

REBa₂Cu₃O_y線材における 自己組織化ピンニングセンター

～ 薄膜結晶成長シミュレーション ～

Self-Organized Pinning Centers in REBa₂Cu₃O_y Coated Conductors
～ Crystal Growth Simulation～

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Outline

1. Flux pinning centers

1.1 Pinning centers with a dimension

1.2 Self-organization of flux pinning centers in REBCO films

Self-organization of Ba-M-O (BMO) nanostructures

2. Crystal growth of REBCO films

2.1 Basics of film crystal growth

nucleation, crystal growth modes

2.2 Simulation of film crystal growth

Self-organization depending on growth temp., deposition rate, BMO addition

3. Summary

1. Flux pinning Centers

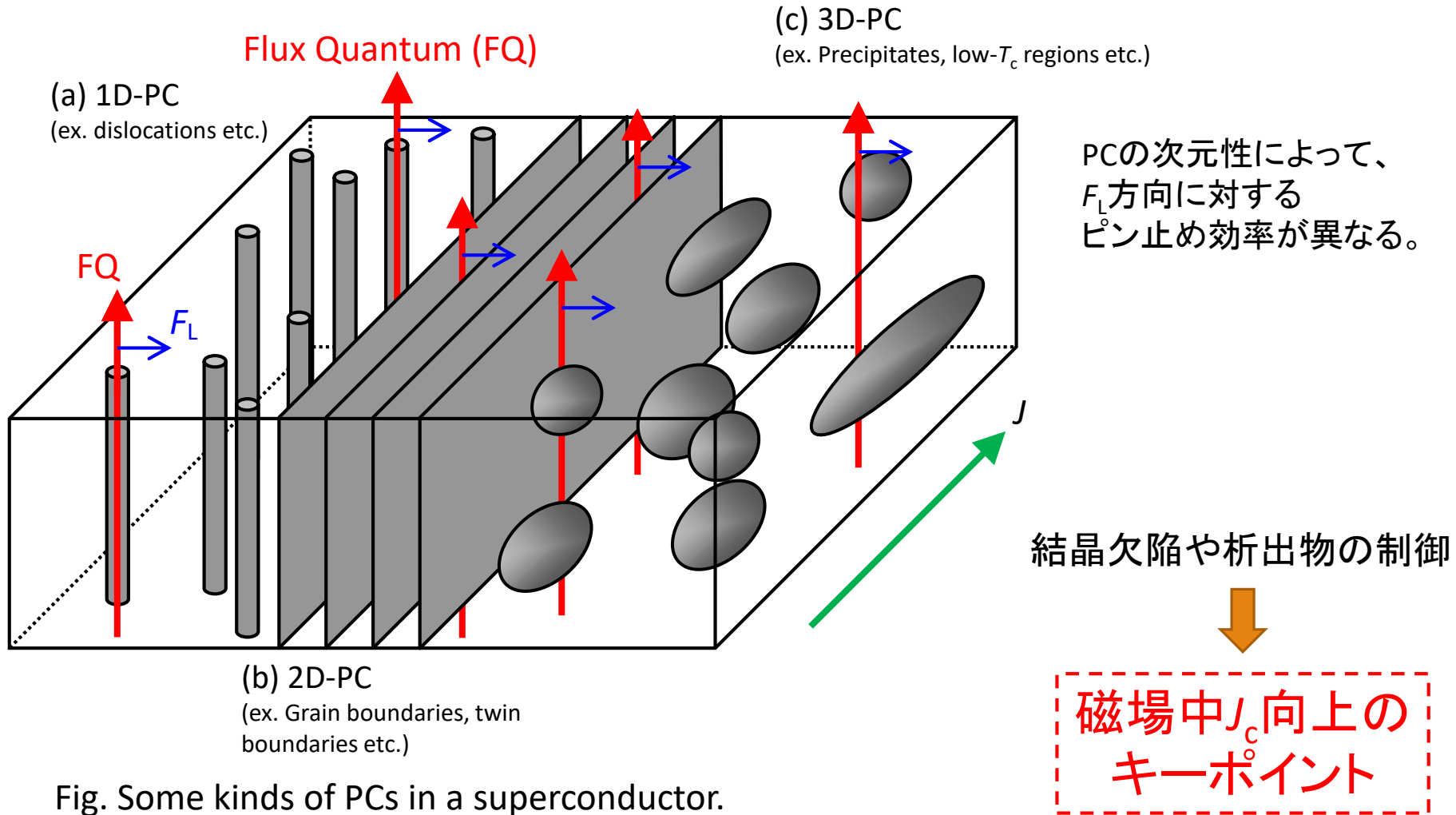
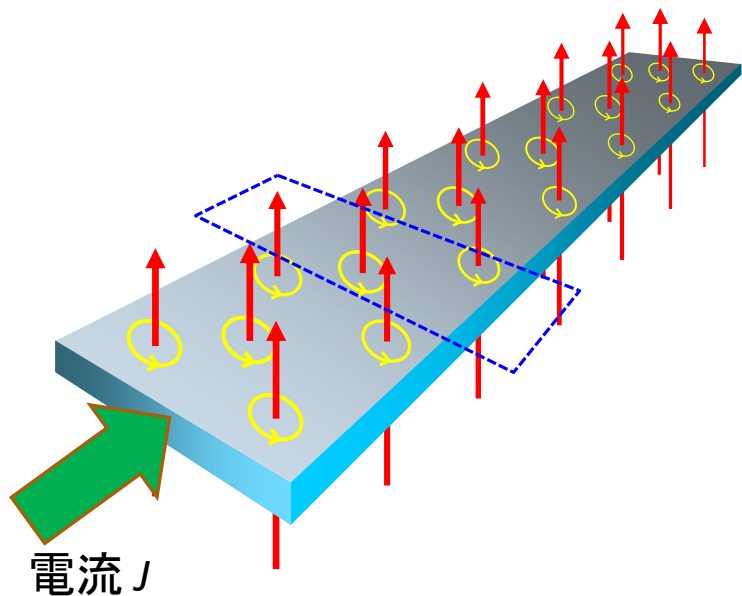


Fig. Some kinds of PCs in a superconductor.

Simulation of FQ motion (2D)

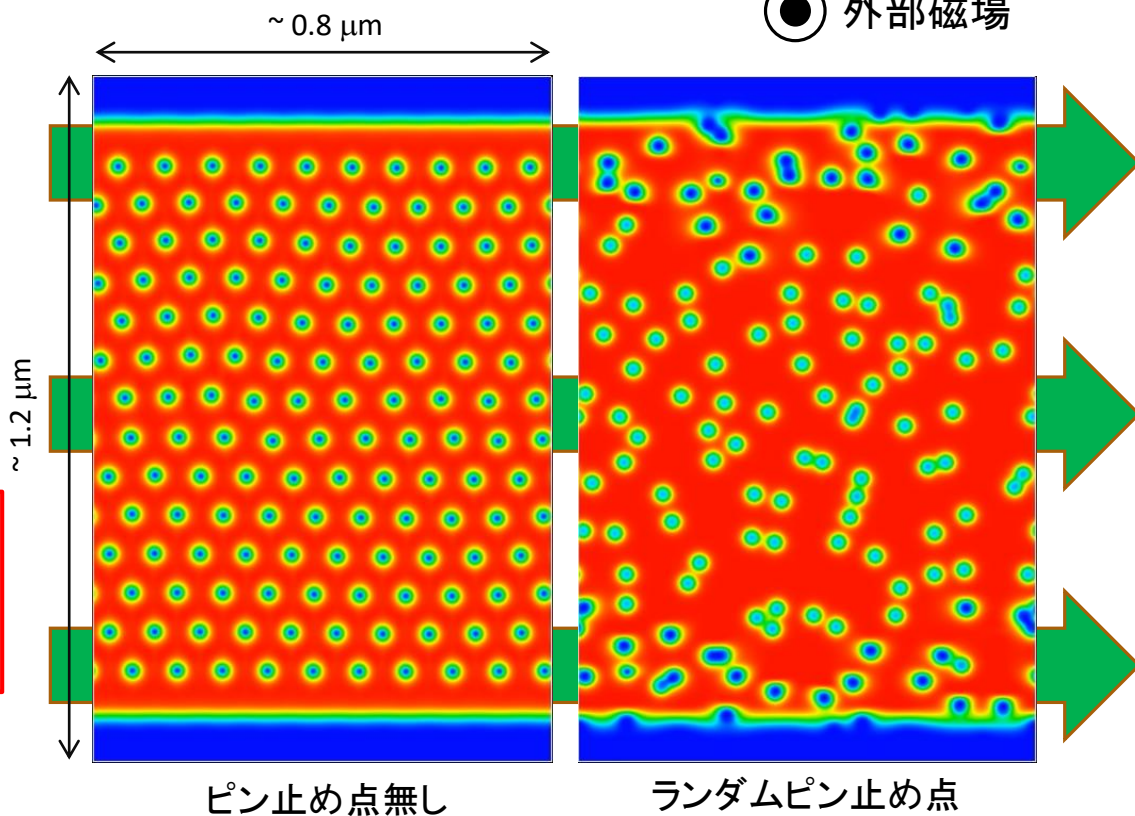


- ・磁束量子のサイズはナノメートル。
- ・直接観察は困難 → 電気特性から推測。
- ・時間依存Ginzburg-Landau(TDGL)方程式の数値計算 → 電場、磁化、超伝導電流 etc.

