

Stripe pattern formation in Ag/Sb co-electrodeposition

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Keywords: pattern formation; Turing instability; spiral pattern; Fourier power spectrum

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Transient changes in surface morphologies of Ag-Sb electrodeposits have been studied using a laser scanning confocal microscope. Measurements of the potential and current density in Ag-Sb electrodeposition reveal that the stripe pattern of the Ag-Sb electrodeposits emerges at the initial stage according to an experimental condition related to a necessary condition for the Turing instability in reaction-diffusion systems. In addition, pattern instabilities in this system give rise to a variety of patterns such as hexagonal patterns, stripe patterns with dislocations, and a small spiral emitted from a large spiral pattern. Their geometrical characteristics are similar to those of Turing pattern in reaction-diffusion systems, which result suggests that the patterns observed in this system are a kind of Turing pattern formed on the solid surface.

1. Introduction

Spatial patterns¹⁻² found in physical, chemical and biological fields have received considerable attentions. Among them, Turing pattern that has been investigated experimentally³ and theoretically⁴ is a good candidate for the mechanisms of pattern formation due to the diffusion-driven instability. Linear instability analysis applied to the Turing instability in reaction-diffusion systems leads a necessary condition for the Turing instability, which is often referred to as local activation and long range inhibition⁵. Experimental observations in diffusion-reaction systems with the famous chlorite-iodide-malonic acid (CIMA)³ and Belousov-Zhabotinsky (BZ)⁵ reactions have mainly been presented.

On the other hand, recent progress in surface morphologies of electrodeposits exhibits the presence of characteristic patterns in Ag-In⁶ and Ag-Sb⁷⁻⁸ electrodeposits as well as spiral patterns in CIMA and BZ reactions. However, there have been very few quantitative investigations into the transient pattern formation of electrodeposits.

In this paper, we present new experimental results on pattern formation of Ag-Sb thin films electrodeposited on copper substrates. First, a potential impulse expressed by a step function is applied across electrochemical circuits, and the current density passing through the electrochemical cell in Ag-Sb electrodeposition is recorded. Experimental conditions in which the stripe patterns emerge are examined with a laser scanning confocal microscope. Fitting an analytical solution of electrode reactions to the measured current density-time curves, we determine the ratios of the kinetic constants to diffusion coefficients, which ratios are discussed in view of the Turing instability condition in reaction-diffusion systems. Secondly, instabilities of the time-series patterns formed on the Ag-Sb electrodeposits are investigated. It is found that the patterns in Ag-Sb electrodeposition have the same structures as Turing pattern⁹⁻¹¹. Pattern formation observed in this system will lead one to the conclusion that the patterns of Ag-Sb electrodeposits are a kind of Turing pattern formed on the solid surface.

2. Experimental setup

Experiments were performed in an electrolyte that includes the following components (g/l): AgNO_3 , 25.5; $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, 72; KSCN , 146; $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, 59.3; $\text{C}_8\text{H}_4\text{K}_2\text{O}_{12}\text{Sb}_2 \cdot 3\text{H}_2\text{O}$ (APT), 6.7, 10 and 13.3; K_2CO_3 , 31.3. The mixed solution of AgNO_3 , K_2CO_3 and $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, which solution was boiled for 30 minutes and yielded burnt umber precipitates of iron hydroxides. After removal of the iron hydroxide, the remaining components were added into the solution.

Poly-crystalline copper and carbon plates of 20 mm long and 10 mm wide were prepared for working and counter electrodes, respectively. The copper substrates of 99.9 wt% purity appear to be mirror-like. These electrodes cleaned by a wet process were located parallel in a still cell including the chemical compositions mentioned above. A potential step was applied across the electrochemical cell. Transient current (potential)-time curves passing through the cell maintained at 300K were recorded using a digital oscilloscope. The applied potential was in a range of 0.75-0.9V.

The surface morphologies were observed with a laser scanning confocal microscope and analyzed using the digitized microscope surface images with a resolution of 780x564 pixels.

3. Results and Discussion

Typical microscope images of Ag-Sb surfaces electrodeposited for 120-2100 sec from the electrolyte including 6.7g/l APT are shown in Fig.1. The surface image in Fig.1 (b) seems to be stripe patterns that comprise bright and dark regions. The observed patterns are very similar to the patterns produced by computer simulations^{2,12} based on the reaction-diffusion systems.

