

Simulations of chemical vapor deposition - diamond film growth using a kinetic Monte Carlo model

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**Computational Physics
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Introduction

Thin film deposition is a major experimental technique that is widely used in Condensed matter physics for the study of material characteristics and interactions and provides us with the basic understanding in material sciences. While innovation continues by the hand of theorists and experimentalists alike, computational physics has emerged as a complement to help generate realistic solutions to complex problems.

Computational physics has long served in the field of molecular modeling. The complex nature of inter- and intra-molecular interaction as well as the formation of the material from an atomic scale and the physics associated with it have been suitably simulated to give proper solutions. For this report, we shall see the thin film growth of diamond on a diamond (100) surface with the help of kinetic Monte-Carlo method.

Computational aspect

The Monte-Carlo method

The Monte-Carlo(MC) method is an experimental technique that uses randomness in a given system to approximate required quantities without the need for an explicit analytical solution. The main implication of this method is that a point in a freely moving system will visit every point in the space that the system moves in, in an uniform and random sense.

It uses the probability distributions for any variable in the system. Working with a specified number of trials, random values are worked out in the domain of the problem eventually resulting in a set of distinct outcomes with the probability of each outcome. The generic algorithm of the method can be summarised in the following steps :-

1. Identification of all the dependent and independent variables in the system and the defining of their domains
2. Determination of a probability distribution to randomly generate values in the specified domain.
3. Computation of the output for the problem based on the random value.
4. Repetition of the above steps for N no. of times and aggregation of results. (The larger the value of N, the more likelihood of the outcomes to converge.)

Kinetic Monte-Carlo method

The kinetic Monte-Carlo(kMC) simulation method is a branch-off of the Monte-Carlo process that allows us to study the time evolution of the problem under consideration. It relies on user-defined rates of changes in between the transition states of the

problem. The process itself can not predict the rates of such changes. The algorithm of the process is as shown below :-

1. Initialise simulation time $t = 0$.
2. For all the individual processes in the system, form a list of the rates(r_i) of those processes.
3. Compute the rate sum(R)

$$R = \sum_{i=1}^N r_i \quad (1)$$

4. Generate a random number $\rho \in [0, 1)$.
5. Find the event to carry out i by finding i such that ρ lies in the normalised range of rates.

$$\frac{R_{i-1}}{R} < \rho \leq \frac{R_i}{R} \quad (2)$$

6. Carry out the event “i”.
7. Recalculate all the rates that have changed due to the event “i”.
8. Generate a new random number $\rho_2 \in [0, 1)$.
9. Update the simulation time to $t + \Delta t$ where

$$\Delta t = -\frac{\ln(\rho_2)}{R}; \quad (3)$$

10. Repeat from step 2 for the fixed number of iterations.

For our simulation, we rely on this kMC method to predict the deposition of diamond thin film. We construct a model of a diamond surface and a set of relevant processes and mechanisms are constructed. Deposition occurs by random bombardment of C species(here CH_3) on the surface with pre-fixed impact rate. Some of these might get adsorbed into the surface depending on the probability distribution of the rates that have been determined by experiments. The adsorbed sites may then partake in several processes(that will be discussed further) with each individual rates.

Here we take into consideration a simplistic one-dimensional model(*May et. al.*). While standard kMC models have been put to use for a while, the limitation of these models lies in the computational expense required. A detailed three-dimensional model of the surface on an atomic scale requires rates for several kinetic parameters that are not known with any precision at all. Moreover, these kMC models face an intrinsic problem for diamond, as the gas phase particles mostly bounce off the inert H-terminated surface. As such, a lot of computational time is wasted on non-events

that have no contribution of growth. The used 1D model uses an interplay between processes like adsorption, desorption, surface migration and addition to lattice with well known rates to provide a quality solution.