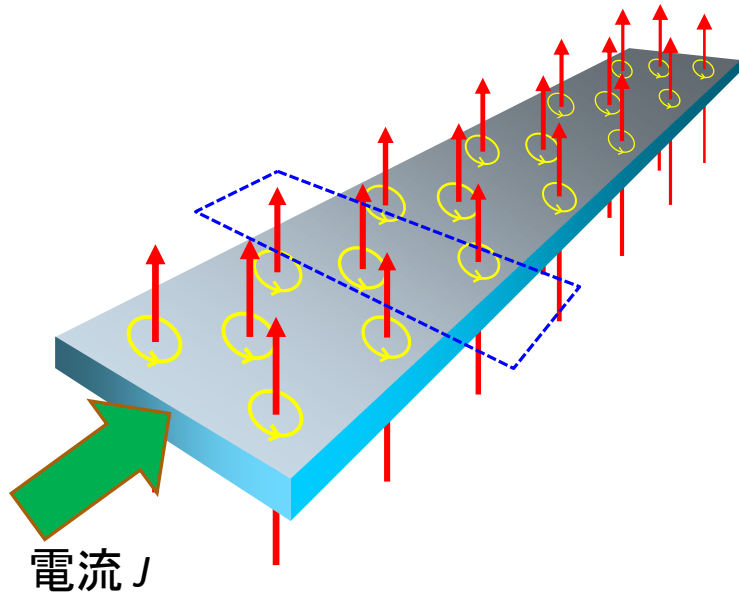
超伝導体内を運動する磁束量子のシミュレーション

- ・左図青破線部分のFQの運動をシミュレーション
- ・磁場印加後、電流値を徐々に上昇。

● 外部磁場



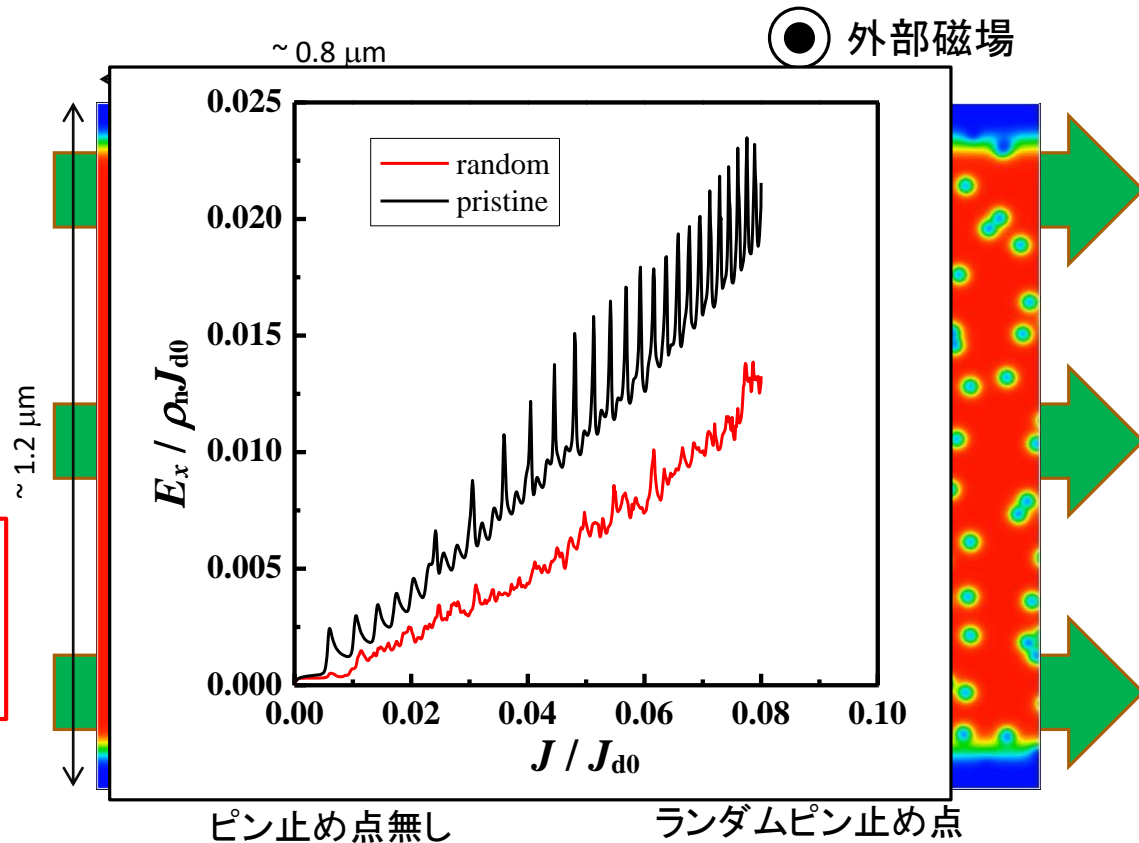
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1.2 Self-organization of flux pinning centers in REBCO films

