The 81st Fujihara seminar
Mathematical Aspects for Interfaces and Free Boundaries

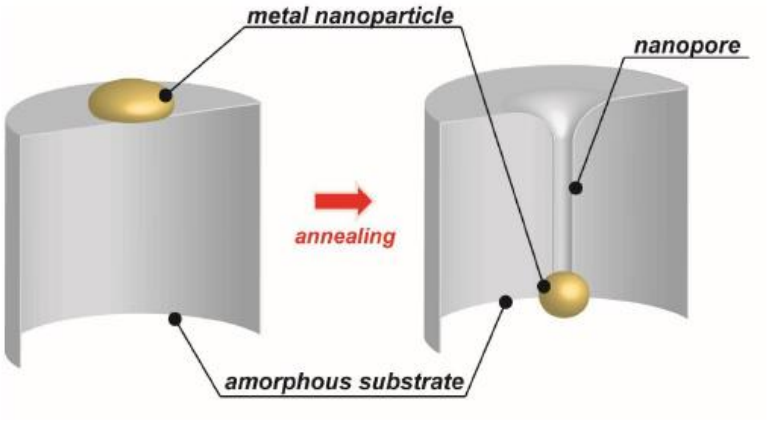
Geometric model of nanoparticle-assisted nanopore formation on solid substrates

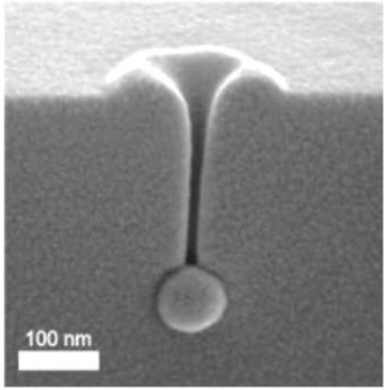
Koichi Sudoh

Sanken, Osaka University

Collaborators: M. Naito (Konan Univ.) and Y. Kohsaka (Kobe Univ.)

Nanopore formation by annealing of metal nanoparticles on ceramic substrates





Nanoscale pores are formed by annealing Au particles on ceramic substrates (SiO_2 and Si_3N_4) at high temperatures.

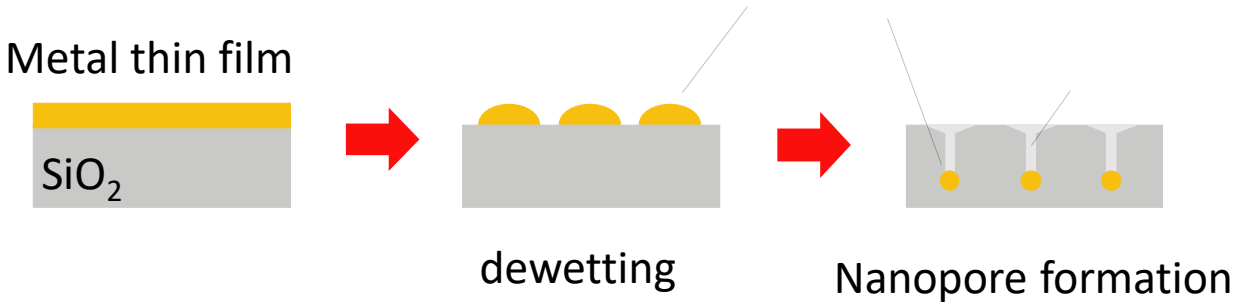
L. J. de Vreede et al., Nano Lett. 15, 727 (2015)

Contents

1. Experiments on nanopore formation by annealing metal nanoparticles on SiO_2
2. Modeling of the nanopore formation based on the experimental results

