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Kinetic Monte Carlo simulation of Ta deposition on Ta (100) surface

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A resistive heater is a main component in the thermal inkjet print head that controls the ejection of the ink droplet [1, 2]. Fast heat transfer from the resistive heater vaporizes the ink, and pressure of the vapor bubble ejects the ink droplet. Since the size and the velocity of the ink droplet as well as the existence of the satellite droplet determine the print quality of the inkjet printer, it is important to control how the bubble is ejected. The bubble ejection mechanism is determined by many factors, including nozzle design, heat flux transient, and bubble nucleation [1, 3, 4]. Asai *et al.* showed that the bubble nucleation is highly affected by the surface roughness of the resistive heater, and showed film bubble created from the smooth film is advantageous to the print head operation [5].

The outermost layer of resistive heater in contact with ink is a Ta thin film deposited by physical vapor deposition process. Ta is particularly useful due to its desirable properties, such as good corrosion resistance and high melting point [6]. Since surface roughness of Ta layer is determined by various process conditions, such as processing pressure, flow rate of Ar, and chamber geometry, the optimization of the surface roughness is performed by trial-and-error experiments in practice. Therefore, in order to reduce the design cycle, it is useful to develop a quantitative simulation tool that can relate the process parameters to the surface roughness of Ta thin film.

One possible simulation technique to model Ta surface roughness would be the molecular dynamics (MD) technique. However, as has been pointed out [7–9], the MD technique can only model deposition processes with unrealistically high deposition rates (10^{10} ML/s, where ML stands for monolayer). This is the consequence of vastly different time scales between molecular vibrations (1fs-1ps) and real deposition processes (1–100 s).

The only feasible simulation technique that can be applied to model the surface evolution with atomistic detail over such a long time scale is the kinetic Monte Carlo (KMC) method [10–12]. In KMC, the transition probabilities and the actual time evolution of a system are formulated as a function of real reaction rates including adsorption, desorption, diffusion and incorporation rates. KMC has been used to model various deposition processes including metal deposition [13] and compound semiconductor deposition [14, 15]. To the best of our knowledge KMC simulation of Ta thin film deposition has not yet been attempted. In this work, a KMC code is developed to predict and characterize Ta thin film deposition processes.

In the implementation of KMC, a table of all possible moves needs to be generated at each time step [14]. The rates in the deposition of PVD include adsorption, desorption and surface diffusion. Adsorption dictates how many atoms deposit on different locations on the wafer and is determined by the conditions in the reactor chamber. Since predicting adsorption with different reactor chamber conditions is beyond the scope of this paper the flux value is used as an input parameter. The binding energy of Ta adatom on the surface is around 6.5 eV. This is too large for thermal fluctuations to overcome this barrier under realistic operating conditions. Therefore, the desorption event is ignored in the simulation. The atomistic event that requires particular attention is the diffusion of Ta on the surface.

The diffusion rates are expressed as transition state theory [16]. Using an universal prefactor, 10^{13} s^{-1}, the diffusion frequency is formulated as follows.

$$\nu = 10^{13} \exp(-E_d/k_B T)\,\mathrm{sec}^{-1} \qquad (1)$$

where E_d is the diffusion barrier, k_B Boltzman constant and T the surface temperature. In this work, the diffusion barrier E_d is calculated using a semi-empirical potential, the embedded atom method (EAM). EAM has been widely used to describe metallic systems [17, 18]. In this work, out of the many EAM potentials developed for Ta [19–22] we have chosen EAM potential developed by Doyama and Kogure because of its simple form and high accuracy in reproducing various physical properties of Ta. For the calculation, five layers of a Ta (100) surface were constructed. In the course of simulation, the bottom two layers were fixed and the top three layers and the z-coordinate of the adatom was relaxed as the x-y coordinates of the adatom were changed within a rectangular mesh of 41 by 41. The minimized total energy was used to construct the potential energy surface. The obtained potential energy surface of Ta adatom on Ta (100) surface is shown in Fig. 1. The location of the transition state is evident from Fig. 1, and the diffusion barrier is obtained from the reaction pathway as shown in Fig. 2. The diffusion barrier is estimated to be 2 eV. The diffusion barrier is