パルスレーザー蒸着法: YBCO + BaZrO₃ → YBCO中にBZOナノ構造が自己組織化

Ref. J. Driscoll et al., Nature mater. 3 (2004)439

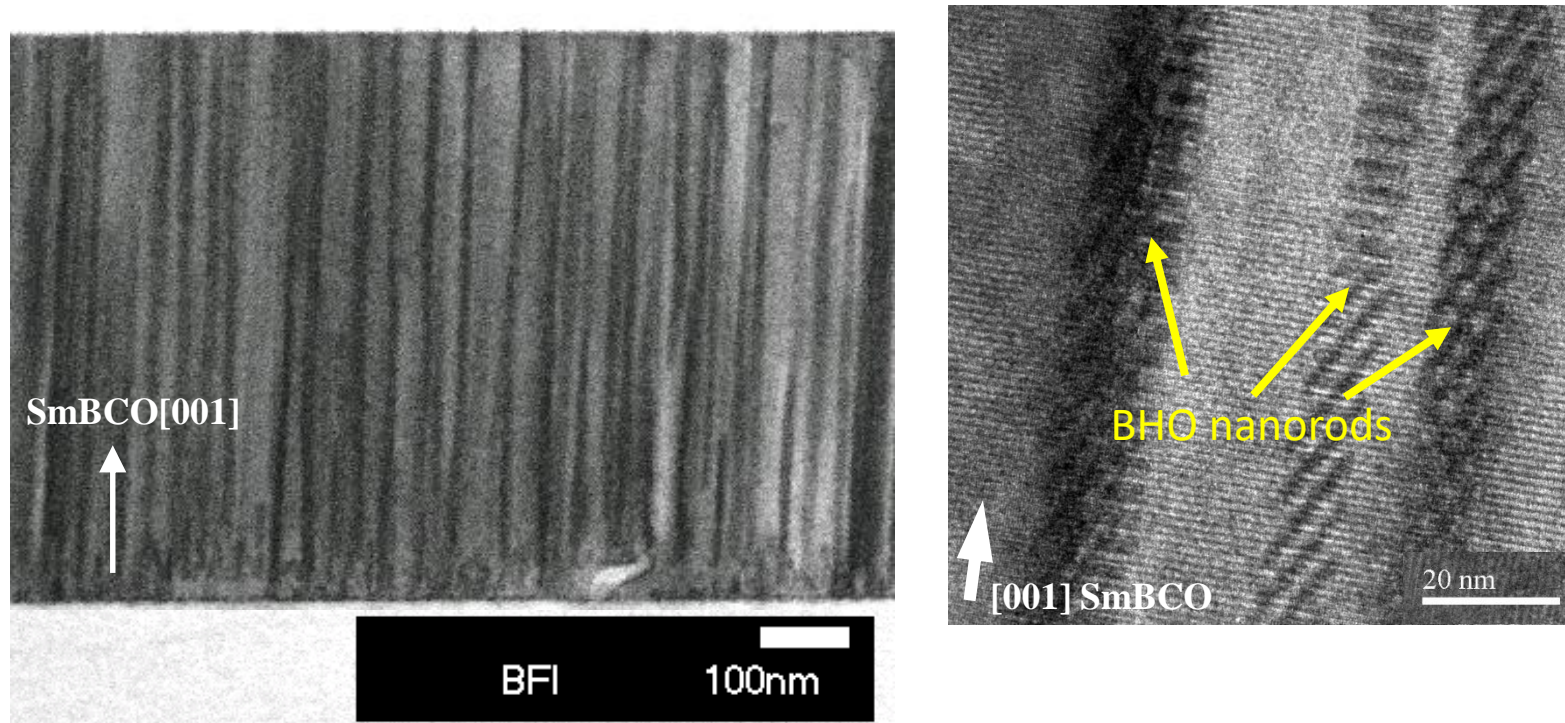


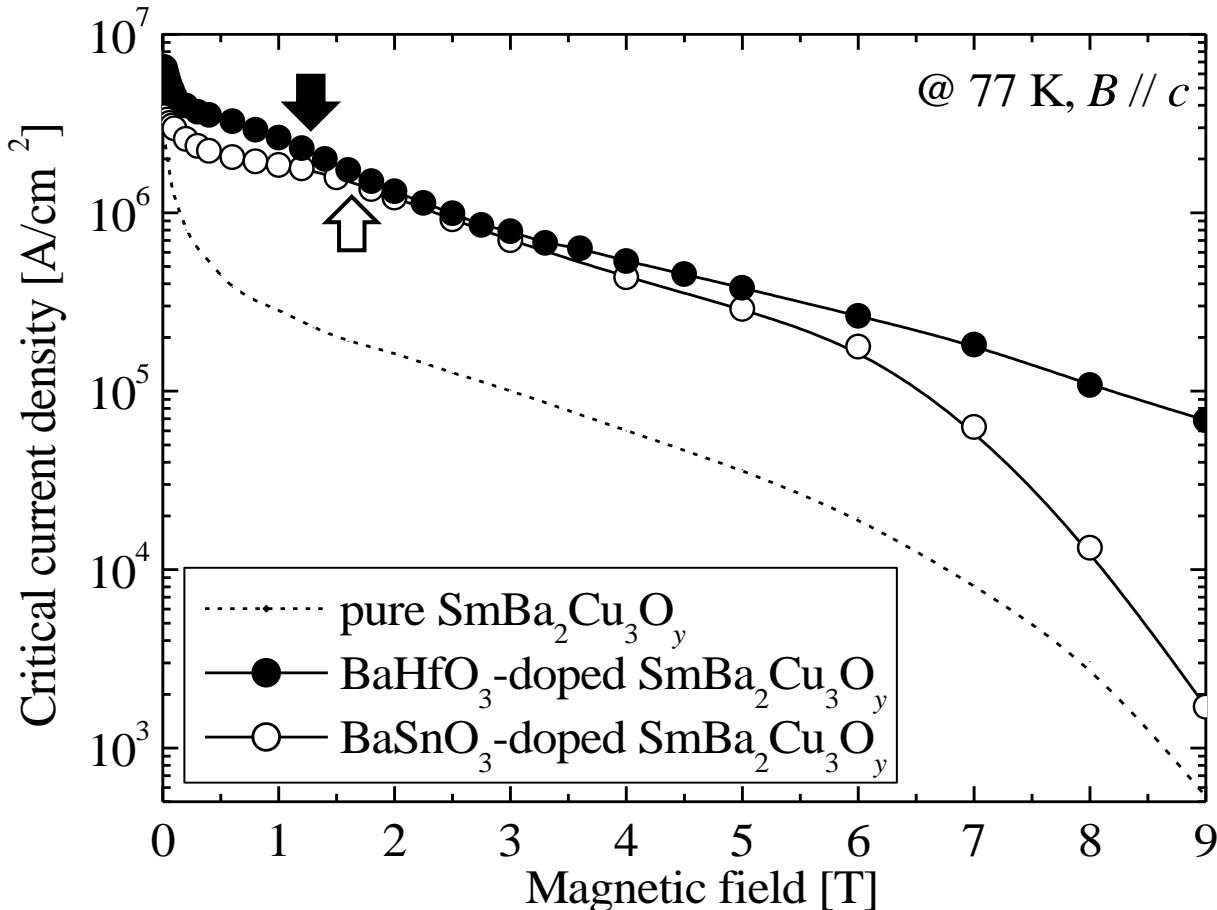
Fig. Cross-sectional TEM images of BaHfO₃ (BHO) doped SmBCO film.

Ref. Tsusuta et al., (2014)

Ba-M-O (BMO) : M = Zr, Sn, Hf, Nb
ナノストラクチャーに自己組織化

FQのサイズと同程度なため、
効率の高いピン止め点

Effect of BMO addition on J_c - B in SmBCO films



BMOナノロッドによる
FQ運動のピン止め



磁場中 J_c の大幅な向上

- ・磁場中 J_c はBMOナノロッドの形状に大きく影響される。
- ・ナノロッド形状は成長条件に影響される。

Fig. J_c - B curves of BMO-doped SmBCO films.

Ref. A. Tsuruta et al., Supercond. Sci. Technol. 27(2014)065001

Effect of growth temperature on nanorod configurations

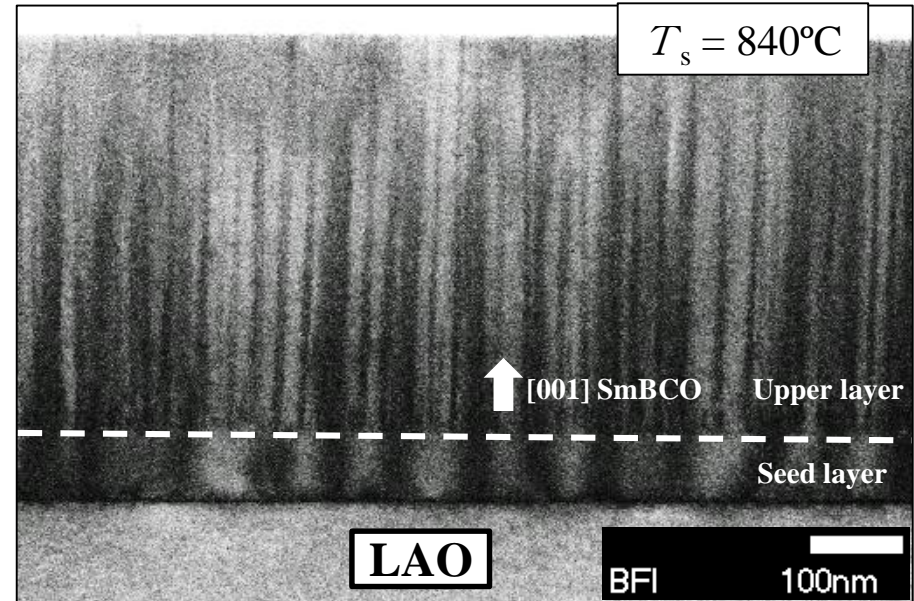
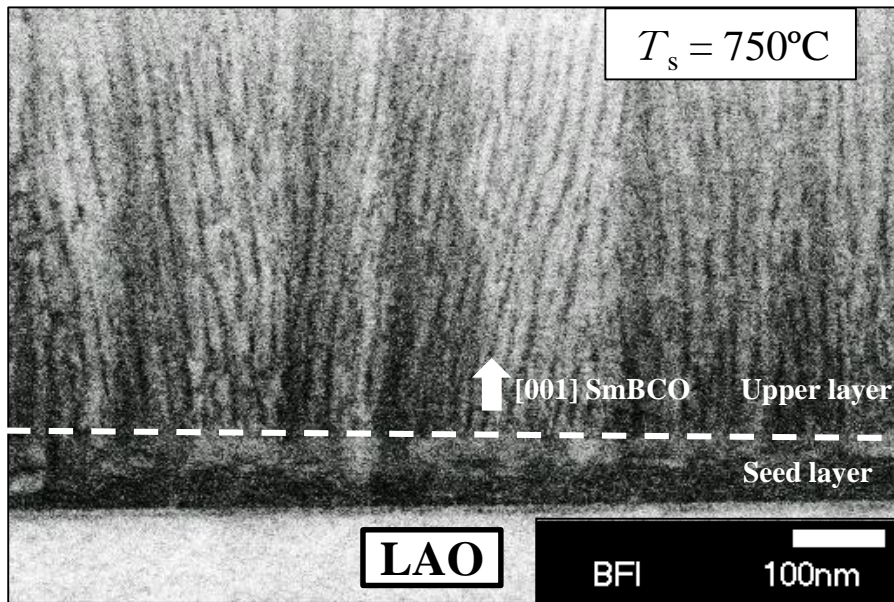


Fig. Cross-sectional TEM images of 3 vol.%BHO-doped SmBCO films deposited at different substrate temperatures (T_s).

Ref. S. Miura et al., J. Phys. 507(2014)022021

成長温度 [$^\circ\text{C}$]	750	840
直径 [nm]	5.7	8.5
傾き	傾斜	直線 //c
数密度 [$1/\mu\text{m}^2$]	2,300	1,440

- ・成長温度が低いほど細く高密度なナノロッド。
- ・添加量や成膜レートにも依存する。



自己組織化機構の
解明が必要

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2. Crystal growth of REBCO films

2.1 Basics of film crystal growth

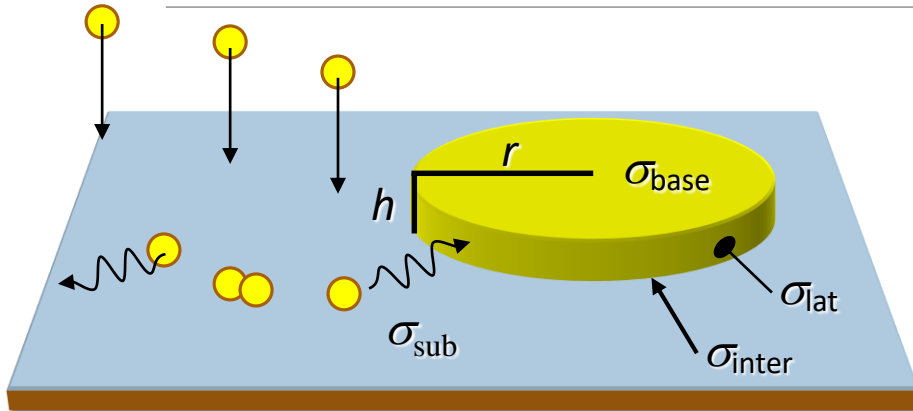
nucleation, crystal growth modes

2.2 Simulation of film crystal growth

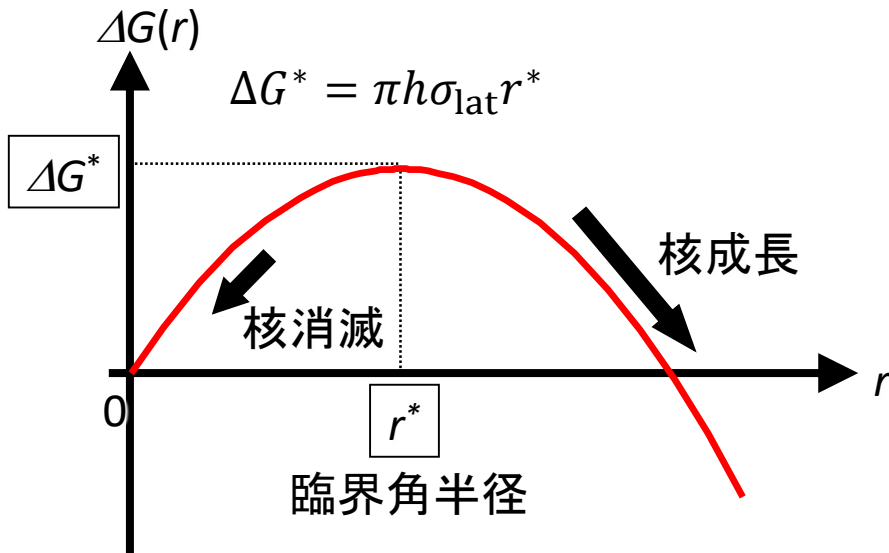
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3. Summary