Experimental method

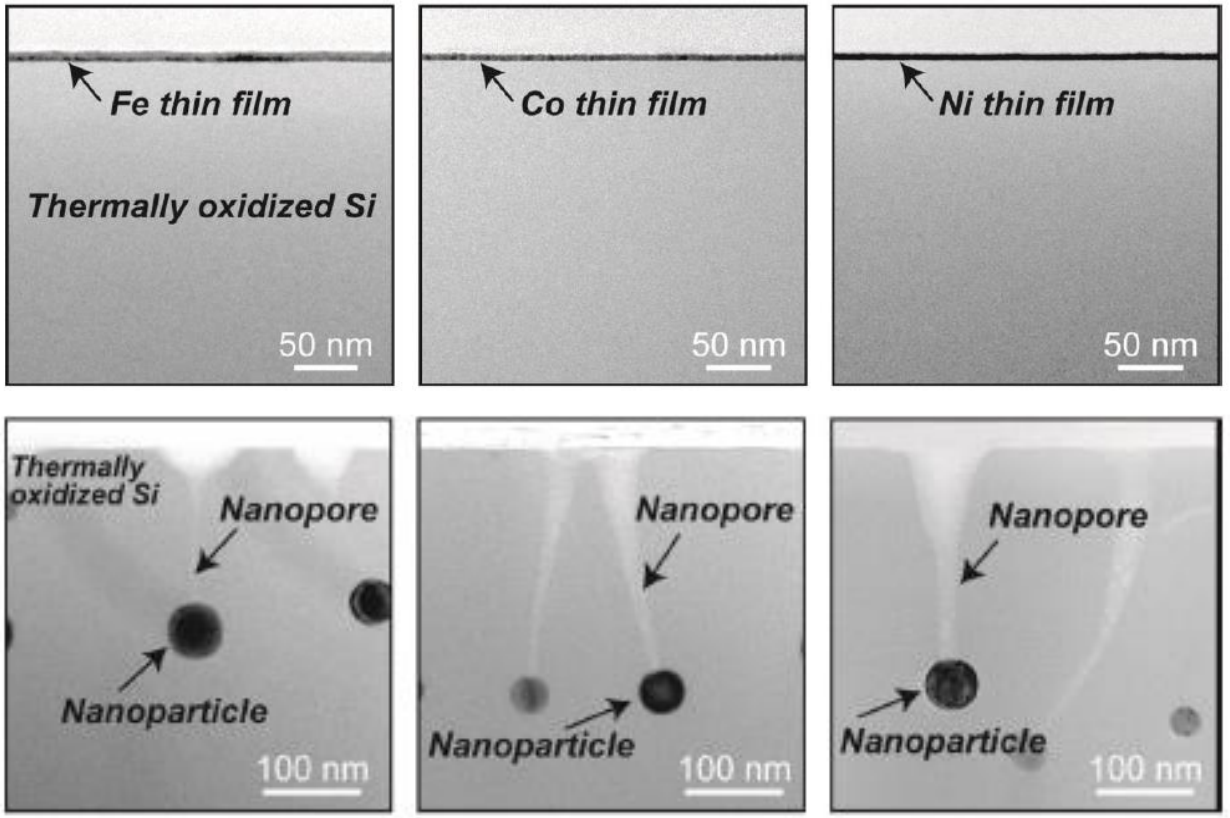
We have performed experiments on nanopore formation by annealing nanoparticles of Fe, Co, and Ni on SiO2.



Structural change by high-temperature annealing

- Prepare samples of metal thin films (5~10 nm thick) on SiO_2
- Anneal thin film samples at 1000~1100 C to cause nanopore formation

