. Therefore, computer modeling could be supportive in understanding CVD graphene growth mechanism on Ni thin film. COMSOL Multiphysics is used to investigate the CVD graphene growth on Ni films. Factors affecting CVD graphene synthesis include carbon solubility in Ni, growth time, growth temperature, cooling rate, as well as Ni film thickness. Our COMSOL model uses transport of diluted species, heat transfer in Ni thin film as well as deformed geometry. In this particular research, the number of simulated graphene layers on Ni film is compared with experimental data. Also, the effect of many parameters on graphene film fabrication is stated.
Keywords: CVD graphene, CVD graphene growth mechanism on Ni.

1. Introduction

Graphene is a nanomaterial consisting of a one-atom-thick layer of carbon atoms arranged hexagonally as shown on Figure 1 [1]. Recently, graphene has gained a significant consideration due its fascinating and potentially very worthwhile properties [2].The exceptional graphene properties are attainable only in high quality defect-free graphene samples. In addition, graphene film properties depend on the number of graphene layers [3].

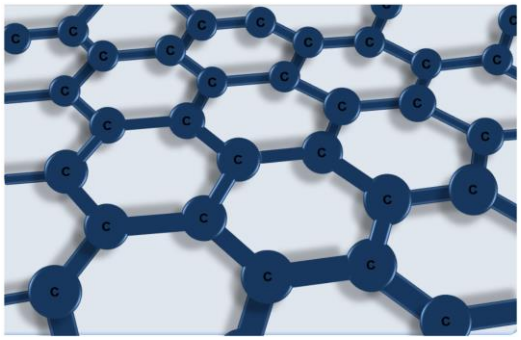


Fig.1: Graphene structure

To date, among graphene synthesis methods, only chemical vapor deposition (CVD) method has shown the capability for growing high-quality graphene film and controlled graphene nucleation over a large area [4]. The quality and continuity of the graphene film could be affected by numerous CVD parameters such as temperature, hydrocarbon (e.g. CH_4) concentration, hydrocarbon pressure, and cooling rate. Also, the graphene growth mechanism is significantly affected by catalyst type, structure, quality, and carbon solubility [5].

In general, two CVD graphene growth mechanisms have been proposed (Figure 2) [6]:

A. Carbon atoms surface segregation: Here it is suggested that decomposed carbon atoms diffuse into the catalyst (e.g. Ni) bulk during the annealing stage at high temperature. Then, carbon atoms precipitate on the catalyst during cooling period.
B. Carbon atoms surface deposition: Here carbon atoms are directly deposited on catalyst (e.g. Cu) surface without segregation resulting in a graphene layer.

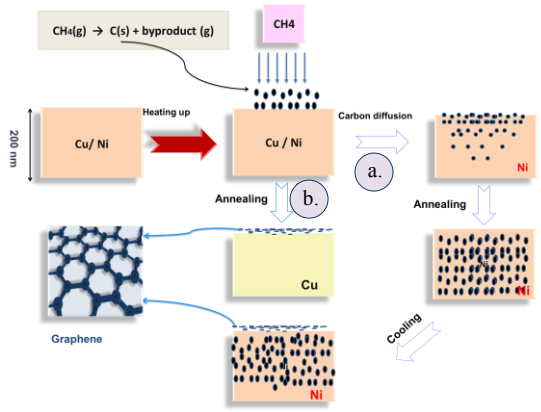


Fig. 2: Graphene growth mechanisms (a) Graphene growth dissolution-precipitation mechanism (b) Graphene growth direct deposition mechanism

Presently, CVD graphene synthesis is widely conducted utilizing transition metal substrates such as Ni and Cu as a catalyst. However, graphene synthesis process is still not fully understood in terms of the growth mechanism and the optimum CVD conditions for graphene growth [6].

In this work, COMSOL Multiphysics was employed to clarify the growth mechanism of CVD graphene on Ni thin film. Also, growing graphene film on Ni thin film at different condition such as CVD growth time, CVD growth temperature, carbon solubility, and Ni film thickness were investigated.