2.1 Nucleation



σ : surface free energy density [J/m²].
 base: top surface, lat: lateral surface, inter: interface between nuclei and subst.
 sub: substrate plane
 v_{cell} : Unit cell volume of REBCO [m³]

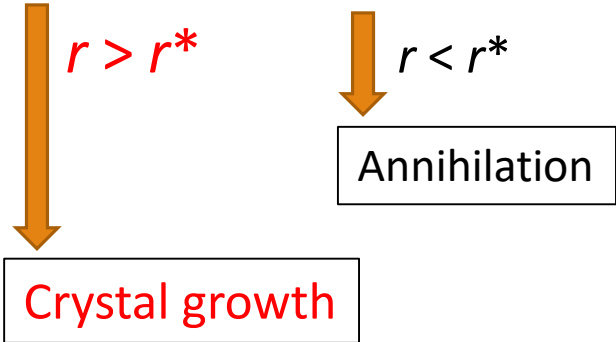


核生成時の系の自由エネルギー変化 ΔG [J]

$$\Delta G(r) = -\frac{\pi r^2 h}{v_{\text{u.c.}}} \Delta\mu + 2\pi h r \sigma_{\text{lat}} + \pi r^2 \sigma_{\text{base}} + \pi r^2 (\sigma_{\text{inter}} - \sigma_{\text{sub}})$$

$\Delta\mu$: Chemical potential difference between vapor and solid phases [J/unit cell]

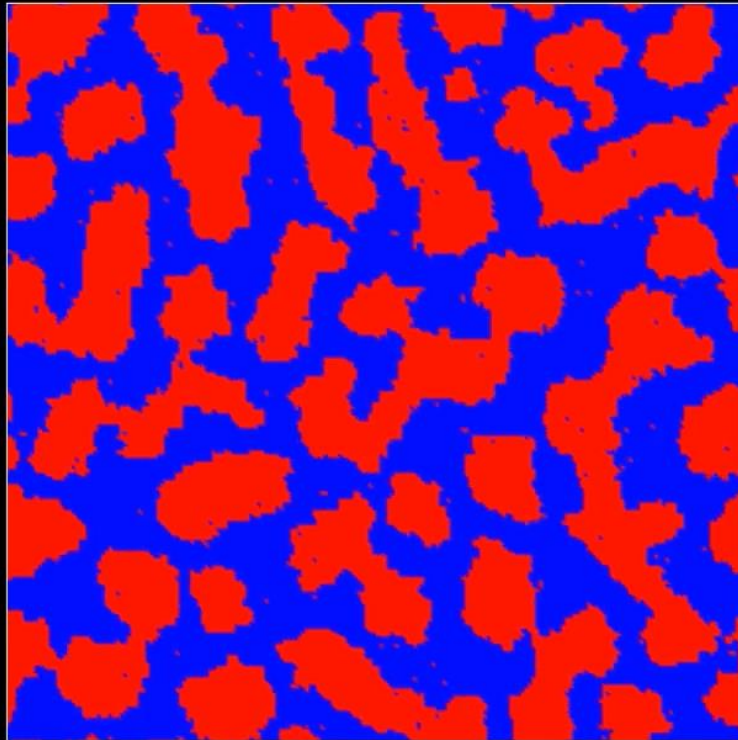
熱揺らぎで、半径 r の核が生成



T_s	low		high
r^*	small		large
ΔG^*	low		high

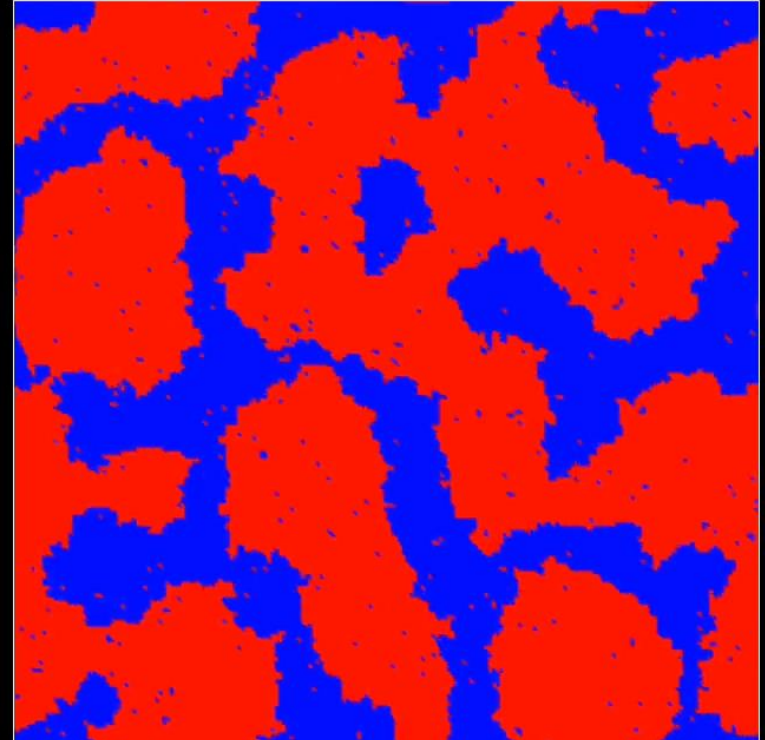
Nucleation (2D Monte Carlo simulation)

$T_s = 1,023$ K (low growth temperature)



step_0000000341.csv

$T_s = 1,193$ K (high growth temperature)



step_0000002998.csv

- ・核生成 → 核が成長し、島を形成 → 成長した島が結合
- ・臨界核半径以下の核は、生成しても消滅する。
- ・基板温度が高いほど臨界角半径が大きいため、核生成しにくい。
→ 基板温度が高いほど島の数密度低い。

Number density of nucleus and growth conditions

Diffusion equation of particles on a substrate

$$\frac{\partial C(\vec{r}, t)}{\partial t} = D(T_s) \nabla^2 C(\vec{r}, t) + F$$

$C(\vec{r}, t)$: concentration of the particles [/m²]

$$D(T_s) = D_\infty \exp\left(-\frac{E_d}{k_B T_s}\right): \text{diffu. const. [m}^2/\text{s]}$$

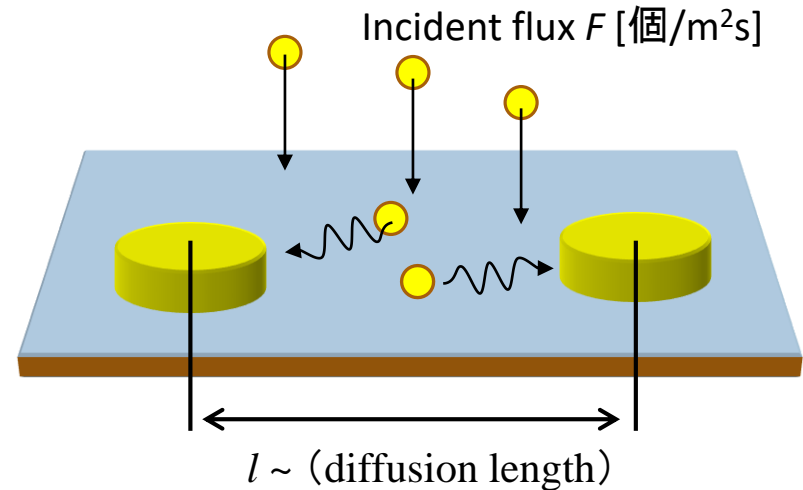
E_d : activation energy [J]

T_s : substrate temperature [K]

$$F = V_{d.r.}/v_{u.c.}: \text{incident flux [}/\text{m}^2\text{s]}$$

$V_{d.r.}$: deposition rate [m/s]

$v_{u.c.}$: unit cell volume [m³/unit cell]



Dimensionless diffusion equation

$$\frac{\partial \bar{C}(\vec{r}, \bar{t})}{\partial \bar{t}} = \bar{\nabla}^2 \bar{C}(\vec{r}, \bar{t}) + R$$

※ $\bar{\quad}$ means a dimensionless parameter.

$$\text{Growth kinetic factor: } R \equiv \frac{F a^4}{D(T_s)} = \frac{a V_{d.r.}}{D(T_s)}$$

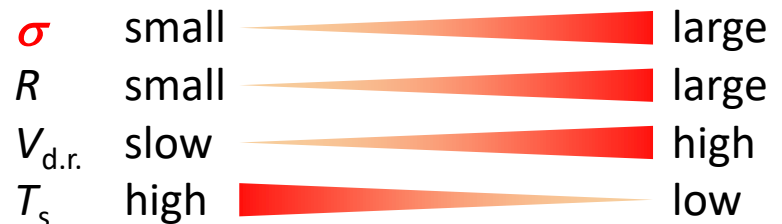


a : lattice const. of the particles [m]