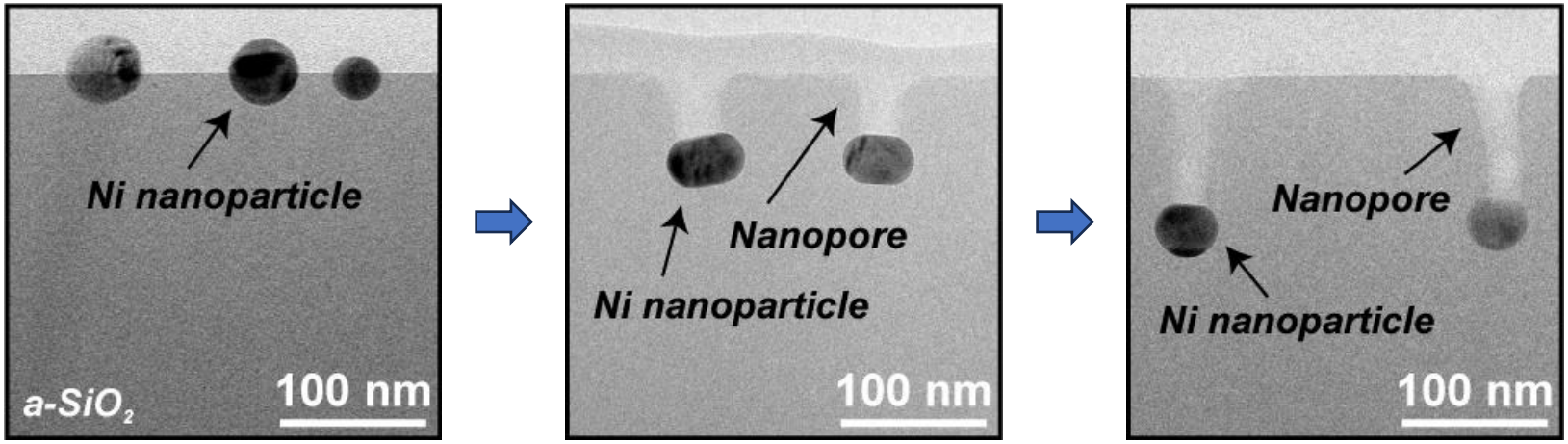
Nanopore formation by nanoparticles of Fe, Co, and Ni



Fe Co Ni

Nanopore formations by annealing metal nanoparticles are considered to be ubiquitous phenomena that arise regardless of the species of metal nanoparticles.

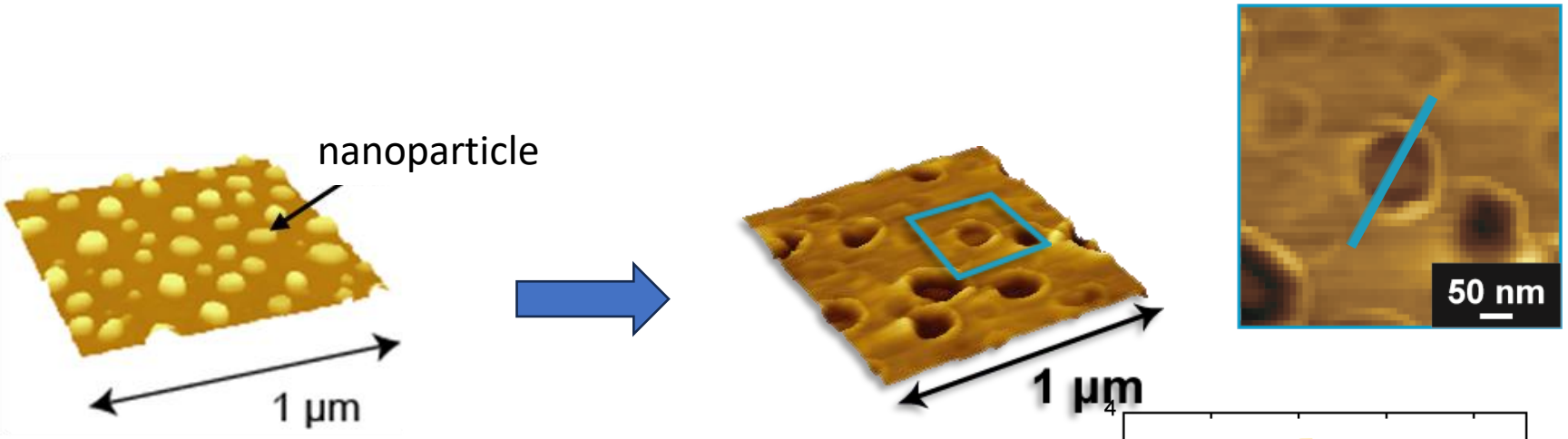
Nanopore formation process



1 min *30 min* *60 min*

The structures after annealing at 1000 C for different times.

