# *Phase-separation between conductive and insulative materials under the static electric field: Modeling for Ag and Sb spatiotemporal patterns on the electrode surface*


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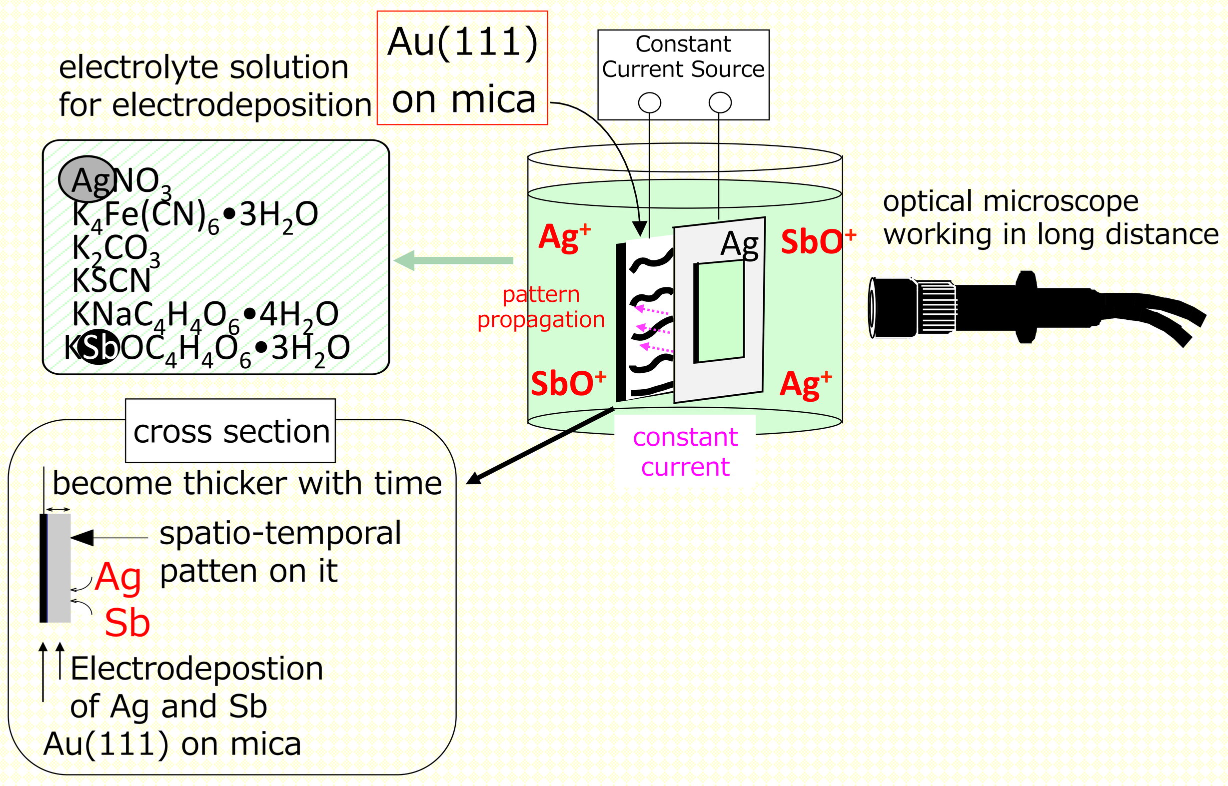
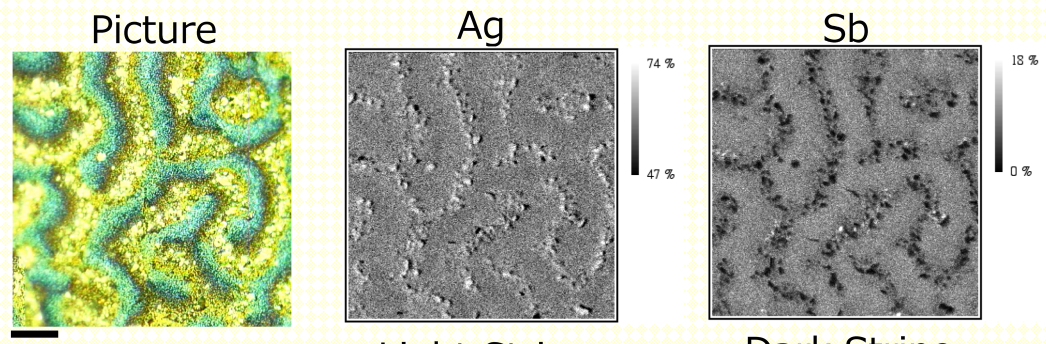
## I. Experimental setup




## II. Element analysis result

Y. Nagamine et al., Phys. Rev. E, 72, 016201 (2005).

For the complex labyrinthine structure

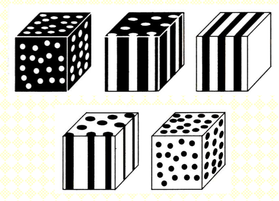



Spatial Separation for Ag and Sb ?