2. Mathematical Model of CVD Graphene Growth on Ni

2.1 Process Descriptions and Problem Formulation

COMSOL Multiphysics software was utilized to model graphene CVD growth on Ni at high temperatures. As illustrated on Figure 3, graphene synthesis is conducted in two essential steps:

A. Carbon diffusivity: carbon atoms are catalytically produced by methane decomposition process that occurs on Ni surface at high temperatures. CH_4 decomposition is generally described by the following chemical reaction [7]:

$$CH_4(g) \rightarrow 2H_2(g) + C(s) \qquad (1)$$

The solubility and diffusivity of the decomposed carbon atoms in Ni in the range 700°C to 1300°C can be described by an empirical relation that was proposed by Lander *et al* [5].
The solubility of carbon atoms (***S***) in Ni is expressed by [5]:

$$S = S_0 \exp(H/kT) \text{ (in atoms.cm}^{-3}) \qquad (2)$$

where, $S_0 = 5.33 \times 10^{22}$ atoms cm^{-3}, an entropic pre-factor associated with the density of the locations where solute atoms be seated; $H = -0.42$ eV; the heat of precipitation; and k is the Boltzmann's constant $= 8.617\,3324 \times 10^{-5}$ eV K^{-1}.

The diffusion coefficient of carbon atoms (***D***) in Ni is given by [5]:

$$D = D_0 \exp(-E_D/kT) \text{ (in cm}^2\text{.s}^{-1}) \qquad (3)$$

where, $D_0 = 2.48$ cm^2 s^{-1}, an entropic pre-factor; E_D, the diffusion activation energy $= 1.74$ eV; and ***k is the*** Boltzmann's constant.

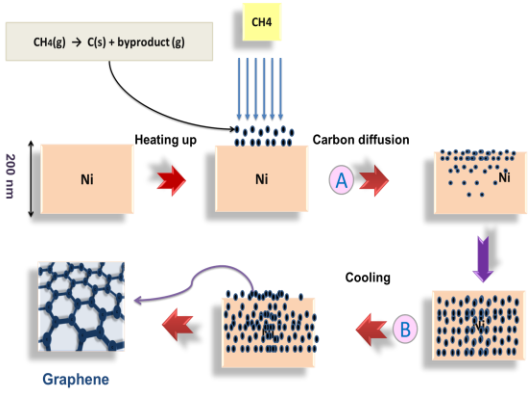


Fig. 3: Graphene CVD growth on nickel film

B. Carbon precipitation: during the cooling period, carbon atoms precipitation on Ni surface occurs due to supersaturation of the diluted carbon in Ni.

2.2 Model definition

i. Assumptions:

To simplify CVD graphene synthesis model, we made the following assumptions:

a. Carbon atoms diffusion via grain boundaries is negligible.
b. There is no diffusion thru the bottom side of the nickel film.
c. Carbon atoms are uniformly distributed in the Ni film during the annealing stage.
d. Precipitated carbon atoms are homogeneously segregated and distributed on the Ni film surface during cooling period.
e. There is no direct deposition on Ni surface for carbon atoms in dissolution process.
f. No carbides in the Ni film are formed.

ii. Geometry

The geometry of the CVD graphene synthesis model created in COMSOL is illustrated in Figure 4.

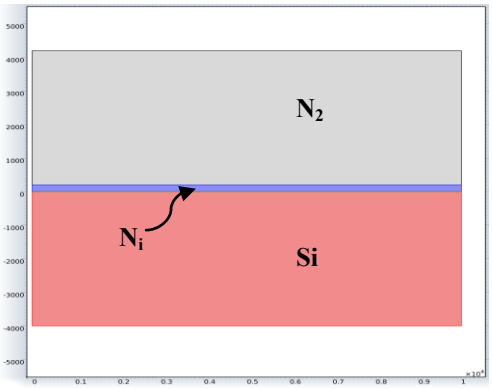


Fig. 4: Model schematic of graphene growth using Ni thin film.

iii. Governing equations

Mass Diffusion

During Carbon dissolution and precipitation stage, mass is transferred mainly by diffusion from the surface of the Ni film into its bulk. Hence, Using conservation of mass, the governing equation for carbon atoms transport is mathematically described by Eq. (4)

$$\frac{\partial c}{\partial t} = \nabla.\ (D\ \nabla c) \qquad (4)$$

Where **c** is the carbon atoms concentration and **D** is the carbon diffusion coefficient defined by Eq. (3).