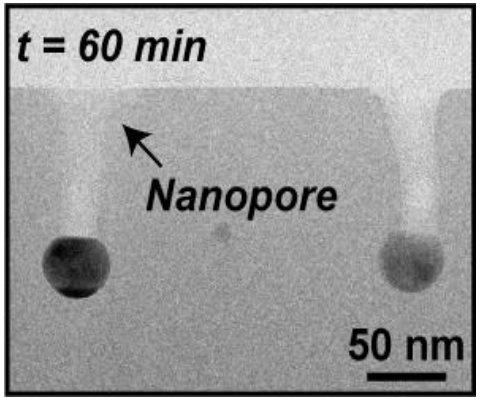
Morphology of the interface between nanoparticles and the substrate

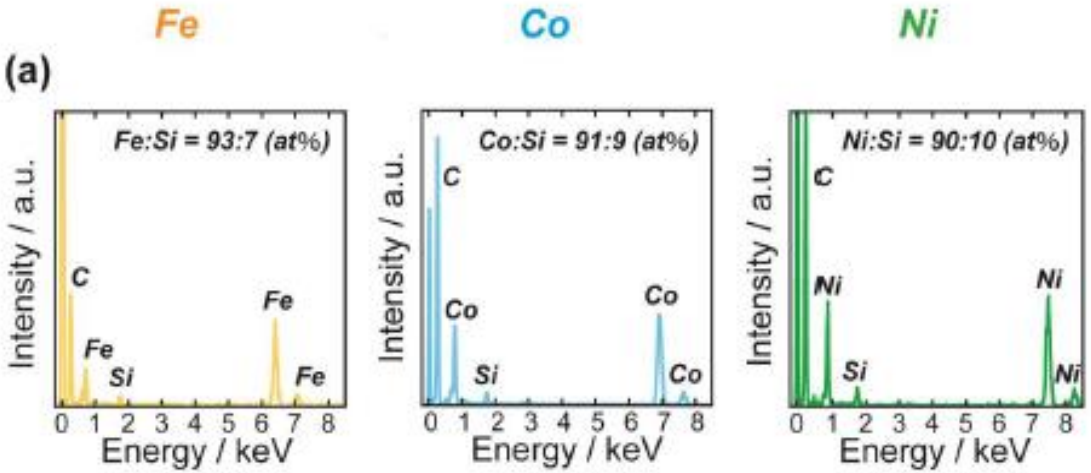


Selective etching of nanoparticles

Considerable structural changes are observed around the triple line.