**Phase Separation ?**

## III. Academic meaning for phase separation under non-equilibrium system

Micro phase separation in Closed System

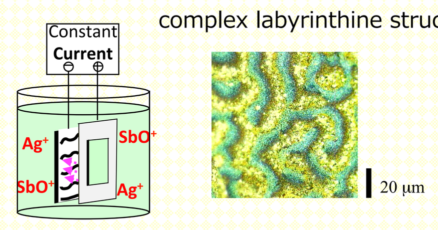


Dynamic pattern in the relaxation process

Stationary pattern in a steady state

No propagation

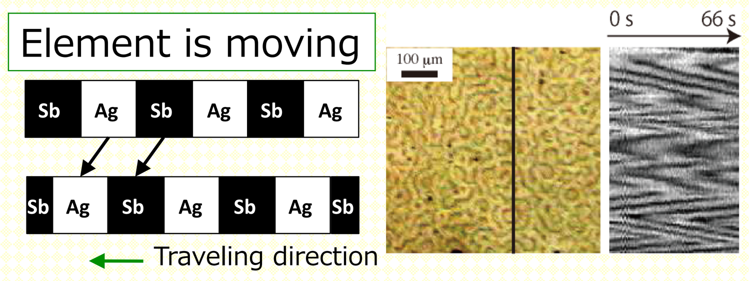
**Micro phase separation in Non-equilibrium System**




Propagation in a steady state

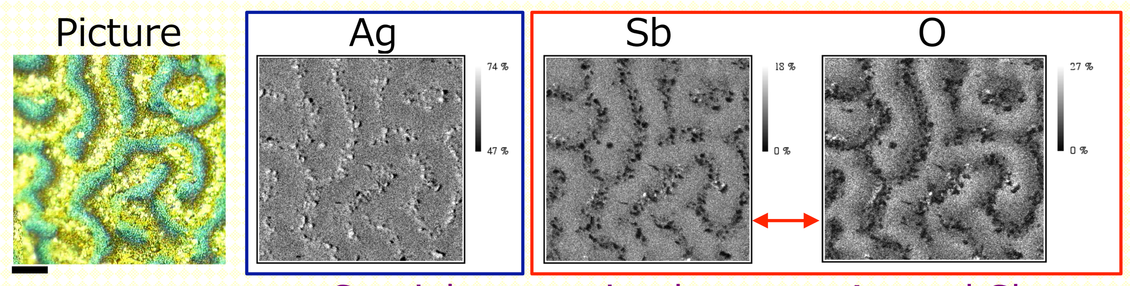
Dark stripe Sb, Light stripe Ag — Different element

Element is moving



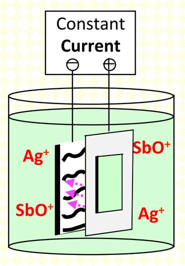

## IV. Characteristics of Ag/Sb pattern

Y. Nagamine et al., Phys. Rev. E, 72, 016201 (2005).




Spatial separation between Ag and Sb

| Conductivity | $63\times10^6\ \mathrm{m^{-1}\Omega^{-1}}$ | | $2.9\times10^6\ \mathrm{m^{-1}\Omega^{-1}}$ |
|---|---|---|---|
| | 25 | : | 1 |

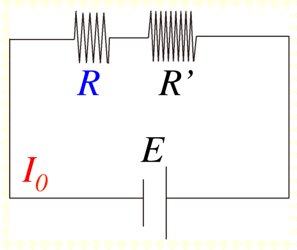


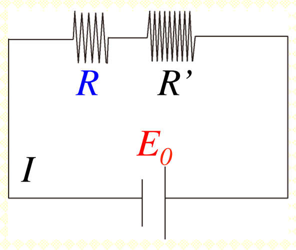
Ag $63\times10^6\ \mathrm{m^{-1}\Omega^{-1}}$ Conductor — **Phase Separation** — Oxidized Sb $\sim 0\ \mathrm{m^{-1}\Omega^{-1}}$ Insulator