- ・粒子の吸着と拡散のバランス
- ・成膜条件によって変化 → 粒子拡散に影響

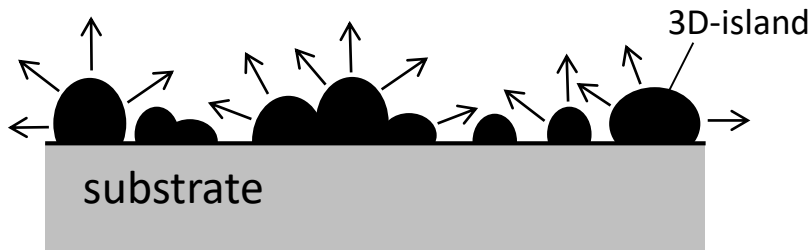
Number density of nuclei σ [/m²]

$$\sigma = l^{-2} \sim \left(\frac{R}{a^6}\right)^{2p} \quad \text{where, } p = \frac{1}{6}$$



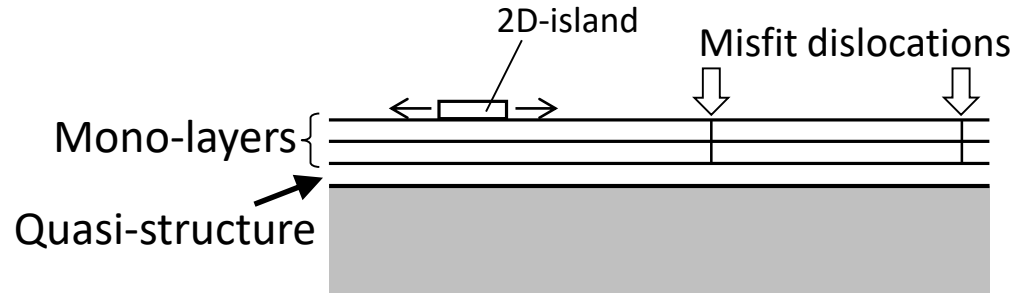
Crystal growth modes

(a) Volmer-Weber (VW) mode
or 3D-island mode



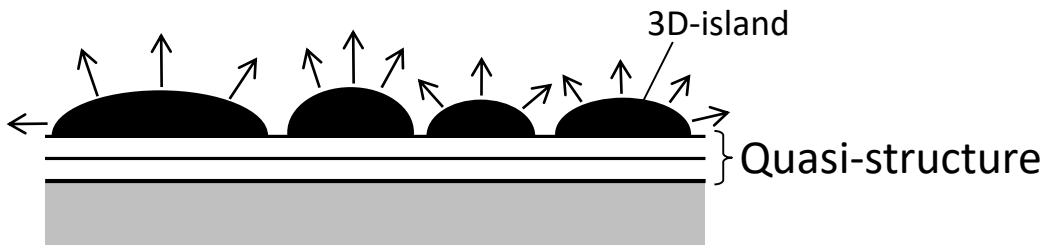
- σ_{inter} 大きい場合 (異種材料、ミスフィット大)。
- 全ての方向に成長。

(b) Frank-van der Merwe (FM) mode
or layer-by-layer mode



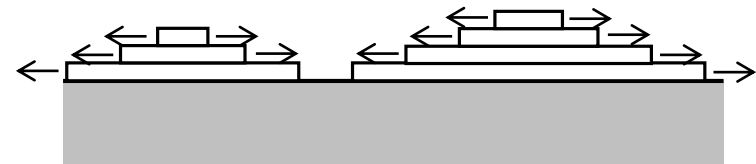
- σ_{inter} ゼロ or 十分小さい場合 (同種材料)。
- 熱揺らぎで2D核が一つ生成。
横方向にのみ成長。
- 一層覆った後、熱揺らぎで2D核生成。

(c) Stranski-Krastanov (SK) mode



- σ_{inter} 十分小さいが格子定数異なる場合。
- 初期FMモード、後にVWモード。

(d) 2D-island mode (REBCO films)



- σ_{inter} ゼロ or 十分小さい場合 (同種材料)
- $\Delta\mu$ (過飽和) の高いFMモード。
- 一層覆う前、新たな2D核が生成。
- 横方向成長がメイン。
小さな縦方向成長成分も持つ。

2.2 Simulation of film crystal growth

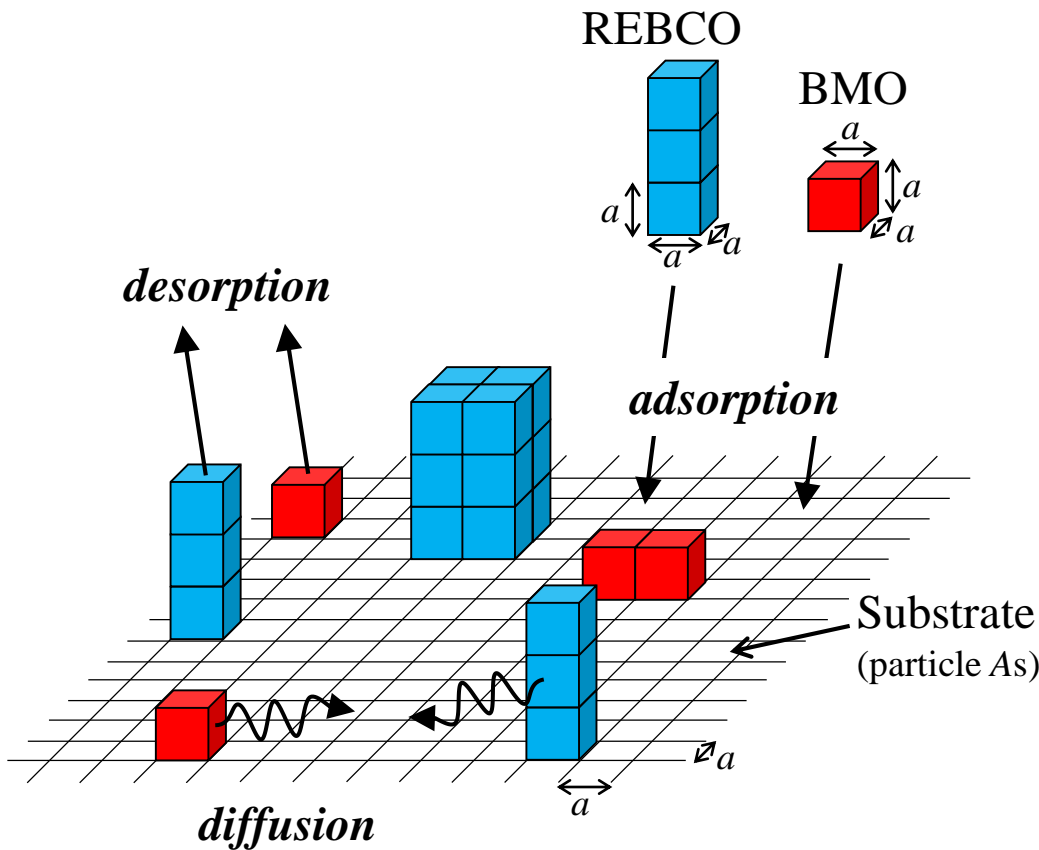


Fig. Schematic illustration of Monte Carlo events in our simulation. Two types of particles are used in this model. Substrate is consisted of REBCO particles.

- Coordination energies of the particles
 - Isotropic bond energy density
 - Counting bonds between the nearest neighbors

$$\Delta E = E_f - E_i \quad \begin{array}{l} E_i : \text{initial state} \\ E_f : \text{final state} \end{array}$$

- Particle motions
 - Two types of particles are deposited onto the substrate.
 - One of adsorption and diffusion motions is randomly chosen by a probability of R .

$$R = \frac{(\# \text{ of adsorp. in unit time})}{(\# \text{ of diffu. in unit time})} = \frac{Fa^2}{D/a^2} = \frac{Fa^4}{D} \quad \begin{array}{l} F: \text{incident flux [}/m^2s] \\ D: \text{diffu. const. [}/m^2/s] \end{array}$$

- Moving only to a nearest neighbor site.
- A desorption of a particle occurs a probability of $\exp(-E_{\text{des}}/k_B T)$.
- Periodic boundary conditions (x, y directions)

Coordination energy (bond energies)

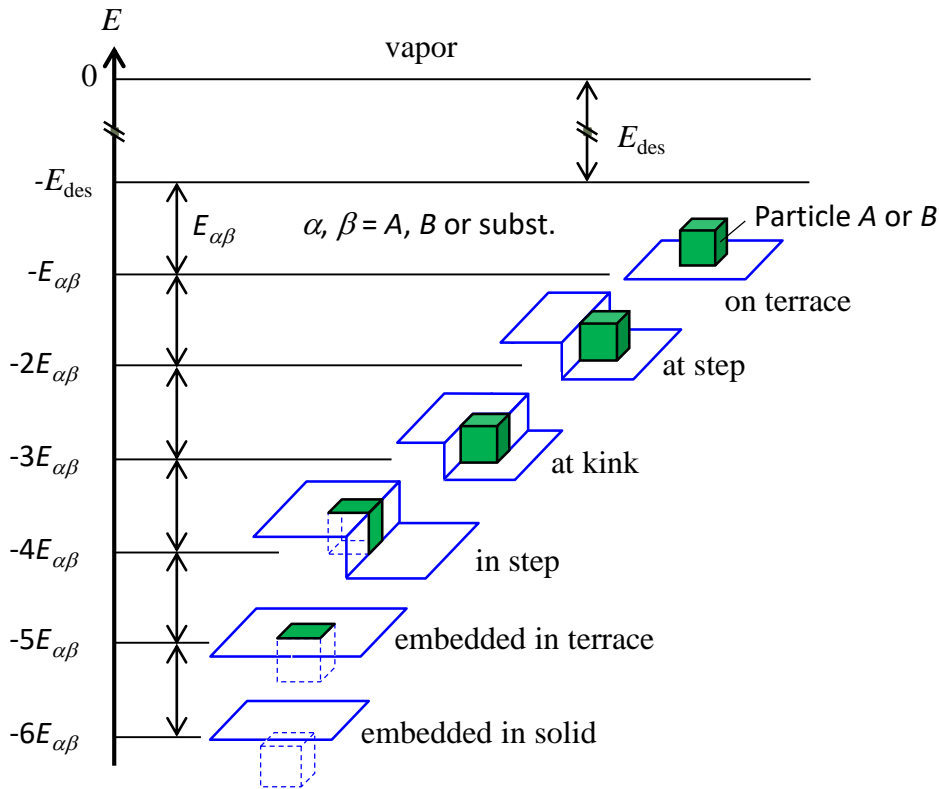


Fig. Energy state diagram of the adsorbed particles on the substrate.