Chemical composition of metal nanoparticles



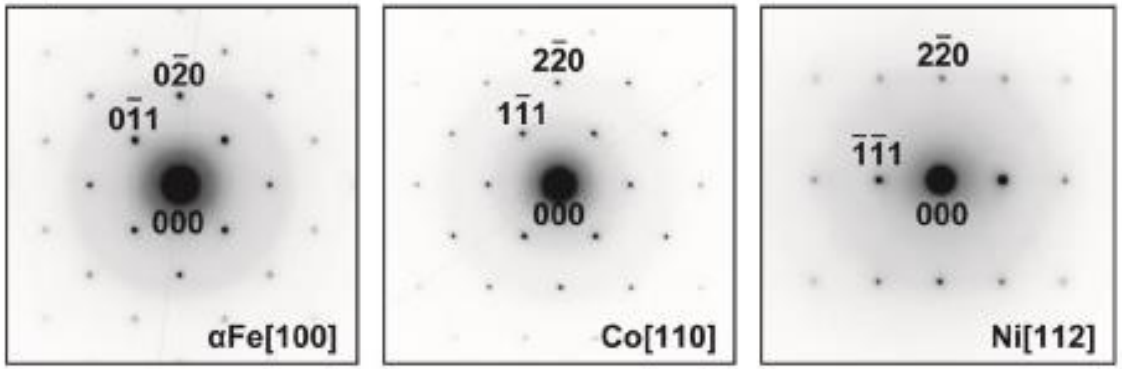


EDS spectrum

- The chemical compositions of nanoparticles has been examined by energy-dispersive X-ray spectroscopy (EDS) measurements.
- There is no signature of the formation of compounds.

Nanoparticles act as catalysts in the nanopore formation.

Crystal structures of metal nanoparticles



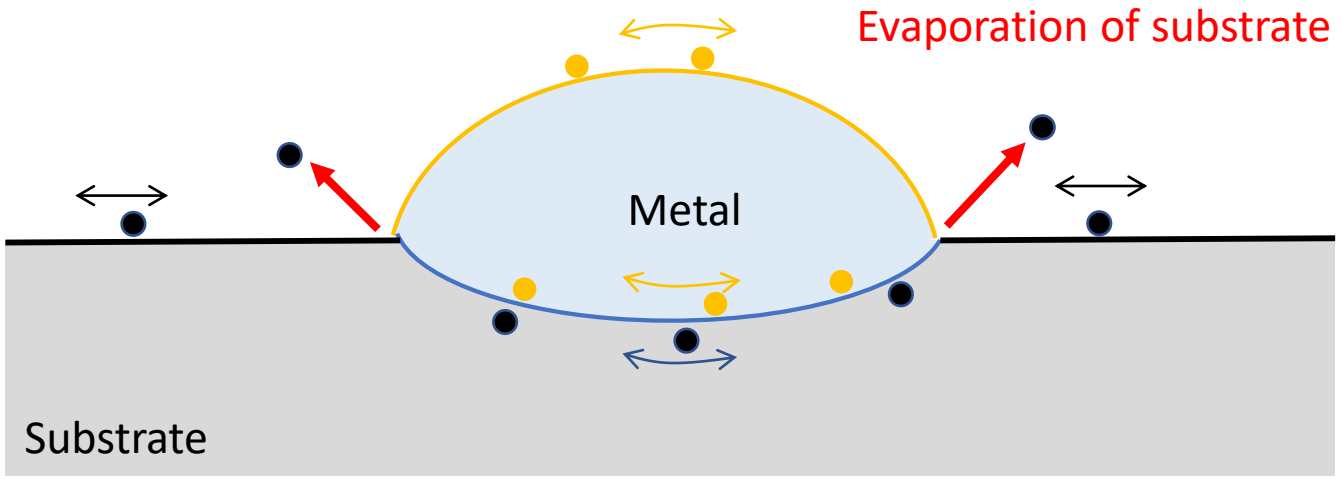
- The measured diffraction patterns of the nanoparticles indicate that the metal nanoparticles exist as a single crystal of pure metal during annealing.

Decomposition of SiO_2 catalyzed by metal nanoparticles

$$SiO_2 \rightarrow \frac{1}{2}O_2 + SiO \uparrow$$

- Evaporation of substrate atoms occurs by decomposition of SiO_2 due to catalysis of metal nanoparticles
- Evaporation of substrate atoms occurs in the close vicinity of the triple line.

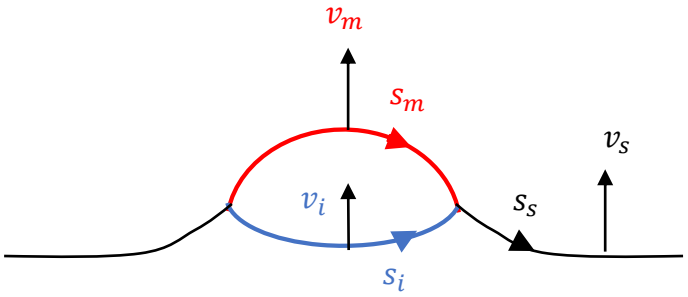
Modeling of nanoparticle-assisted nanopore formation



- Diffusion along the surfaces and interfaces
- Localized evaporation of substrate atoms around the triple line
- The interface remains compact during structural changes.