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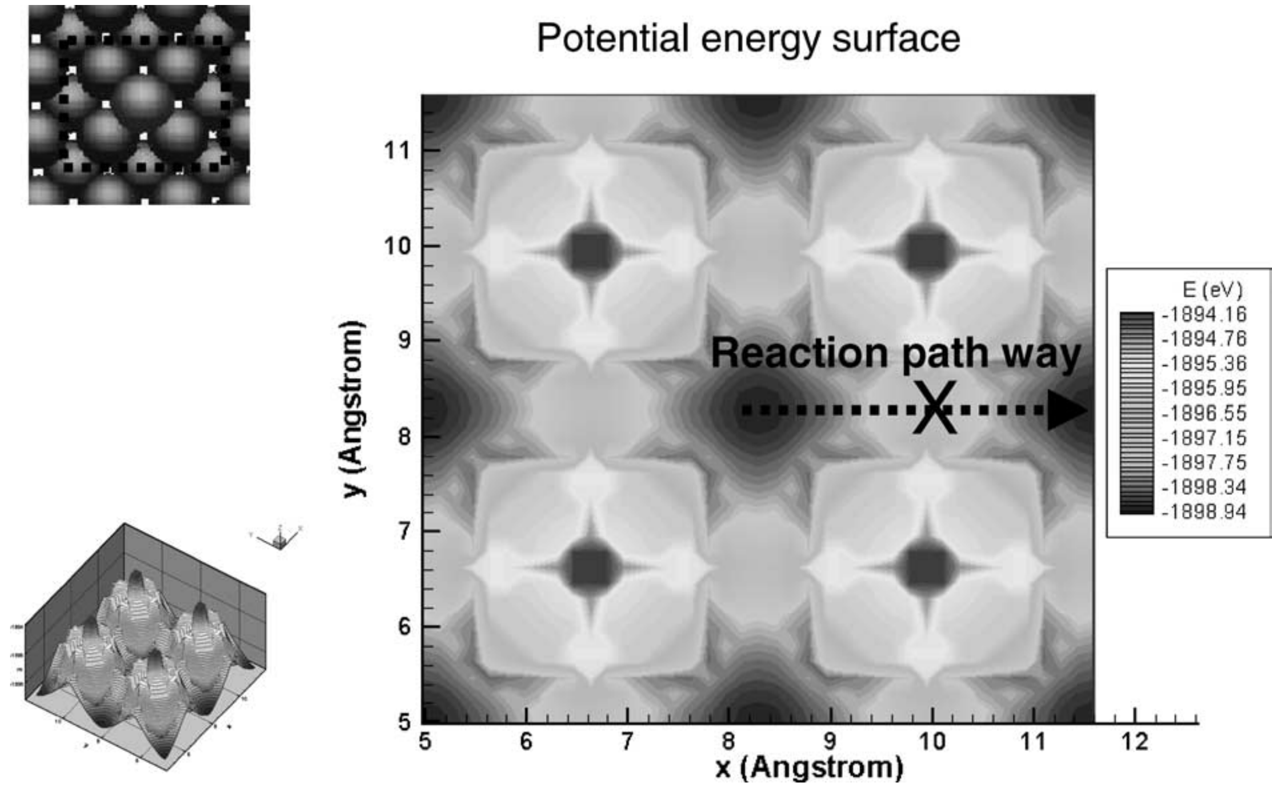

Figure 1 Potential energy surface of Ta adatom on Ta (100) surface.

affected by the number of the nearest neighbors. Including only the first nearest neighbor, the diffusion barriers are summarized in Table I.

Table of all possible reactions, including adsorption, desorption, and diffusion, is set up in every time step, and a random number is generate to select the move. Then, the time evolution is described using the following equation [10].

$$\tau = -\frac{1}{\sum_i n_\mathrm{i} r_\mathrm{i}} \ln(U), \tag{2}$$

where U is a random number on uniformly distributed between 0 and 1, and n_i is the number of species capable of undergoing a transition with a rate r_i. Once a particular move is selected, the surface configuration is modified accordingly and the table of possible moves is updated to account for the new configuration. This procedure is repeated until a desired time is elapsed. The flowchart of the simulation is depicted in Fig. 3.