The static electric field is applied

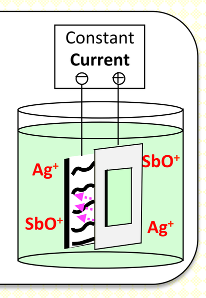
## V. Applied mode of static electric field

| Constant Current Mode | Constant Voltage Mode |
|---|---|
| $I_0$: Constant | $E_0$: Constant |



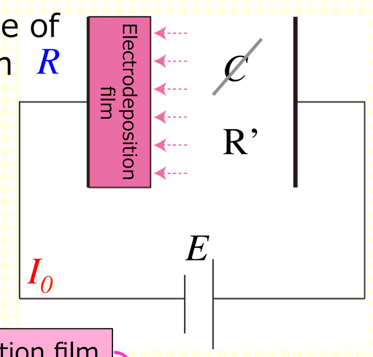




Constant Current $I_0$

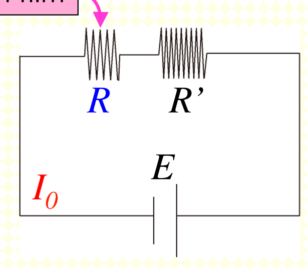


## VI. Elelctrodeposition system under constant current mode

Constant Current Mode — $I_0$: Constant




Electrodeposition film




Composition of electrodeposition film

| | Resistivity=1/Conductivity | Volume ratio |
|---|---|---|
| Material A | $R_A$ ( $f$ times larger) | 1 |
| Material B | $R_B$ | 1 |

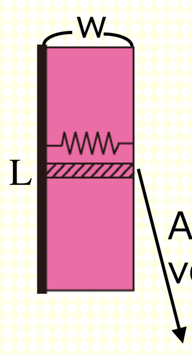
$R_A = f * R_B$

Resistance of the entire film $R$

## VII. Modeling for phase separation between conductor and insulator under the electric field

### VII-1. Qualitative calculation

Electro-deposition film — Homogeneous mixing condition — Phase separation condition




In-line calculation for local resistance in homogeneous mixing condition

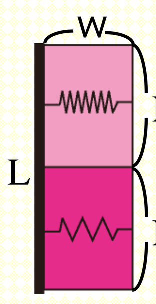
Assuming that material volume ratio is 1 : 1

$$\left(\frac{R_A+R_B}{2}\right)\times w$$

The entire resistance $R_{mix}$ is

$$R_{mix} = \left(\frac{R_A+R_B}{2}\right)\times w \Big/ L = \frac{f+1}{2} * (wR_0/L)$$

$R_A = f * R_B = f * R_0$




$L/2 \rightarrow R_A \times w/(L/2)$

$L/2 \rightarrow R_B \times w/(L/2)$

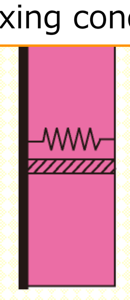
The entire resistance $R_{sep}$ is

$$\frac{1}{R_{sep}} = \frac{1}{R_A\times w/(L/2)} + \frac{1}{R_B\times w/(L/2)}$$

$$R_{sep} = R_A R_B w \Big/ (R_A+R_B)\left(\frac{L}{2}\right) = \frac{2f}{f+1} * (wR_0/L)$$

$R_A = f * R_B = f * R_0$

Homogeneous mixing condition



The entire resistance $R$ is

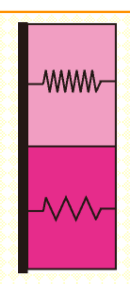
$$R_{mix} = \frac{f+1}{2} * (wR_0/L)$$

For example, if 100 is substituted into resistivity ratio $f$

$$R_{mix} = \frac{101}{2} * (wR_0/L) \approx 50 * (wR_0/L)$$

$$\Delta R = R_{mix} - R_{sep} = \frac{(f-1)}{2(f+1)} * (wR_0/L) \geq 0$$

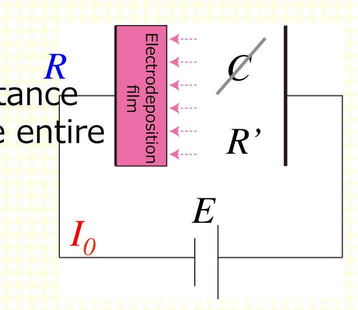
Phase separation condition



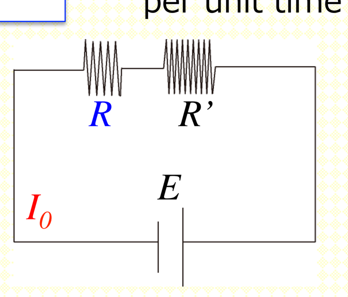
$$R_{sep} = \frac{2f}{f+1} * (wR_0/L)$$

$$R_{sep} = \frac{200}{101} * (wR_0/L) \approx 2 * (wR_0/L)$$

Resistance in phase separation condition is lower.