Evolution equations

m :metal surface
s :substrate surface
i :metal/substrate interface



Mullins equation

W. W. Mullins, J. Appl. Phys. 28, 333 (1957).

Normal velocity of the surfaces and interface

metal surface

$$v_m = D_m \gamma_m \frac{\partial^2 K_m}{\partial s_m^2}$$

metal/substrate

$$v_i = D_i \gamma_i \frac{\partial^2 K_i}{\partial s_i^2}$$

substrate surface

$$v_s = D_s \gamma_s \frac{\partial^2 K_s}{\partial s_s^2} - R_e \exp\left(-\frac{s_s}{\sigma}\right)$$

evaporation term

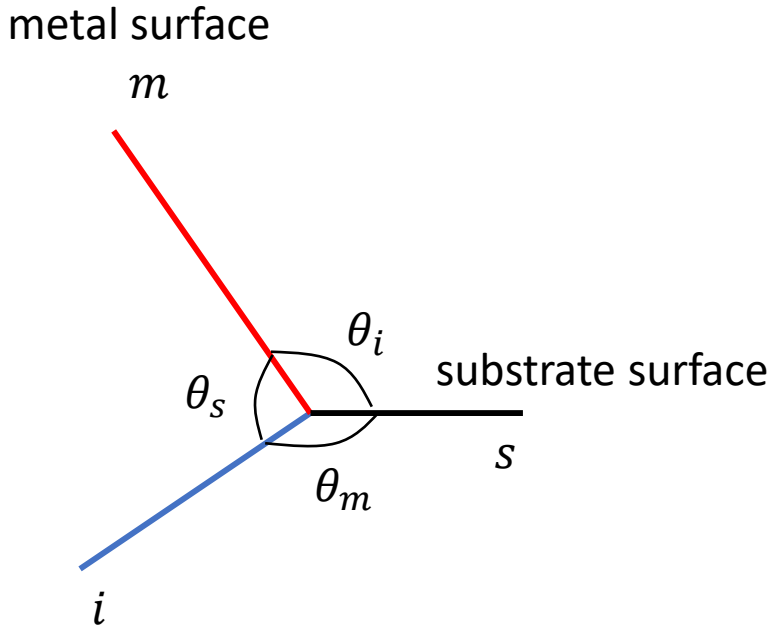
s: arc length from the triple point

K: mean curvature

D_m, D_i, D_s: diffusion constants

$\gamma_m, \gamma_i, \gamma_s$: surface/interface free energies

Boundary condition at the triple point



Local equilibrium condition

$$\frac{\gamma_m}{\sin\theta_m} = \frac{\gamma_i}{\sin\theta_i} = \frac{\gamma_s}{\sin\theta_s}$$

Mass conservation condition

$$j_i = j_m = j_s$$

where $j_\alpha = -\gamma_\alpha D_\alpha \frac{\partial K_\alpha}{\partial s_\alpha} \quad (\alpha = m, s, i)$