Table Bonding energy densities per α^2 .

E_{AA} (A-A) 2,000 K

E_{BB} (B-B) 2,500 K

E_{AB} (A-B) 500 K

E_{AS} (A-subst.) E_{AA}

E_{BS} (B-subst.) E_{AB}

E_{des} 50,000 K

Table Simulation conditions

Diffusion const., D $\sim 10^{-13} - 10^{-11} \text{ cm}^2/\text{s}^*$

a 0.4 nm

Molar fraction of B 8.5 mol.% (3 vol.%)

Depo. rate, v_{dep} $10 \sim 3,000 \text{ nm/h}$

* B. Dam et al., Physica C 305 (1998) 1

➤ The coordination energies are calculated based on the bond-counting model.

3D Monte Carlo simulation (3D-MC)

$T_s = 1,193$ K

20 nm
(50 sites)

80 nm
(200 sites)

80 nm (200 sites)

step_0000000000000000434.csv

 REBCO
 BMO

Fig. Bird's-eye view of the BMO self-organization in REBCO. The REBCOs are shown transparent for ease of viewing.

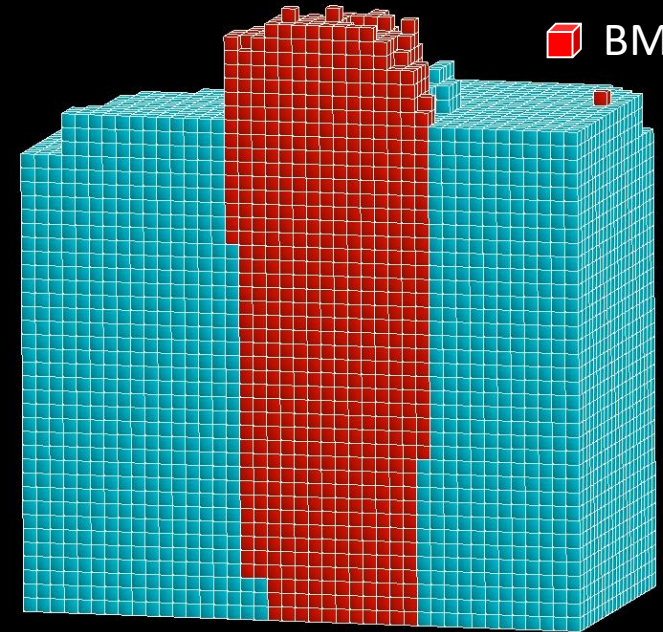


Fig. Enlarged and cross-sectional view of a single nanorod in the right movie.

- BMOs grow into 3D-island (VW mode) and REBCOs show SK mode.
- Top of BMO nanorods is always higher than a REBCO layer.
 - This result is consistent with experimental results

Substrate temperature dependence

- BMO volume fraction 3 vol.%, deposition rate 70 nm/h.
- The REBCOs are also shown transparent for ease of viewing.

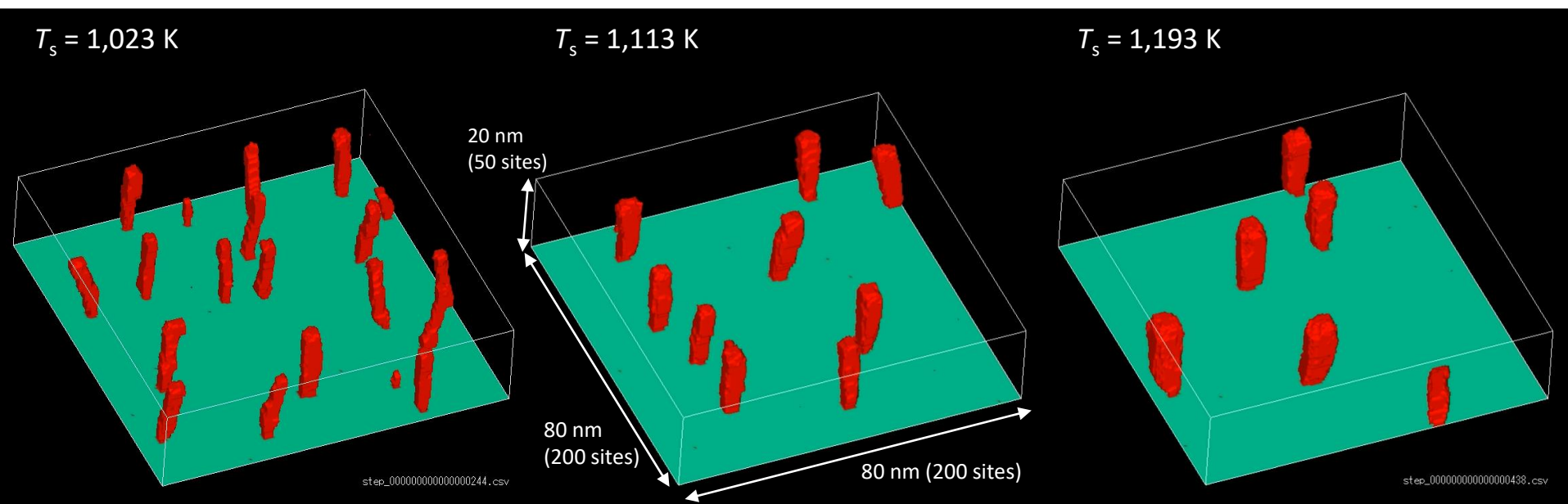
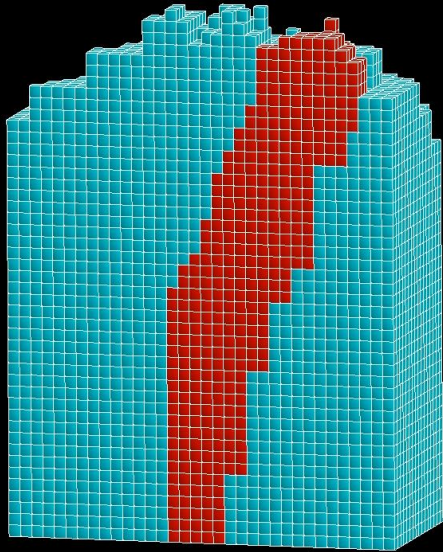


Fig. Simulation on self-organization of BMO nanorods at various growth temperatures.

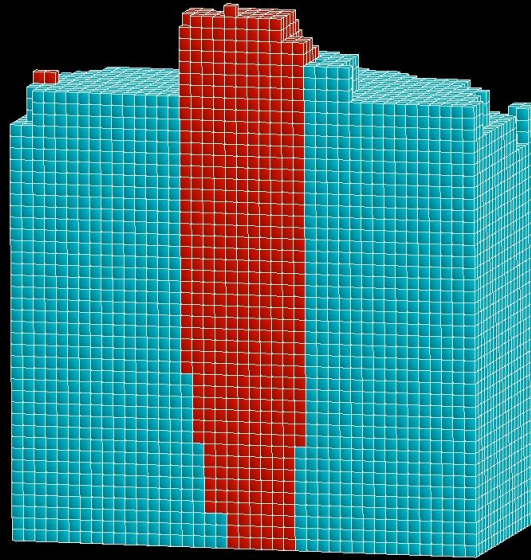
- 数密度は T_s の上昇に伴って減少。
- $T_s = 1,023$ Kでは、傾いたナノロッドが見られた。(実験結果と同様の傾向)
- 低い T_s では数密度高い分、ナノロッド一本当たりのBMO供給量が少なく、ナノロッド成長速度が遅い。→ 傾いたナノロッド