The Physical aspect

For the simulation we consider CVD growth on an diamond substrate with crystallographic orientation of (100). The reaction chamber gas mixture is taken to be a mixture of hydrogen(H_2) and methane(CH_4). The key physical processes that have been taken into account are :-

1. CH_3 adsorption

The adsorption of CH_3 radical into the radical site depends on the concentration of the gaseous radical at the surface of diamond. The rate for this is given by

$$R(site^{-1}s^{-1}) = \frac{P \times [CH_3]_s \times 3757 \times \sqrt{T_{ns}}}{4 \times 1.56 \times 10^{15}} \quad (4)$$

where P is the probability of adsorption. It has been taken as 0.1 in the used model.

2. CH_2 activation and Deactivation

These concern the activation and deactivation of surface radical sites due to H abstraction and vice versa.

$$Activation\ Rate = (k_1[H]_s + k_{-2})U \quad (5)$$

$$Deactivation\ Rate = (k_2[H]_s + k_{-1}[H_2])A \quad (6)$$

where U and A are the number of unactivated and activated sites respectively. The rate constants associated with the gas concentrations used above are given by the following expressions.

$$k_1 = 3.2 \times 10^{-12} T_s^{0.5} \exp(-3430/T_s)$$

$$k_{-1} = 3.2 \times 10^{-13} T_s^{0.5} \exp(-7850/T_s)$$

$$k_2 = 9.6 \times 10^{-13} T_s^{0.5}$$

$$k_{-2} \sim 0$$

Figure 1: The rate constants used in above equations(values taken from <https://aip.scitation.org/doi/10.1063/1.3437647>)

3. Surface Migration

An activated CH_2 bridge group can move along or across a dimer row provided a suitable neighbouring radical site is present. The rate of this migration is given by

$$Migration\ Rate = 1 - (1 - R)^4 \times 6.13 \times 10^{13} \times e^{\frac{-128400}{RT_s}} \times M \quad (7)$$

where R is the fraction of surface radical sites and is given by

$$R = \frac{1}{1 + 0.3e^{\frac{3430}{T_s}} + 0.1e^{\frac{4420}{T_s}} \frac{[H_2]}{[H]}_s}$$

T_s and M represent the substrate temperature and the number of sites capable of migration respectively.

4. β -scission

This refers to the release of free C_2H_4 radical from the diamond surface. This occurs when there is an activated 2-block column on the substrate surface. The rate is given by

$$\beta - scission\ rate = \frac{k_B T_s}{h} e^{\frac{-1.8 \times 10^5}{RT_s}} B \quad (8)$$

where B is the number of activated 2-block columns.

The KMC Model

We use pre-existing parameters for substrate temperature(T_s), near-substrate gas temperature(T_{ns}) and concentration of gaseous phases($[H_2]$, $[H]_s$, $[CH_3]_s$).

T_s/K	T_{ns}/K	$[H]_s/(10^{14}\text{ cm}^{-3})$	$[H_2]/(10^{17}\text{ cm}^{-3})$	$[CH_3]/(10^{13}\text{ cm}^{-3})$
573	781	18.0	3.37	2.03
673	857	9.34	2.87	2.50
773	935	5.48	2.50	2.55
973	1094	2.63	1.99	2.00
1173	1266	1.84	1.65	1.44
1373	1442	1.63	1.41	1.13

Figure 2: The parameters(adapted from <https://aip.scitation.org/doi/10.1063/1.3437647>)

0	Hydrogenated unactivated surface layer
1	Dehydrogenated activated surface radical site(dangling bond)
2	Hydrogenated(unactivated) adsorbed CH_2/CH_3 unit
3	Dehydrogenated activated adsorbed CH_2 unit

We construct a 1000×600 working grid. Each block at the surface is assigned a number according to the state it is in as per the given table The model follows the following steps