Continuity condition for the chemical potential of substrate atoms

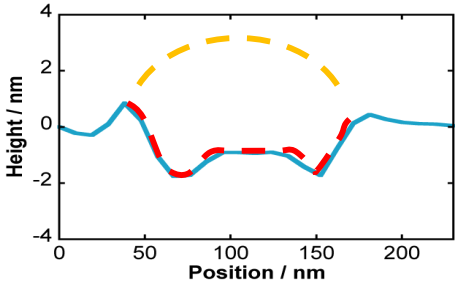
$$\gamma_i K_i = \gamma_s K_s$$

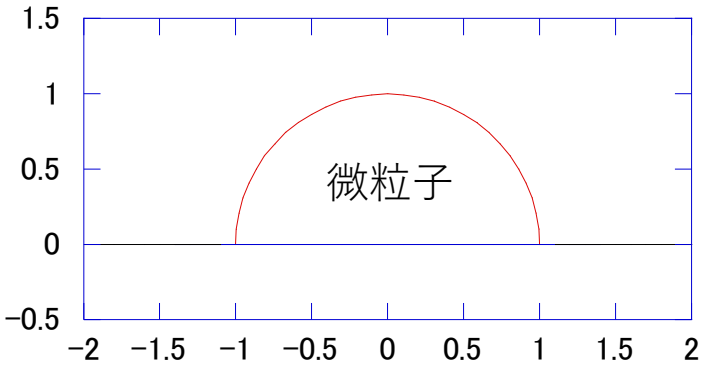
Structural evolution without evaporation