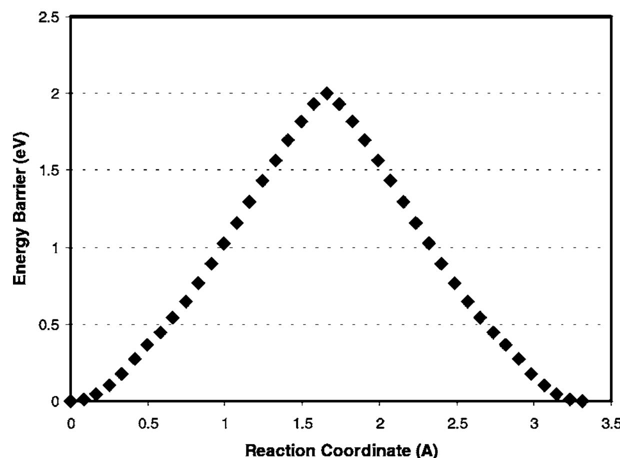

Figure 2 Potential energy surface of Ta adatom on Ta (100) surface along [100] direction.

Using the KMC code, a representative Ta film growth is modeled. The simulation condition is as follows:

- Flux: 0.2 μm/h
- Substrate temperature: 1000 K
- Computational domain size: 20 nm $\times$ 20 nm

Surface roughness, defined as a standard deviation of film thickness in different locations, is shown in Fig. 4. The surface roughness oscillates in the early stages; indicating that the surface grows in the layer-by-layer fashion, where the surface roughness increases as the density of adatoms increases, and the surface roughness decreases as the adatoms are incorporated into the layer of the film. As the film grows further, the oscillation disappears and the roughness increases progressively. Fig. 5 shows the surface morphologies after the deposition of 20, 40 and 60 layers of monolayers, indicating

TABLE I Diffusion barriers for different number of nearest neighbors

Number of nearest neighbors	Energy barrier (eV)
0	2.00
1	2.57
1	2.35
2	2.80
2	3.12
3	3.27

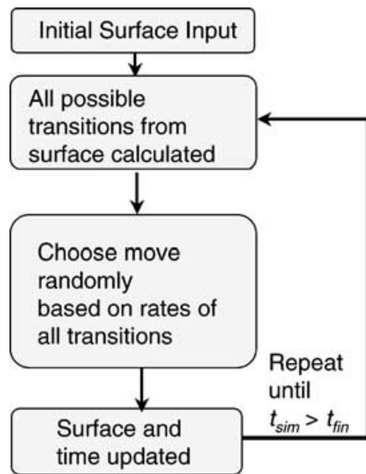

Figure 3 Algorithm of KMC for the simulation of film growth.

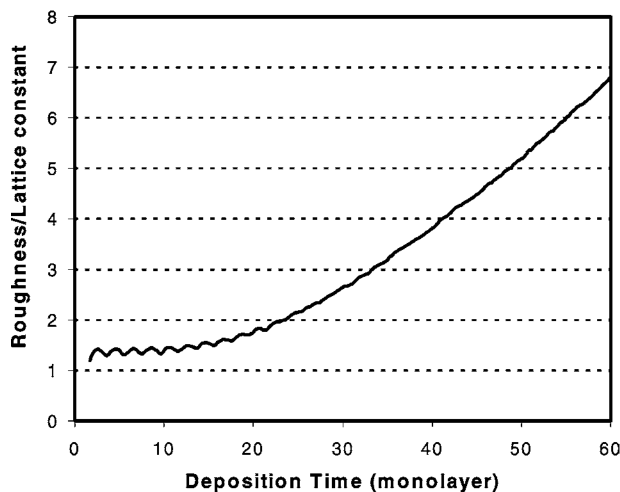

Figure 4 Time evolution of surface roughness.

again that the film is very smooth in the early stages (after 20 monolayers), and is getting rougher as the film grows (after 40 and 60 monolayers).