Substrate temp. dependence of nanorod shape

$T_s = 1,023 \text{ K} (R = 10^{-5})$



$T_s = 1,113 \text{ K} (R = 7 \times 10^{-6})$



$T_s = 1,193 \text{ K} (R = 2 \times 10^{-6})$

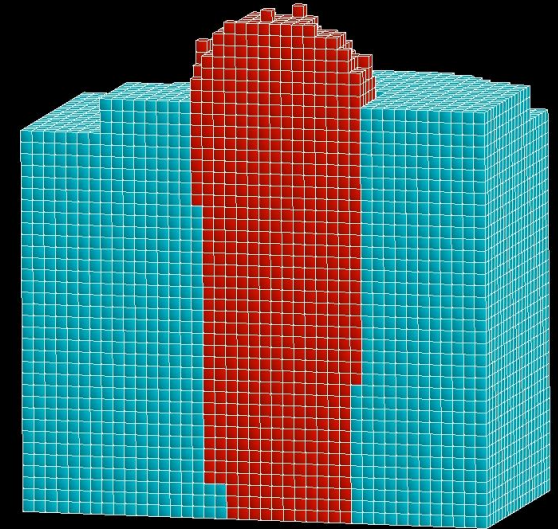
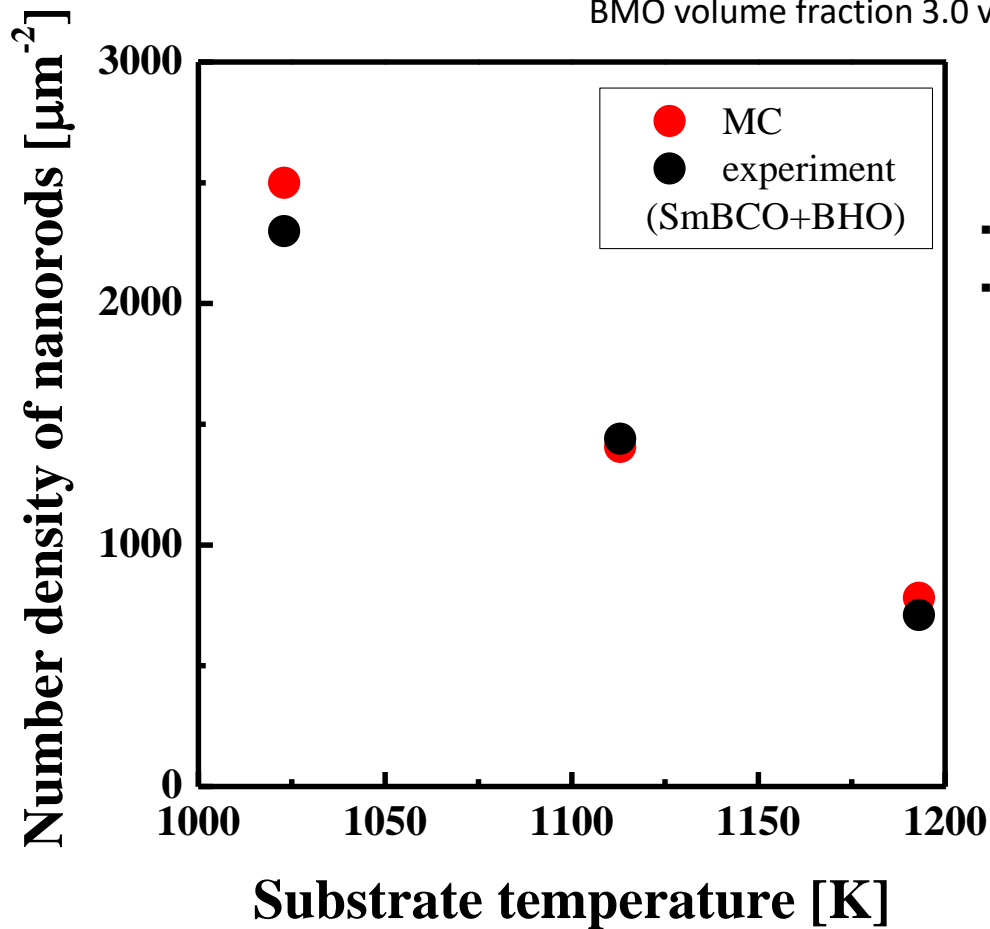


Fig. Enlarged and cross-sectional views of self-organization of BMO nanorods at various growth temperatures.

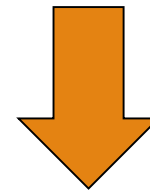
- T_s 高い場合: ナノロッド数密度が少ない分、一本当たりに供給されるBMO粒子数多い。
→ ナノロッドの3D島成長が速く、常にナノロッドの頭がREBCO層の上に出る。
- T_s 低い場合: ナノロッド数密度多く、一本当たりに供給されるBMO粒子少ない。
→ ナノロッドの3D島成長が遅い。REBCOによって成長が阻害され易くなる。
- $T_s = 1,023 \text{ K}$ の場合、ナノロッドの左側がREBCOステップによって覆われたため、ナノロッドが右側にしか成長できず、右側に傾いたナノロッドが形成された。

Comparison of simulation results with experimental results

BMO volume fraction 3.0 vol.%



- ・シミュレーションパラメータを最適化。
- ・数密度の T_s 依存性に関する実験データをシミュレーションで再現。

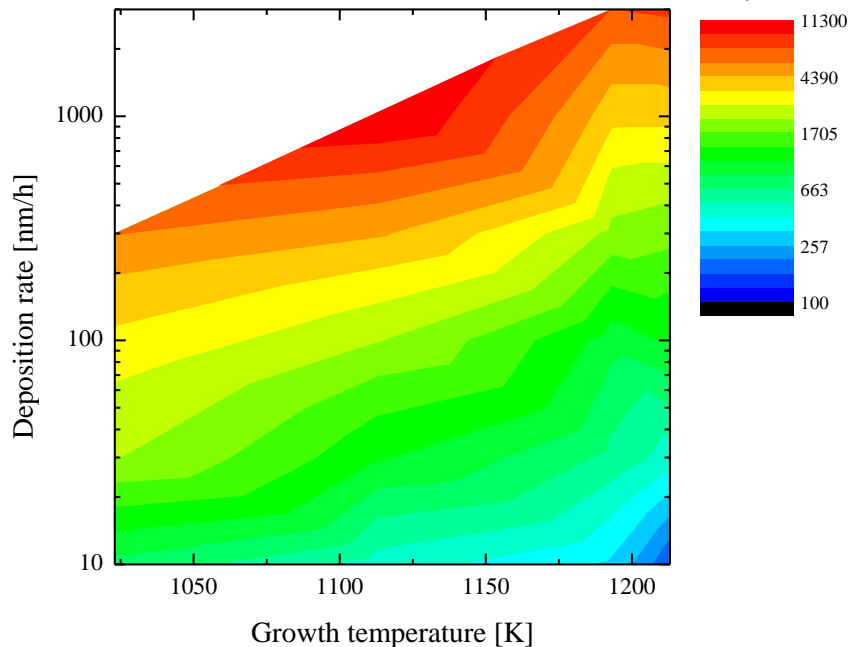


数密度やナノロッド形状に種々の成膜条件(基板温度、成膜レート、BMO添加量)が与える影響をシミュレーション

Fig. Number density of BMO nanorods as a function of substrate temperature.

Number density and shape of nanorods depending on T_s and deposition rate (BMO 3 vol.%)

(a) Contour plot of number density



(b) Phase diagram of nanorod shapes

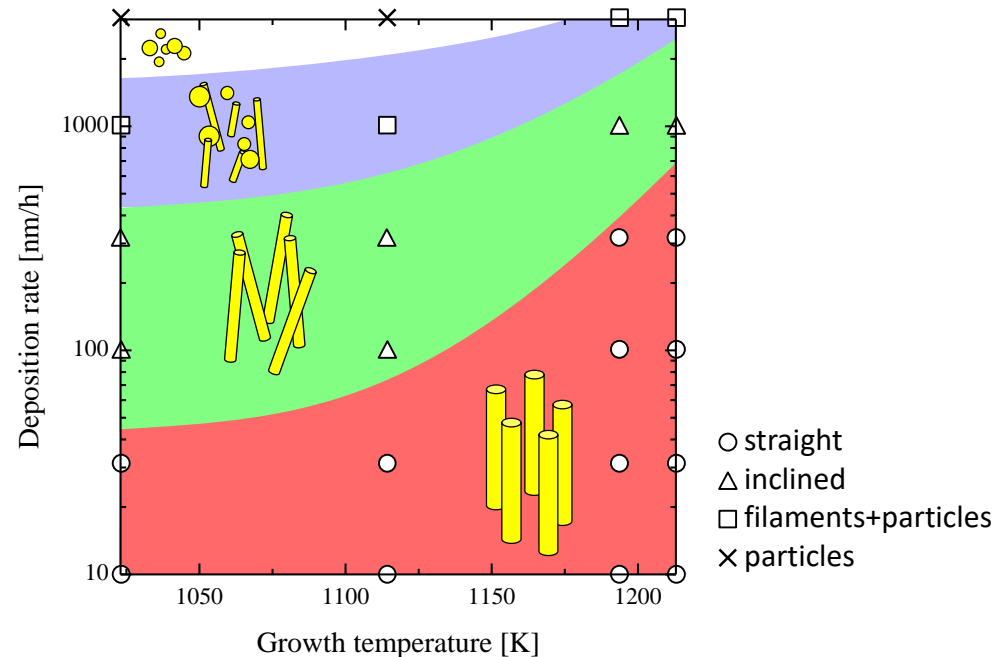
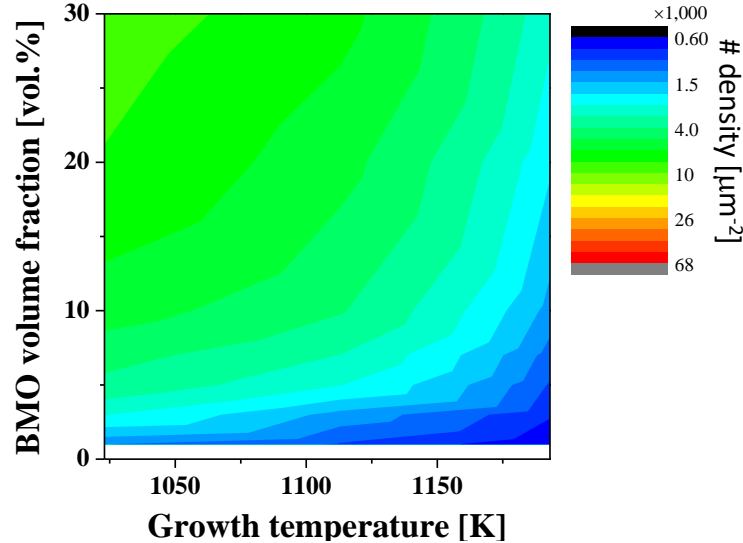


Fig. (a) Contour plot of number density and (b) phase diagram of nanorod shape depending on growth temperature and deposition rate.

