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Research paper

Dewetting dynamics of nickel thin film on alpha-quartz substrate: A molecular dynamics study

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ABSTRACT

Dewetting dynamics of the nickel thin film on the alpha-quartz substrate is closely investigated by molecular dynamics simulation. Morphology after the spontaneous dewetting of thin films changes from multi-droplets, single-droplet and cylindrical structure as the film thickness increases. In the thin cylindrical structure, a neck is induced to break into the droplet due to the Plateau–Rayleigh instability whereas the thick cylindrical structure does not break. Nucleation and subsequent solidification happen only in the large droplet after the dewetting due to the size effect, which is dominated by the kinetic factor of nucleation in the small system.

1. Introduction

Dewetting of the metal thin film is a promising way to synthesize metal nanoparticle assembles, which is widely employed for application. For example, metal nanoparticles monodispersed on the substrate are widely used as a catalyst of the synthesis of vertically-aligned carbon nanotubes [1–3]. Since size and density of nanoparticles strongly affect quality and yield of products [3], there are many studies focusing on the pattern formation and self-organization of metal nanoparticles on the substrate via the dewetting [4–7]. Moreover, dewetting is proactively used to synthesize various nanomaterials such as graphene-nanoribbon [8,9], nanowire [10] and nanoparticle-array [11,12]. Therefore, it is important to control the dewetting process with a high degree of accuracy to synthesize the nanostructure as planned. However, it is not straightforward to control the dewetting process since the dewetting is governed by the nonlinear dynamics related to the capillary effect, which results in various patterns of morphology even in the same condition. Therefore, instability of nanoscale liquid metals on the substrate is widely studied [7,12,13]. For example, collapse and breakup of the nanostructure due to the capillary effect is closely discussed on the basis of the Plateau–Rayleigh instability [11–13], which originally explains the breakup of the falling stream of fluid into smaller droplets with same volume [14,15].

In addition to many experimental observations, computational simulations have also contributed to understanding the fundamental aspect of the dewetting [11–13,16]. Especially, molecular dynamics (MD) simulation [13,16] is a powerful tool since it can trace the motion of metal atoms directly during the dewetting. For example, Nguyen et al. [13] performed an MD simulation of the breakup of thin rings and lines due to the Plateau–Rayleigh instability. Moreover, Li et al. [16] studied dewetting and subsequent detachment of Pt nanofilms on the graphite substrate and compared results with analytical models. These studies [13,16] employed the Lennard-Jones potential for the interaction between the liquid metal and the substrate for simplicity since the force field between metal atoms and the inorganic substrate such as graphite, silicon and silicon oxide are not established. On the other hand, it is known that the parameter of the Lennard-Jones potential are sensitive to the wettability of metal nanoparticle on the substrate [17–19], which should affect the dewetting behavior seriously. Therefore, the unified force field should be employed both for metal–metal and metal-inorganic interactions in order to discuss the wetting property more accurately.

In this study, the dewetting dynamics of the Ni amorphous thin film on the alpha-quartz (SiO_2) substrate, which is a typical combination for catalyst/substrate for the carbon nanotube growth, is closely investigated by the MD simulation with an unified force field, the Condensed Phase Optimized Molecular Potentials for Atomic Simulation Studies II (COMPASS II) [20,21]. In particular, the effect of thickness of thin films on the dewetting dynamics is closely examined. Then, nucleation and solidification in dewetted nanoparticles is discussed both from thermodynamic and kinetic points of view.

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2. Simulation methodology

Dewetting of the Ni amorphous thin film on a (100) SiO_2 substrate is examined by the classical MD simulation using the MS Forcite plus module in Materials Studio 8.0 [22]. The COMPASS II [20,21], which covers most elements universally, is employed for the force field between all atoms. The short range interactions are cut in 12.5 Å, and the Coulomb interactions are calculated using the Ewald method. The charge property of each atom in the SiO_2 substrate is assigned by the COMPASS II force field in the same manner as our previous studies [23,24]. The classical equation of motion is solved by the velocity Verlet algorithm with a time step of 2.0 fs. The temperature is controlled using a Nosé thermostat [25].

Fig. 1 shows an overall view of the simulation cell. In the bottom of the rectangular box of $10.31 \times 10.26 \times 15.00\ nm^3$ with a periodic boundary condition, SiO_2 layers 1.35 nm in height are placed and an amorphous Ni film z nm in height (z = 0.3–1.1 nm at intervals of 0.1 nm) is placed on the SiO_2 substrate. The amorphous Ni thin film is created by 'Amorphous cell' module in Materials Studio 8.0. A top of the SiO_2 substrate is oxygen-terminated, and all atoms in the bottom layer are fixed during the calculation. A small simulation cell of $5.89 \times 5.92 \times 10.12\ nm^3$ is also prepared to investigate the size effect of the dewetting dynamics in Section 3.2. The detail property of each simulation cell is listed in Table 1. After the geometric optimization by the steepest descendant and conjugate gradient methods for 5000 steps, the main calculation is performed for 500 ps at 1500 K for all configurations. Three replicate calculations are performed for each condition to gather statistics.