The effect of two input parameters, flux and substrate temperature on the surface roughness, is examined. The surface morphology after depositing 15 monolayers at different flux values, 0.2, 2.0 and 20.0 μm/h is shown in Fig. 6. With the smallest flux, 0.2 μm/h, the film is smooth except for islands with one monolayer thickness. As the deposition rate increases, the surface becomes significantly rougher. This can be understood in the following way. The surface roughness is determined by the competition between surface diffusion and adsorption. If the diffusion is faster than the adsorption, the adatoms have a higher chance of finding stable sites such as at the kinks and terraces. On the other hand, if the diffusion is slow compared to the adsorption, the adatoms have higher chance of encountering other adatoms and of forming immobile islands before they find stable sites, which increases the chance of roughening the film. The same trend is observed from the surface morphology change with different substrate temperatures, 300, 600 and 900 K shown in Fig. 7. In this case, as substrate temperature increases, the surface becomes smoother, because a high substrate temperature increases the mobility of the adatoms.

Aforementioned case studies showed that one needs to use highest substrate temperature and lowest flux rates that the PVD equipment can handle, in case that depositing smooth film is the goal of the process engineers. However, applying this result directly to real operation will be problematic; in actual operation, low substrate temperature is often desirable not to interfere already deposited other films underneath the Ta layer, and high flux is desirable to increase production rates. Furthermore, in the particular application of Ta film to resistive heater in inkjet printhead, the smoothest film might not be the best choice, because some degree of roughness will increase the bubble nucleation rates by enhancing microscopic heat transfer from the film to the ink. Thus, one needs to determine the desired surface roughness after considering all the constraints.

Once desired surface roughness is selected, corresponding substrate temperature and flux can be obtained using the simulation tool presented in this paper. In order to apply these results to the actual process operation, the simulation parameters, in particular the flux, need to be directly related to the process variables, such as chamber geometry and operating condition. Commercial process simulators can be used for this purpose [23]. In the cases where a commercial tool is not readily applicable, one could use the experimental data and interpolate operating conditions that result in the optimum flux. However, since a large number of experimental data is required to account for wide operating condition and possible nonlinearity of the process, and

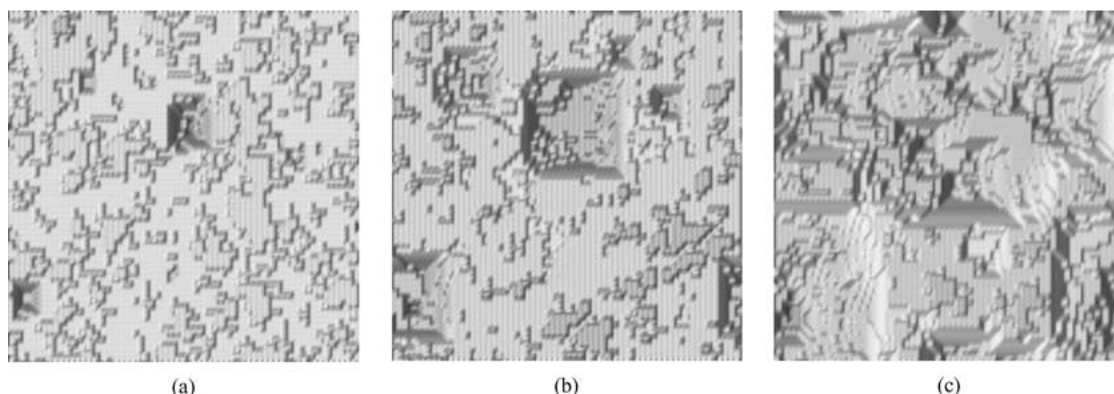

Figure 5 Surface morphology at different time after depositing: (a) 20 ML, (b) 60 ML, and (c) 140 ML.

