Colliding Spiral Waves Propagating on the Electrode

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Spiral waves consisted of deposited Ag and Sb were propagating two-dimensionally on a copper electrode surface while the electrochemical co-deposition of the metals was proceeding. A time course of this electrochemically driven wave-propagation was phenomenologically similar to the one driven by a homogeneous non-linear reaction in Belousov-Zhabotinsky (BZ) reaction-diffusion medium. The Ag/Sb co-deposition also formed a layered structure in the depth, finally it made a 3-dimensional super-structure on the electrode.

The non-linear chemical reaction such as BZ reaction forms a spatial pattern (the spiral waves) as well as a temporal pattern (the alternative color change in the solution).[1] The spiral waves observed in the non-stirred BZ solution are one of the most famous pattern produced spontaneously by a chemical reaction.[1,2] The self-sustained spatial pattern formation is interesting because it has the potential to be the new synthetic method for producing a periodic functional structure such as a super-lattice[3] and a photonic crystal.[4] In order to form a specific self-assembled super-structure, we believe it is important to examine a non-linear electrochemical reaction, especially in the cathodic domain. Historically, the non-linearity in the electrochemistry has been well studied in the anodic domain; for example, a metal dissolution accompanied by an oxide film formation.[1,5-7] However, the anodic process is usually unable to form the specific structure because the electrode itself is going to disappear at the end. In this article, the cathodic non-linear electrochemical metal co-deposition reaction[8] was studied, and it formed a three dimensional super-structure in the deposited film.

The composition of an aqueous electrolyte in which the spiral waves were deposited was shown in Table 1.[9] Three electrodes were dipped in this solution; the working electrode was a mirror-polished polycrystalline copper plate and the counter and the reference electrodes were silver plate and the SCE, respectively. The electrolysis was conducted under the constant current condition; -21 ~ -25 mA/cm^2. The reacting surface was magnified by a microscopic optics, Mitutoyo Mplan NUV-20, and recorded by a CCD camera, SONY KV-6AD3. Only when the working electrode was set vertically in the solution, the pattern was obtained. Then, the surface of the electrode was observed in the horizontal direction. The surface structure of the deposited film was analyzed by a spatially resolved X-ray photoelectron spectroscopy (ESCA), Vacuum Generator (VG) ESCALAB250. The ESCA analysis revealed that the white area on the optical image is made of the deposited Ag and the black one is of the Sb. The electrode on which the deposited metallic film had been formed was sliced its depth structure was observed by the optical microscope.

Table 1. Compositions in an aqueous electrolyte for pattern formation of silver-antimony co-deposition

	Solution / mol dm^{-3}
$AgNO_3$	0.15
$K_4Fe(CN)_6 \cdot 3H_2O$	0.17
K_2CO_3	0.22
KSCN	1.5
$KNaC_4H_4O_6 \cdot 4H_2O$	0.21
$KSbOC_4H_4O_6 \cdot 0.5H_2O$	0.04

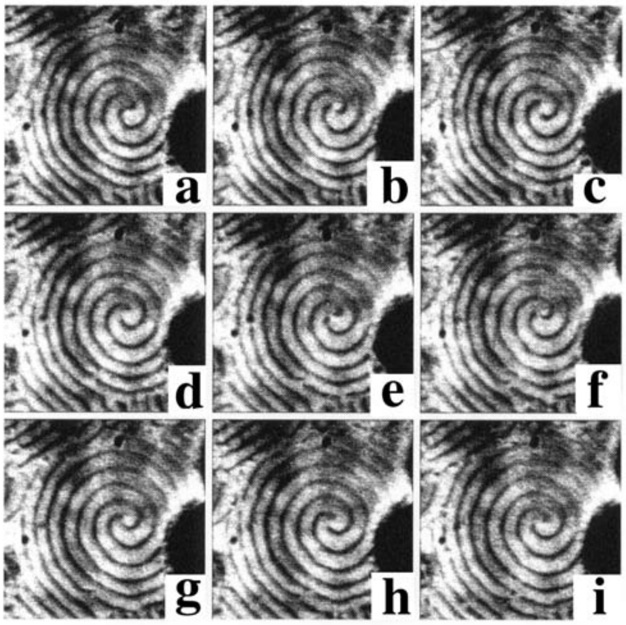

Figure1. Time course of the spiral wave propagation on the electrode.

The time evolution of the propagating spiral waves was shown in Figure 1, in which each picture was sequentially taken from (a) to (i) with the constant time intervals of 5 s. The size of the pictures in Figure 1 was 100 µm × 100 µm. An angular rotation velocity of the spiral wave was about 8 deg/s, which was not changed (neither accelerated nor decelerated) within the observed time period. The deviation of the angular rotation velocity on several spirals was within less than 10%. The center of the spiral wave was not moved spatially within the observation time period.