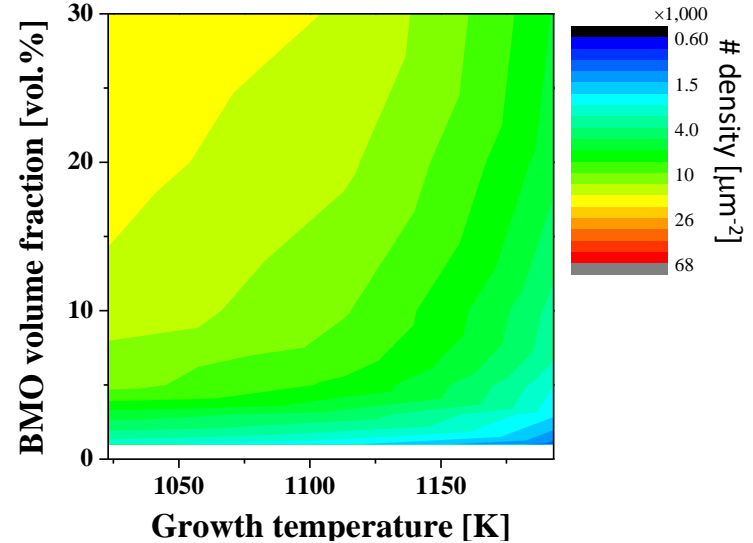
- 数密度は T_s の低下と成膜レートの増加に伴って増加。(直径は縮小。)
- 高い成膜レートと低い T_s ではナノロッドが十分に成長できない。その結果、多数のナノパーティクル(短いナノロッド)が生成。
- 低い T_s では、ナノロッド形状は成膜レートに比較的敏感。

Number density depending on growth temperature and BMO volume fraction

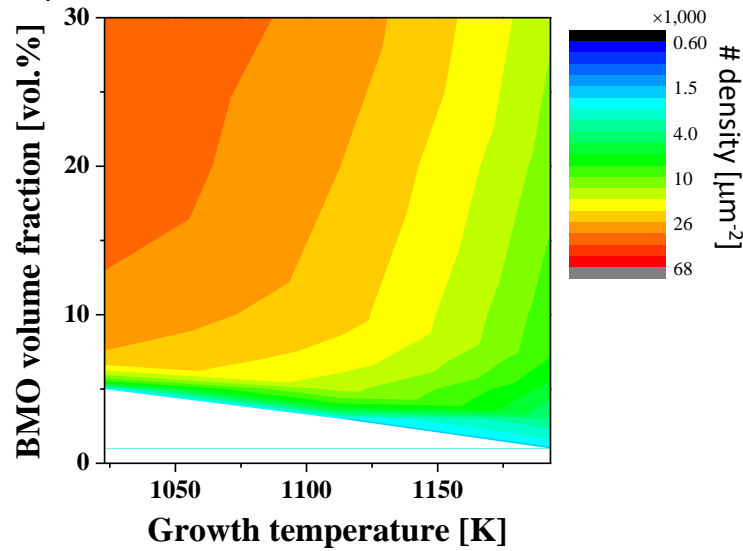
Depo. rate = 70 nm/h



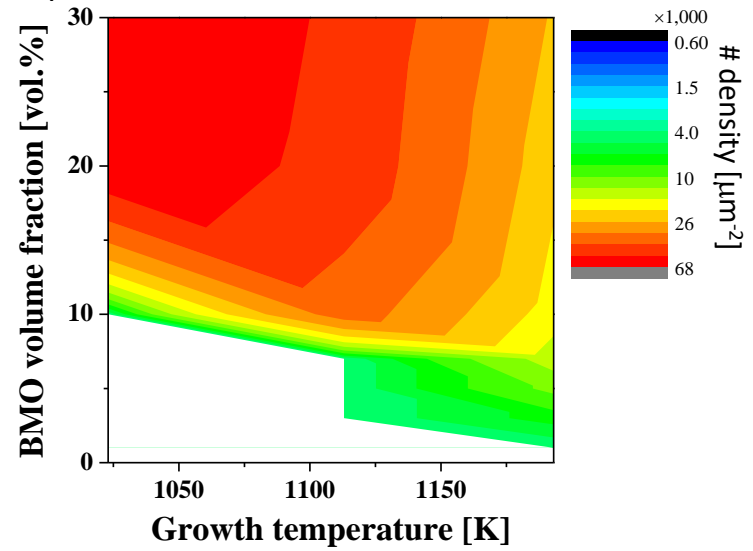
Depo. rate = 300 nm/h



Depo. rate = 1,000 nm/h

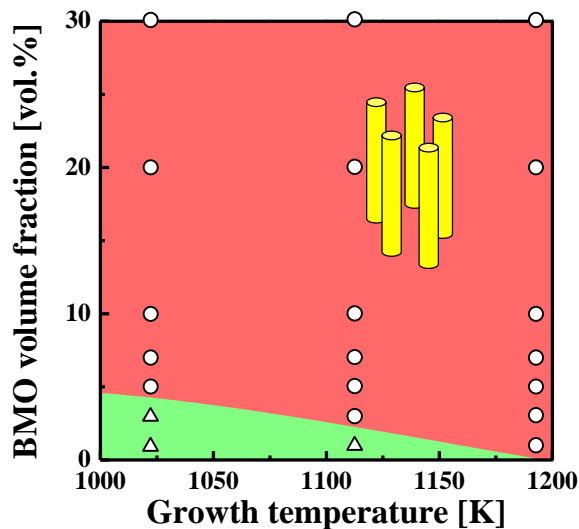


Depo. rate = 3,000 nm/h

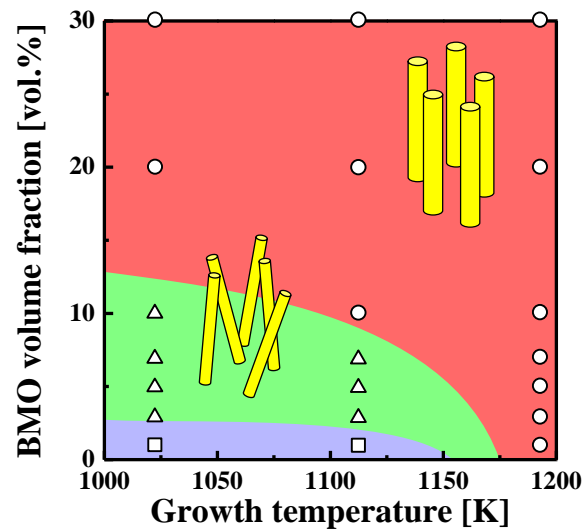


Nanorod shapes depending on growth temperature and BMO volume fraction

Depo. rate = 70 nm/h

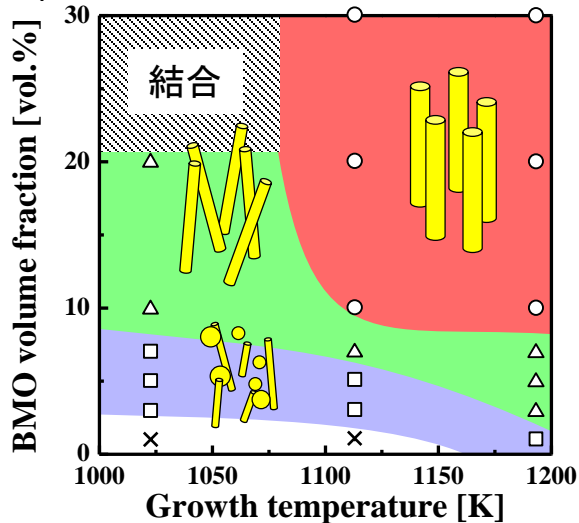


Depo. rate = 300 nm/h

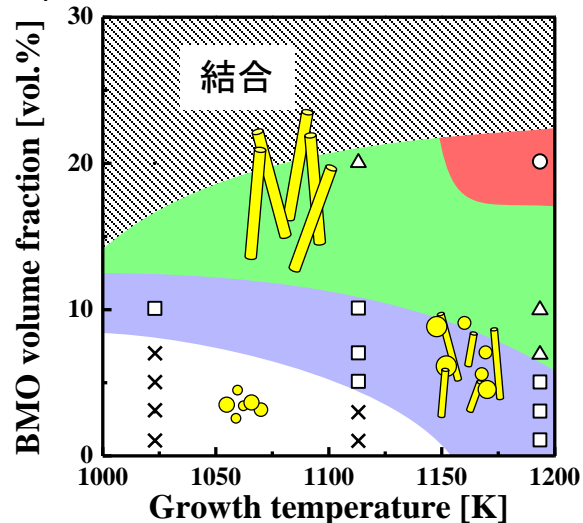


- Straight
- △ Inclined
- Filaments + particles
- × particles

Depo. rate = 1,000 nm/h



Depo. rate = 3,000 nm/h



3. Summary

Self-organized BMO nanorods in a REBCO film are markedly effective for enhancement of flux pinning.

3D Monte Carlo simulation was developed for revealing the BMO self-organization mechanism.

- Self-organization mechanism of BMO nanorods was revealed.
Difference of crystal growth modes between REBCO and BMO is important.
- Morphologies of the BMO nanorods are affected by deposition conditions such as growth temperatures, deposition rates and BMO volume fractions.
- From 3D-MC simulation, we made a contour plots of number density of BMO nanorods and phase diagrams on BMO shapes depending on
- the deposition conditions.

Thank you for your kind attention!