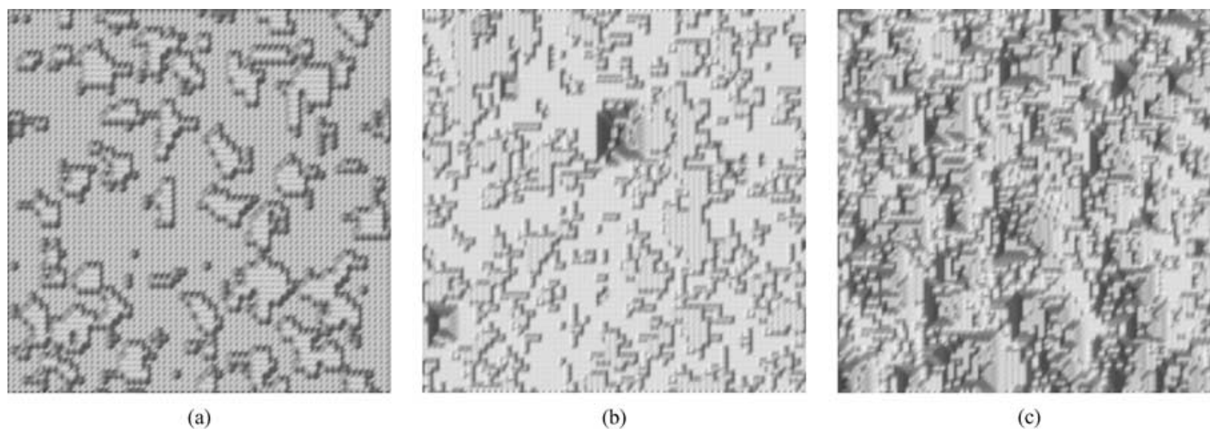

Figure 6 Surface morphology with different flux values: (a) 0.2 μm/h, (b) 2 μm/h, and (c) 20 μm/h.

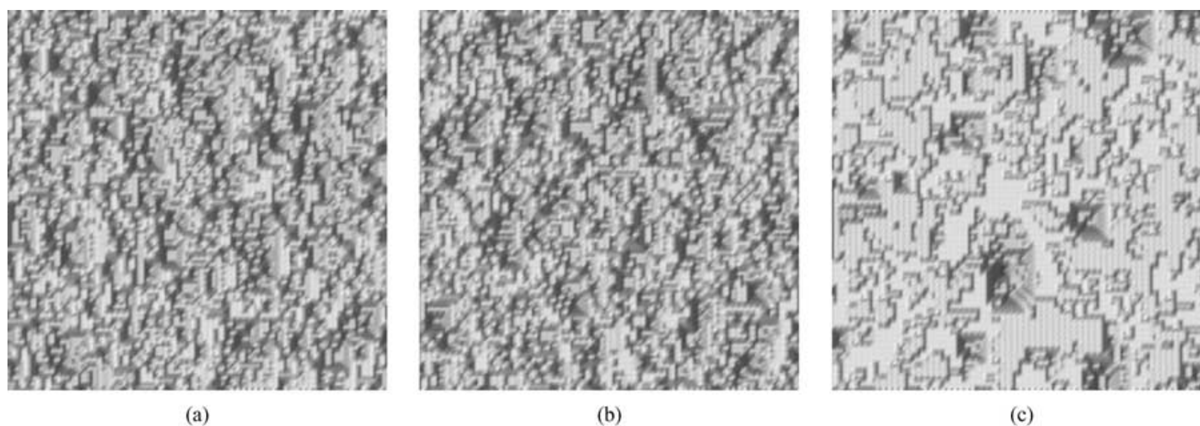

Figure 7 Surface morphology with different substrate temperature: (a) 300 K, (b) 600 K, and (c) 900 K.

such a database is restricted to the specific equipment, it would be still advantageous to use process simulators to increase predictive power.

Surface roughness considered in this paper is governed solely by the competition between deposition and surface diffusion. Surface roughness resulting from other causes, such as polycrystalline structure and inherent stress requires further study.

In this work, a simulation tool based on the kinetic Monte Carlo method was developed to model the surface roughness of Ta deposition on Ta (100) surface. The diffusion barriers were determined using the embedded atom potential. Surface roughness simulation results indicated that high substrate temperature and small deposition rates produce smoother films. However, in the practical applications, low substrate temperature is often desirable in order not to disturb already deposited films, and high deposition rates are needed to meet the production rate. Thus, the presented simulation codes can be used to obtain optimal operating conditions that satisfy surface roughness requirements.

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