The collision of the two propagating spiral waves was obtained in Figure 2 (A). The time interval between the pictures was 5 s and the size of the picture was 100 µm × 100 µm. The two arms of the spiral waves were collided at the centers of the pictures. Schematically, the time course of the waves

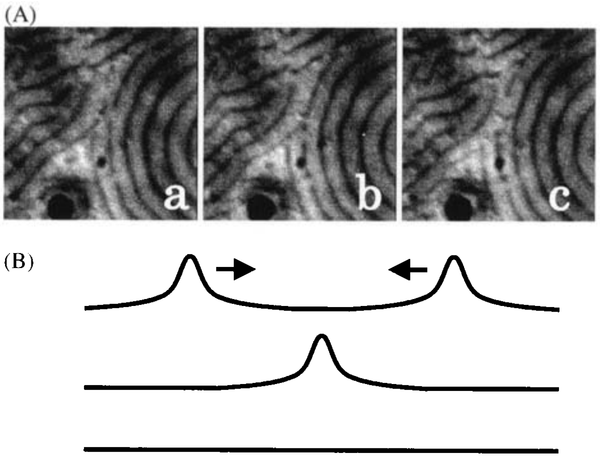

Figure 2. Collision of the spiral waves, (A), and schematic representation of the collision, (B).

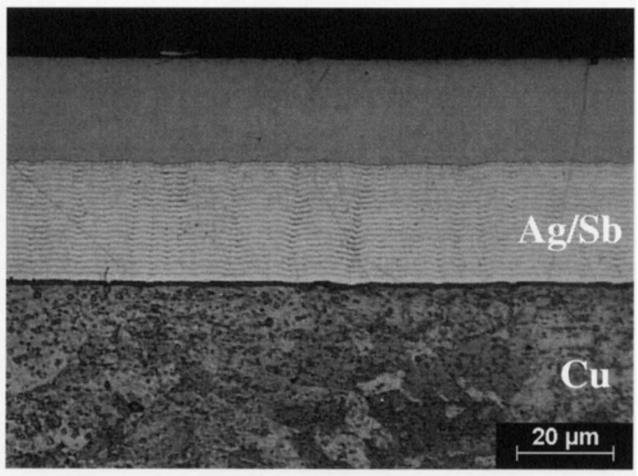

Figure 3. Depth profile in the deposited film.

before and after the collision was shown in Figure 2 (B). In the conventional collision of a couple of the linear waves, the time course can be traced simply by adding the two waves, which was not observed in Figure 2. Actually, both of the traveling waves disappeared after the collision. This is a typical colliding behavior of the non-linear waves observed in the homogeneous non-linear chemical medium.[1,2,10]

The wave propagation on the electrode was identical with the one observed in the BZ reaction medium.[1,2,10] Much has been reported about the mechanism for the spiral wave formation in the homogeneous medium.[1,2,10] These waves are described by the reaction-diffusion scheme as shown in the set of differential equations below,[2,10,11]

$$\partial \boldsymbol{A} / \partial t = \mathrm{F}(\boldsymbol{A}) + D_m \nabla^2 \boldsymbol{A}$$

where $\boldsymbol{A}$ is the vector of the concentration of the chemical species involved in the reaction. t represents the time. $\mathrm{F}(\boldsymbol{A})$ shows the reaction rate equation. D_m is the matrix of the diffusion constants of the reactants. The spatial change in the concentrations by the diffusion is shown by $D_m \nabla^2 \boldsymbol{A}$. The spiral waves, their propagation and the collision are intrinsically able to be reproduced by the equation above.[2,10,11] In this scheme, the spatial pattern formation is qualitatively explained by the competition between the explosive evolution of a certain chemical species (an activator) by the auto-catalytic process and the deceleration of the reaction by an inhibitor. The inhibitor is simultaneously produced by the auto-catalytic process. If it diffuses more quickly than else, it is spatially accumulated around the reaction center by the diffusion. Thus, the reaction proceeds heterogeneously in the space and the spatial pattern is producing.

However, at this stage, there is no candidate for the activator and inhibitor in the Ag/Sb electrochemical co-deposition. Then, the reaction mechanism seems to be different from the reaction-diffusion scheme. Figure 3 shows the side view of the deposited film on the electrode. The alternative accumulation of Ag and Sb was observed in the layered structure. At this moment, we have found a couple of keys to investigate the non-linearity of the reaction; (1) the formation of 2-dimensional Sb cluster needs a relatively large activation over-potential ca. 200 mV and (2) the liquid flows close to the electrode surface which is induced by the density decreasing accompanied by the deposition of the metal ions. Both of them are indispensable for the pattern formation. The numerical modeling to this non-linear electrochemical reaction is on going in this laboratory.

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