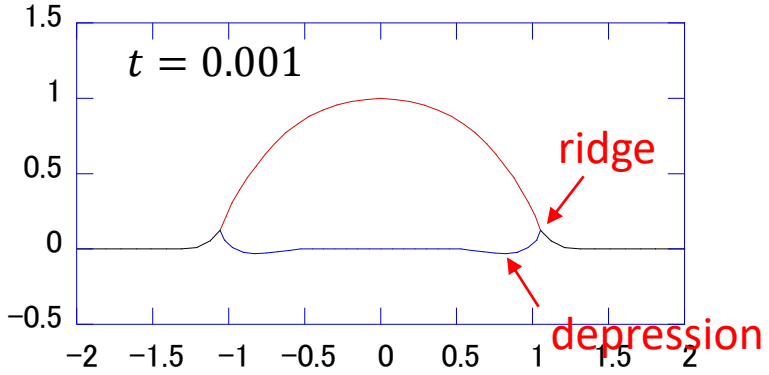
$\theta_i = 135°, \theta_s = 160°$

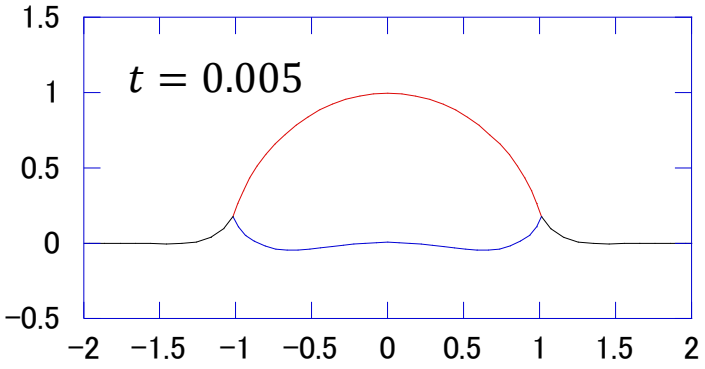
$D_s = 0.01, D_i = 1.0, D_m = 1.0$

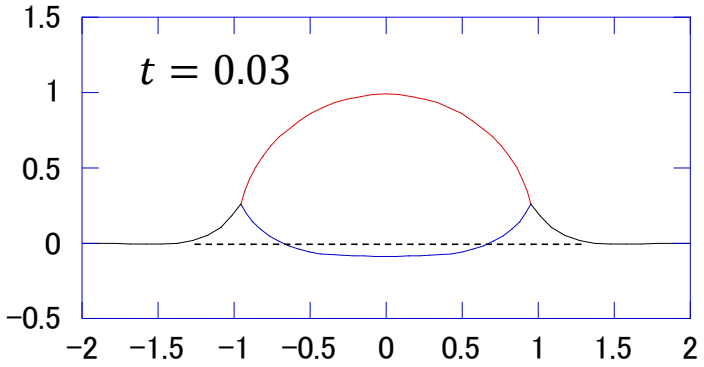
$R_e = 0.0$









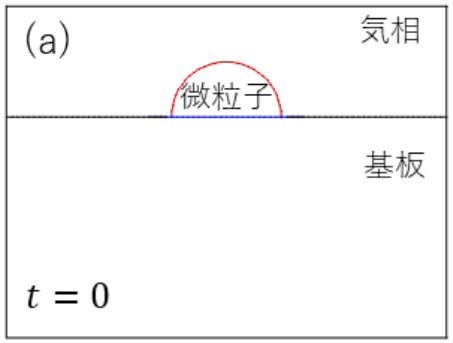


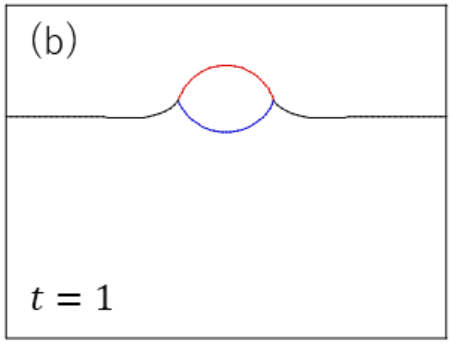
Structural evolution when evaporation occurs

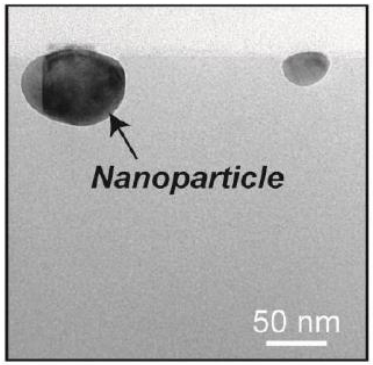
$\theta_i = 135°, \theta_s = 160°$

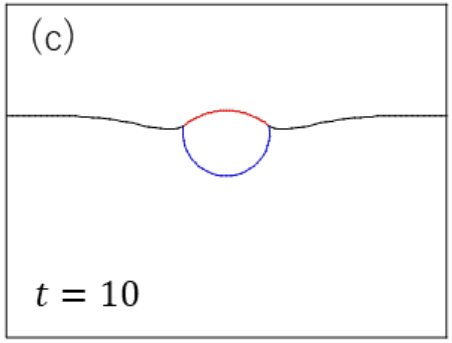
$D_s = 0.01, D_i = 1.0, D_m = 1.0$

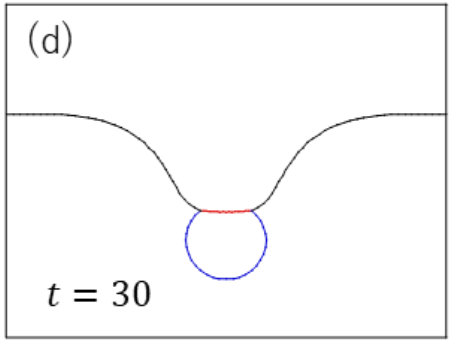
$R_e = 0.001, \sigma = 0.01$

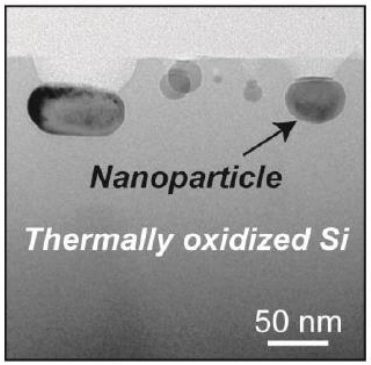












The simulation reproduces the experimentally observed structural evolution.

Summary

- We have investigated the mechanism of nanopore formation by annealing metal nanoparticles on SiO_2 substrates.
- We proposed a simple geometrical model of the nanoparticle-assisted nanopore formation allowing for the localized evaporation of substrate atoms in the close vicinity of the triple line.
- We have demonstrated that our model can reproduce the experimentally observed structural evolution of nanoparticles on SiO_2.