In Section 3.4, an adaptive common neighbor analysis (CNA) [26] is performed using OVITO (open visualization tool) [27] to identify solid and liquid structures in the obtained atomic configuration. The adaptive CNA, which employs variable cutoff distances, distinguishes atomic configurations precisely as fcc (face-centered cubic), hcp (hexagonal closed pack), bcc (body-centered cubic), ico (icosahedron) and unknown coordination structures even at high temperature, although the conventional CNA with fixed cutoff distances usually includes an inherent error to some extent due to thermal vibration [28,29].

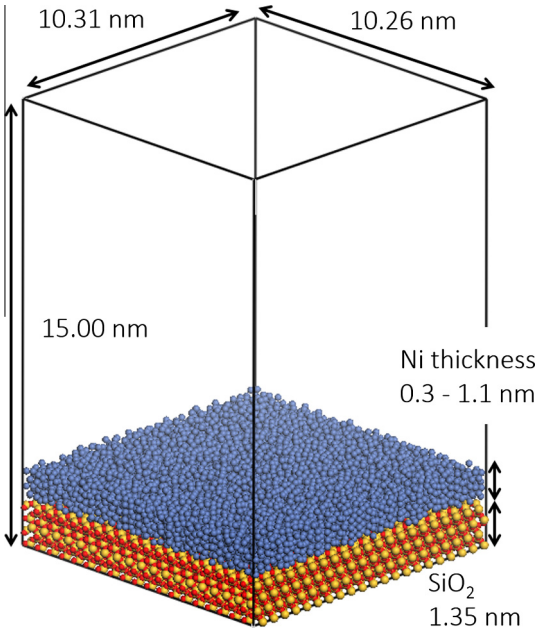

Fig. 1. Initial configuration of the simulation cell with the amorphous Ni thin film 1.0 nm in thickness. Blue, red and yellow atoms represent Ni, O and Si atoms, respectively, and hereinafter the same applies. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Number of atoms in simulation cell.

Element		Number of atoms
(a) Large cell		
Si		4389
O		7930
Ni	0.3 nm	2459
	0.4 nm	3278
	0.5 nm	4097
	0.6 nm	4917
	0.7 nm	5736
	0.8 nm	6556
	0.9 nm	7375
	1.0 nm	8194
	1.1 nm	9013
(b) Small cell		
Si		1584
O		2772
Ni	0.5 nm	1356
	0.6 nm	1627
	0.7 nm	1898
	0.8 nm	2169
	0.9 nm	2440
	1.0 nm	2712

3. Results and discussion

3.1. Morphology of dewetted thin film on the substrate

Fig. 2 shows snapshots of the spontaneous dewetting of Ni thin films with thickness of 0.3, 0.5, 0.6, 1.0 and 1.1 nm. In the initial configuration, the SiO_2 substrate is completely covered by the Ni thin film for all conditions. In the case of the thinnest condition, 0.3 nm, the Ni thin film breaks and bare SiO_2 surface appears via dry patches (parts of the substrate without the film covering) in many areas at the same time just after the calculation starts. As time advances, area of the bare SiO_2 surface expands and dry patches coalesce together. Consequently, three Ni islands appear at 20 ps and these Ni islands move on the SiO_2 substrate easily since they remain as liquid state. Then, adjacent two islands become sintered to form one larger Ni droplet after 60 ps. Another sintering event does not occur and two droplets remain after 500 ps calculation. The contact angle of all droplets is estimated to be approximately 138°. The contact angle θ is calculated on the assumption that the Ni droplet is spherical as follows:

$$\theta = \cos^{-1}\left(\frac{x_2^2 - x_1^2}{x_2^2 + x_1^2}\right), \tag{1}$$

where x_1 is the height of the droplet and x_2 the radius of the cross-sectional circle at the bottom of the droplet [18].

In the case of the thin film 0.5 nm in thickness, the thin film breaks and the bare SiO_2 surface appears via dry patches by 2 ps as same as the case of the thin film 0.3 nm in thickness. However, the number of dry patches in the film of 0.5 nm is less than that of the film of 0.3 nm. One long band-like structure appears at 20 ps and it breaks to form two Ni droplets at 30 ps. Two droplets move on the SiO_2 surface and become sintered at 70 ps, resulting in the formation of one large droplet. The droplet starts solidifying at approximately 300 ps. At 500 ps, the Ni droplet completely solidifies and the facet can be found on the surface. Detail of the solidification process is closely discussed in Sections 3.4 and 3.5. In case