In dissolution period, the initial condition sets the concentration of carbon atoms in Ni film at t=0:

$$\mathbf{c} = 0$$

After dissolution phase, but during the precipitation phase, the concentration of carbon atoms in Ni film at t=0 is set to be equal to the carbon solubility at the initial temperature of the Ni film:

$$\mathbf{c} = \mathbf{S}\ (\mathbf{T_{Ni}})$$

where $\mathbf{T_{Ni}}$: the initial temperature of the bulk of the Ni film

Mass Diffusion Boundary Condition

The mass boundary conditions for this model are:

- $\mathbf{c = S\ (T_{surf})}$ at $\partial\Omega_{\text{ Ni top surface}}$
- No flux: $\mathbf{-n.N_i=0}$ at $\partial\Omega_{\text{ Ni bottom surface}}$
- Symmetry: $\mathbf{-n.N_i=0}$ at $\partial\Omega_{\text{ other}}$

where $\mathbf{T_{surf}}$ is the initial temperature of the surface of the Ni film.

Heat Diffusion

During the precipitation phase, the heat is transferred within the Ni film by conduction. So, the mathematical model for heat transfer in Ni film is expressed by Eq. 5.

$$\rho C_p \frac{\partial T}{\partial t} = \nabla.\ (k \nabla T) \qquad (5)$$

Heat Diffusion Boundary Condition

The heat boundary conditions are:

- Temperature: $\mathbf{T=T_{surf}}$ at $\partial\Omega_{\text{ Ni top surface}}$
- Insulation: $\mathbf{-n.(-k\nabla T) = 0}$ at $\partial\Omega_{\text{ Ni bottom}}$
- Symmetry: $\mathbf{-n.N_i=0}$ at $\partial\Omega_{\text{ other}}$

3. Result and Discussion

3.1 Carbon atoms inward diffusion in Ni film

Carbon diffusion inside Ni film is investigated in this research. To clarify, CH_4 decomposes on the top surface of 200 nm Ni thick and releases carbon atoms at 1000°C. Then, the adsorbed carbon atoms diffuse into the Ni

film at the same temperature. Carbon atoms diffusion field at 0.05 sec is shown on figure 5.

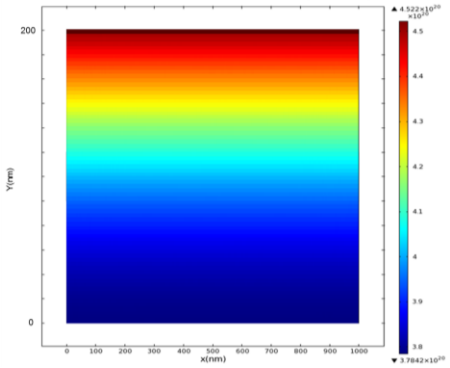


Fig. 5: Calculated carbon atoms diffusion field inside 200 nm thick nickel film using COMSOL.

The carbon diffusion as a function of time is illustrated in figure 6. It is obvious that the carbon atoms concentration in Ni film reaches its saturated state in less than 0.1 second.

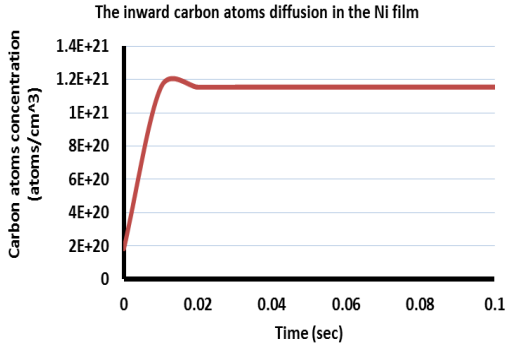


Fig. 6: The inward carbon atoms diffusion in the Ni film

The influence of temperature on carbon diffusion within Ni film is investigated and the results are depicted in figure 7. It is noticeable that higher temperature results in a faster diffusion of carbon atoms.