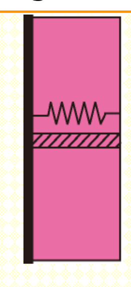



$W = RI^2$ — Consumption energy per unit time




constant current mode $I_0$ is constant

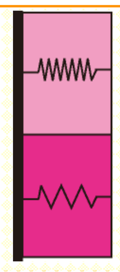
Homogeneous mixing condition



$R_{mix}$ — $W_{mix} = R_{mix} I_0^2$

∨ ∨

Phase separation condition



$R_{separation}$ — $W_{separation} = R_{sep} I_0^2$

Energetically, It is more stable.

### VII-2. Formulation for model

Free energy of the system

$$F(C(x)) = \int dx \left[\frac{\varepsilon^2}{2}(\nabla C)^2 + W(C)\right] + \boxed{\frac{1}{2}RI^2}$$

Term for conventional phase separation

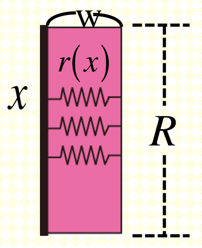
Onsager's variational principal

Term for conventional free energy [interface energy], or [internal energy and entropy]

consumption energy global coupling

Entire resistance

$$R = \left\{\frac{1}{\int \frac{1}{r(x)}dx}\right\}$$




$w \times \int C_A dx = Cons.$

$w \times \int C_B dx = Cons.$

$C_A(x) + C_B(x) = Cons.$

Local resistance

$$r(x) = A_0 \cdot (R_A \cdot C_A(x) + R_B \cdot C_B(x)) \times w$$

$A_0$ : Coefficient — $C_A, C_B$ : Concentrations of Materials A and B

$$F(C(x)) = \int dx \left[\frac{\varepsilon^2}{2}(\nabla C)^2 + W(C)\right] + \frac{1}{2}\left\{\frac{1}{\int \frac{1}{r(x)}dx}\right\} I^2$$

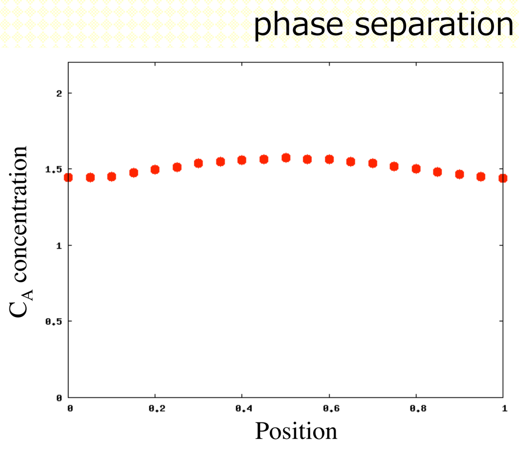
$$= \int dx \left[\frac{\varepsilon^2}{2}(\nabla C)^2 + W(C) + \bar{f}_1\right] \qquad \int \bar{f}_1 dx = \frac{1}{2}\left\{\frac{1}{\int \frac{1}{r(x)}dx}\right\} I^2$$

Extended Cahn-Hilliard equation

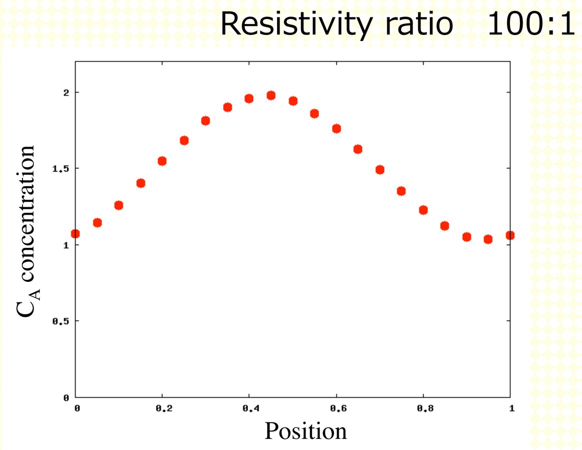
$$\frac{\partial C(x)}{\partial t} = L\nabla^2\left[-\varepsilon^2\nabla^2 C + \frac{dW}{dC} + \frac{d\bar{f}_1(C)}{dC}\right]$$