1. *Surface site activation* - Block “0” changes to “1” following eq(5). U is the number of “0” blocks.
2. *Surface site Deactivation* - Block “1” changes to “0” following eq(6). A is the number of “1” blocks.
3. *Adsorption of CH_3* - A “2” block randomly strikes the surface above a “1” or “3” block. Rate is given by eq(4). Hereafter, it can follow different pathways that are enlisted in the following items.
4. *Activation of adsorbed groups* - Block “2” changes to “3” following eq(5). U is the number of “2” blocks.
5. *Deactivation of adsorbed groups* - Block “3” changes to “2” following eq(6). A is the number of “3” blocks.
6. *Migration* - A “3” block can move left or right depending on the presence of a neighbourhood “1” block. Rate is given by eq(7). M is the number of “3” blocks that can jump.
7. *Addition to lattice* - If an adsorbing block lands next to a step-edge it can directly fuse with the lattice to give a “0” block(**Eley-Rideal process**). Alternatively, if a migrating block lands next to a step edge, it too fuses with the lattice(**Langmuir-Hinshelwood process**). However, for diamond we consider only migration of a “3” block off the top of a side-edge onto a “1” block in the bottom corner as parameter for fusion with lattice.
8. *β -scission* - If a “3” block lies on a 2-column block(activated), it simply breaks off back to the gaseous phase as C_2H_4 .

Results

The simulation results using the given parameters results in the following films.

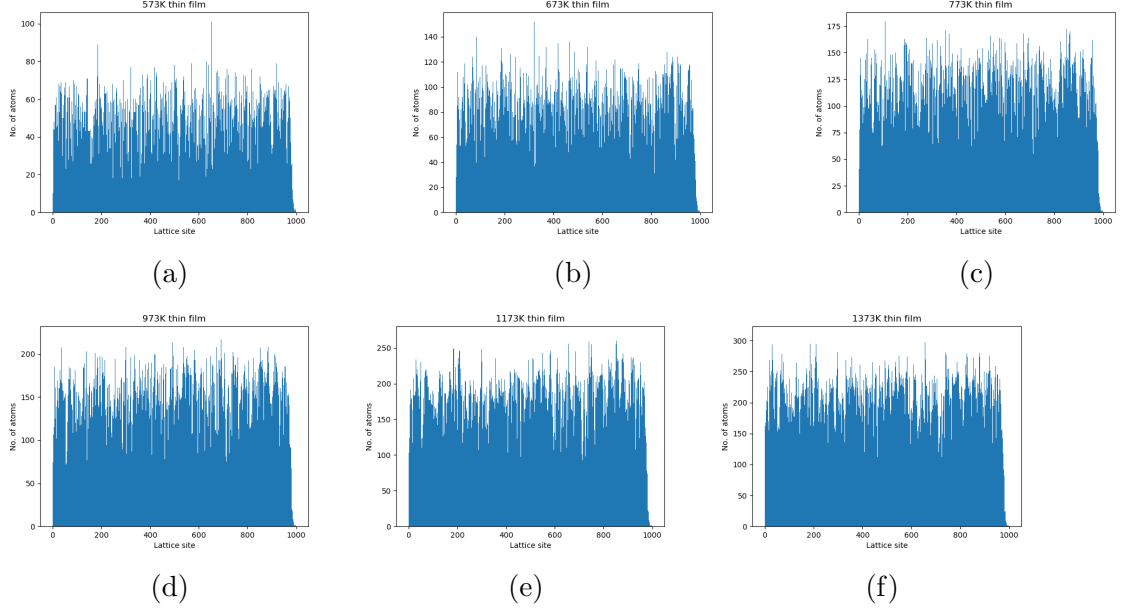


Figure 3: Thickness plot for (a) 573K, (b)673K, (c)773K, (d)973K, (e)1173K, (f)1373K