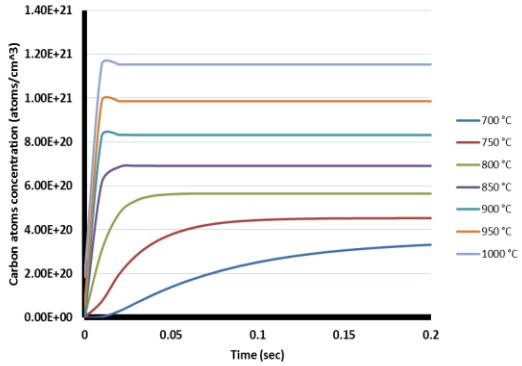


Fig. 7: The influence of temperature on carbon atoms diffusion inside the Ni film.

From the figure 8 it can be seen that as the thickness of the Ni film becomes thicker, more time is required to reach to the saturated state of carbon atoms.

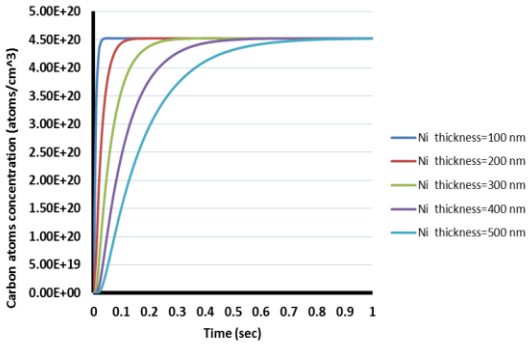
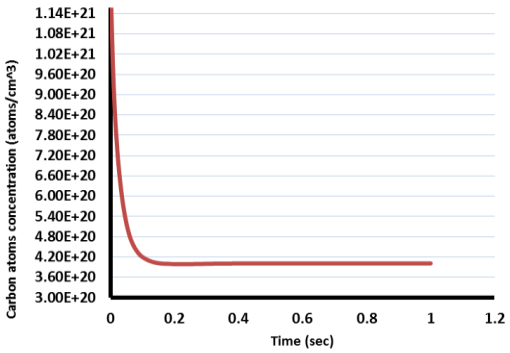


Fig. 8: The influence of the Ni film thickness upon carbon atoms saturation.

3.2 Carbon atoms outward diffusion in Ni film

Supersaturation by cooling leads to segregation of carbon atoms on the Ni film surface. To explain, Ni film at 1000 °C is cooled down to 725 °C to promote the formation of graphene film. It can be observed from figure 9 that the concentration of carbon atoms in the Ni film falls from 1.0 $x10^{21}$ (atoms/cm^{-3}) initially to 4.0 $x10^{20}$ (atoms/cm^{-3}) in less than 0.2 sec due to removal of carbon atoms from the Ni film under the influence of the supersaturation.



4 Fig. 9: The outward carbon atoms diffusion driven by Supersaturation in the Ni film

In this model, in order to simulate the obtained graphene layers, a deforming mesh coupled with diffusion transport model are used. To clarify, the precipitated carbon atoms cause a movement in +y-direction to the interface between Ni film domain and N_2 domain. So, the mass flux in y-direction at the interface divided by the density of carbon atoms being precipitated gives the rate at which the interface is moving. Hence, the velocity of the interface can be mathematically expressed by equation 6.

$$v_y = \frac{\vec{j}_m \cdot \hat{n}_y}{\rho_{carbon}} \qquad (6)$$

where

v_y : The interface velocity

$\vec{j}_m \cdot \hat{n}_y$: The mass flux in y-direction

ρ_{carbon} : The density of graphene; 2.267 g/cm^3

Hence, the thickness (d) of the segregated carbon material can be calculated by equation 7.

$$d = v_y * t \qquad (7)$$

where ***t:*** time

The resulted final graphene thickness obtained in less than 0.2 sec is 7 Å as shown on figure 10.