$$= L\nabla^2\left[-\varepsilon^2\nabla^2 C + \frac{dW}{dC}\right] + L\nabla^2\frac{d\bar{f}_1(C)}{dC}$$

| Conventional Cahn-Hilliard equation | Extended Cahn-Hilliard equation |
|---|---|
| $\frac{\partial C(x)}{\partial t} = L\nabla^2\left[-\varepsilon^2\nabla^2 C + \frac{dW}{dC}\right]$ | $\frac{\partial C(x)}{\partial t} = L\nabla^2\left[-\varepsilon^2\nabla^2 C + \frac{dW}{dC}\right] + L\nabla^2\frac{d\bar{f}_1(C)}{dC}$ |
| Conventional phase separation | Consumption energy, Resistivity ratio 100:1 |



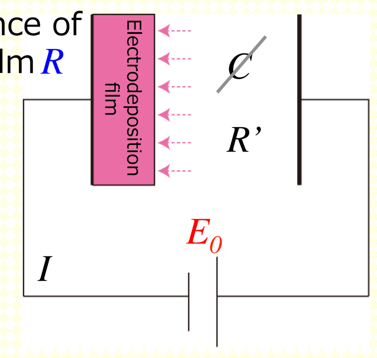

On 4000th step, phase separation does not start yet.

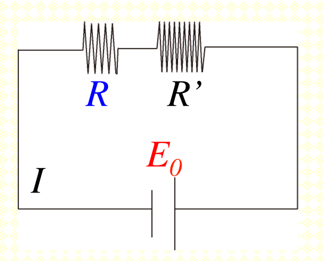



On 4000th step, phase separation has already started.

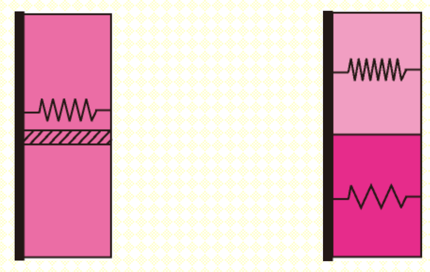
### VII-3. Comparison with constant voltage mode

Constant Voltage Mode — $E_0$: Constant




Homogeneous mixing condition — Phase separation condition



$$R_{mix} = \frac{f+1}{2} * (wR_0/L) \qquad R_{sep} = \frac{2f}{f+1} * (wR_0/L)$$

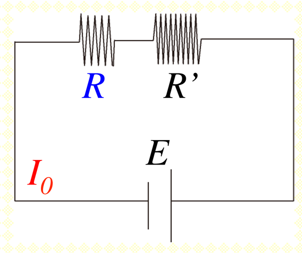
Resistance becomes lower

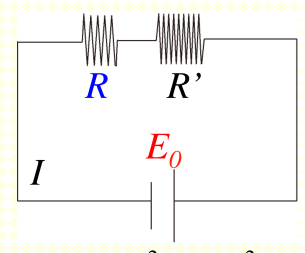
Consumption energy

$$W = RI^2 = R\left(\frac{E_0}{R}\right)^2 = \frac{E_0^2}{R_{mix}} \leq \frac{E_0^2}{R_{sep}}$$

Energy increases

| Constant Current Mode | Constant Voltage Mode |
|---|---|
| $I_0$: Constant | $E_0$: Constant |

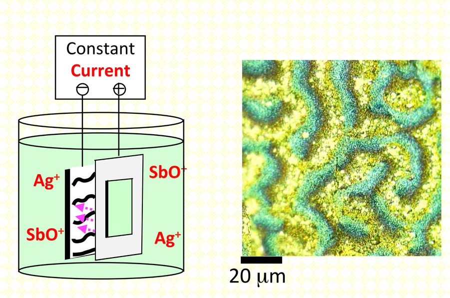


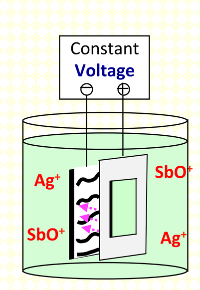

| $W = R_{sep}I_0^2 \leq R_{mix}I_0^2$ | $W = \frac{E_0^2}{R_{sep}} \geq \frac{E_0^2}{R_{mix}}$ |
|---|---|
| If phase separation occurs, consumption energy decreases. | If phase separation occurs, consumption energy increases. |

**Phase separation is energetically more stable under constant current mode**

Phase separation is stable.




Emergence




No Emergence