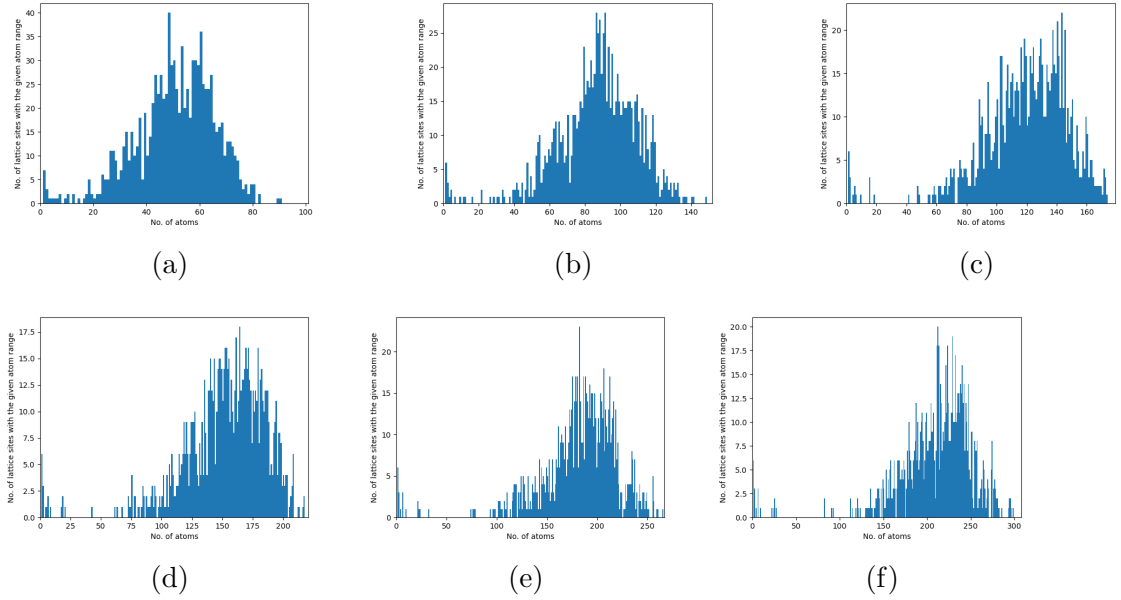


Figure 4: Frequency plot for thickness distribution for (a) 573K, (b)673K, (c)773K, (d)973K, (e)1173K, (f)1373K

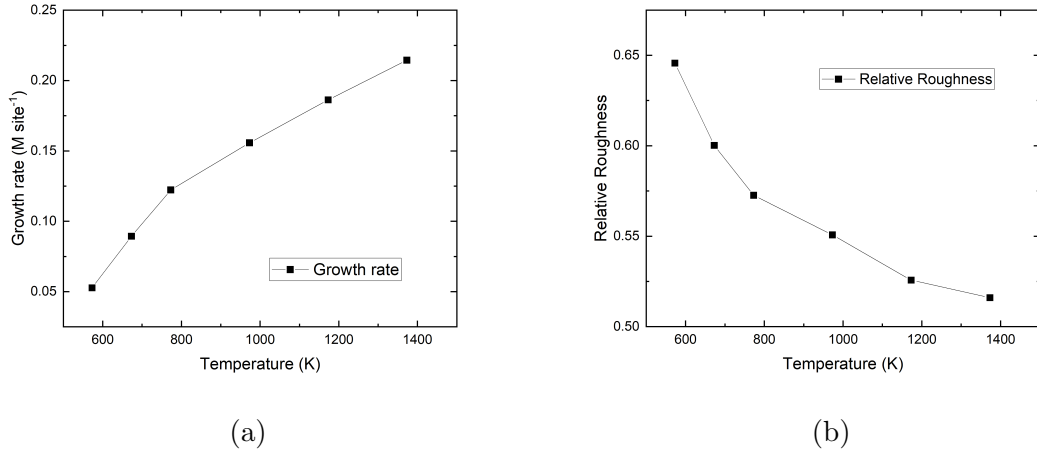


Figure 5: (a)Growth rate vs Substrate Temperature plot (b) Relative roughness of film vs substrate temperature

Results and Conclusion

1. The growth rate is seen to rise with rise in substrate temperature, This can be attributed to the fact that with rise in temperature, the surface radical sites becomes less onert which results in more adsorption of CH_3 and hence more deposition.
2. The relative roughness seems to decrease with increase in temperature. This can be explained by considering the increase in migration rates with increase in surface temperature. This leads to greater LH-contribution to the deposition of the film.
3. The frequency plot of the number of sites with a specific number of deposition events show a rightward shift(towards higher value) with rise in temperature.
4. Overall, the model seems to fall in line with the experimental expectations.

References

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