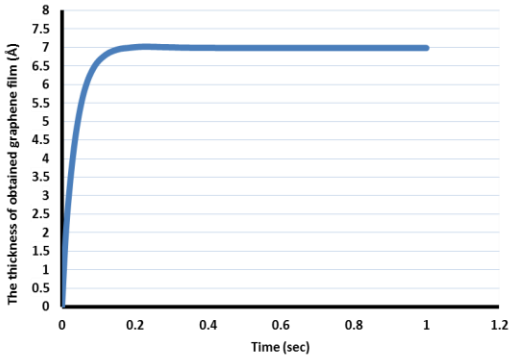


Fig. 10: The thickness of the obtained graphene film on Ni film surface

The number of achieved graphene layer (**N**) can be calculated by utilizing equation 8.

$$N = \frac{d}{\Delta d} \qquad (8)$$

where **Δd** is single layer graphene thick (**Δd**=0.335 nm) [8]. As shown on figure 11, the achieved number of graphene layers when the Ni film is cooled from 900°C to 725°C equals **1.7** layers. It is obvious from figure 11 that 1.7 layers gotten within 0.4 sec.

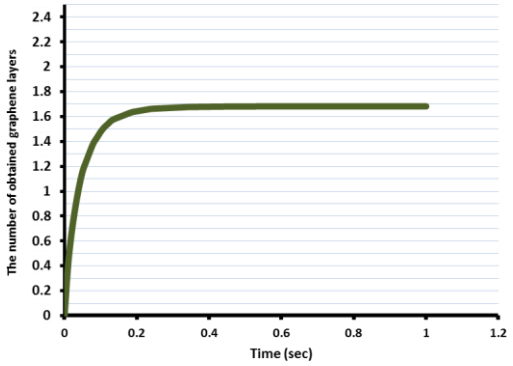


Fig. 11: The number of the obtained graphene layers on Ni film surface after cooling from 900 °C to 725 °C.

Further investigation was conducted in this research to explain the effect of cooling on the obtained graphene layers on the Nickel surface. To explain, Cooling 200 nm thick nickel film from 1000°C to different temperature as show on figure 12. It was simulated in order to determine the number of graphene film formed on the Ni film surface by precipitation mechanism. For

instance, the number of precipitated graphene layer when the 200 nm thick Ni film cool from 1000°C to 725°C equals ~2 layers.

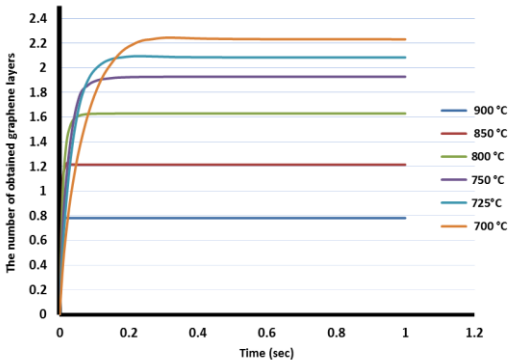


Fig. 12: The number of the obtained graphene layers on Ni film surface after cooling from 1000 °C to different temperature

4. Accuracy Check

As part of this work, the model accuracy was determined by comparing the simulated results with experimental data. To simplify, Baraton et al. had conducted an experiment typical to the one that we have modeled. In their experiment, ion implantation of carbon ions was utilized in graphene growing on 200 nm thick Ni film [9]. Then, the Ni film was annealed at 900°C for more than 30 min in order to ensure that carbon atoms are being uniformly distributed inside the Ni film. After that, the Ni film temperature was decreased to 725°C. Next, Ni film was rapidly quenched to trap the residual carbon within the Ni film. Hence, the rapid quenching process inhibits carbon diffusion to Ni film surface. As a result, two to four layers of graphene were characterized on the Ni film. According to Baraton et al, 2 layers of graphene should only be achieved on the Ni film for a uniform precipitation of carbon atoms. Hence, the experimental work of Baraton et al., in terms of the number of graphene layers, is similar to the obtained value (**1.7** layers) in our simulation utilizing COMSOL MULTI PHYSICS software.

5. Conclusions

In this paper, CVD graphene growth on nickel thin films by dissolution- precipitation mechanism has modeled using COMSOL MULTIPHYSICS. Heat transfer, mass transfer, and deformed geometry models were employed to simulate inward and outward carbon atoms diffusion in the Ni film as well as the number of achieved graphene layers. Cooling 200nm thick Ni film saturated with carbon atoms from 900 °C to 725 °C leads to precipitate 1.7 graphene layers on the Ni film surface. The obtained number of graphene layers was compared with a real experimental data. We have found that COMSOL results are reasonable.

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