3. 1. Characteristic of pattern formation in time domain

Microscope images of Ag-Sb electrodeposits at four different deposition times are shown in Fig.1, which images are obtained by ex situ optical observation.

Linear instability analysis^{1,5} of the reaction-diffusion systems gives us a condition of bifurcation for pattern formation. The conclusions led by the linear instability analysis are that (1) pattern formation in chemical systems including at least two interacting chemicals occurs if their diffusion coefficients differ,

and (2) diffusion destabilizes chemical systems at a particular wave length. For activator-inhibitor systems including two reaction species, a necessary condition for the Turing instability that is referred to as local activation and lateral inhibition is derived,

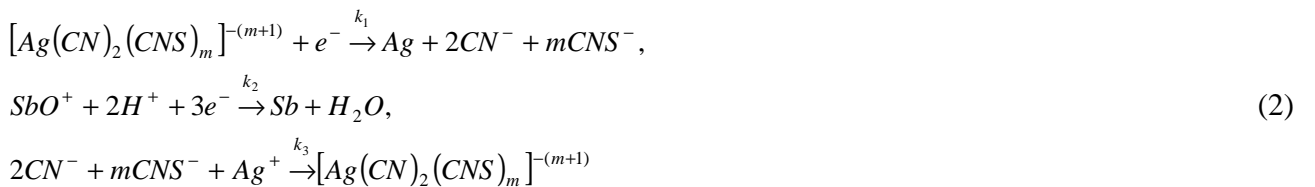
$$D_2 / D_1 > |k_{22} / k_{11}|, \quad (1)$$

where D_1 and D_2 are the diffusion coefficients of the activator and the inhibitor, and k_{11} and k_{22} are the reaction rates for the activator and the inhibitor, respectively. This indicates that the diffusion coefficients D_1 and D_2 should not have anisotropic values but different values that exceed the ratio $|k_{22}/k_{11}|$.

In order to gain insights into an experimental condition for pattern formation in Ag-Sb electrodeposition, we need to determine the ratios of the kinetic constants to the diffusion coefficients of Ag and Sb ions. In the next section, these quantities will be shown to be obtained from measurements of transient current density-time curves and analytical solutions of electrode reactions near cathode electrodes.

3.2 Onset of pattern formation

We have already reported¹³ in detail the existence of a formula for a rate constant and diffusion coefficient in Ag-Sb stripe pattern formation, which relationship is derived from the experimental results. Here, we briefly describe the method for deriving the formula from the experiments in Ag-Sb co-electrodeposition. The electrochemical reactions in Ag-Sb electrodeposition are considered to proceed along the following reactions, which are often presented in the literature^{14,15},



where k_i is the rate constant and m has a value ranging from 1 to 2.

As the concentrations of Ag^+ , CN^- and CNS^- are sufficiently high, the concentration change of the Ag complexing agent, C_1 at the distance between x and $x+dx$ from the cathode electrode located at $x=0$

can be approximated as $\partial C_1 / \partial t = k'_3$ where k'_3 is a constant. Hence the total changes of the concentrations and the boundary conditions in one dimension are given by

$$\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2} + k'_3, \quad (3)$$

$$\frac{\partial C_2}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial x^2}, \quad (4)$$

$$D_i \frac{\partial C_i}{\partial x} = k_i C_i, \text{ at } x=0 \text{ and } i=1,2 \quad (5)$$

$$C_i(x,0) = C_i^o, \quad C_i(\infty, t) = C_i^o. \quad i=1, 2 \quad (6)$$

where C_2 is the concentration of SbO^+ ions, D_i is the diffusion coefficient and C_i^o is the equilibrium concentration. The current density i is equal to the number of ion flux,

$$i = \sum_{j=1}^2 n_j F D_j \frac{\partial C_j}{\partial x} \Big|_{x=0}, \quad (7)$$

where n_j is the number of electrons transferred per ion and F is the Faraday's constant. Using the Laplace transform, the solution that satisfies Eqs. (3)-(7) is given by

$$\frac{i}{i_o} = \frac{F}{i_o} \sum_{j=1}^2 n_j k_j C_j^o e^{\left(\frac{k_j}{\sqrt{D_j}}\right)^2 t} \operatorname{erfc}\left(\frac{k_j}{\sqrt{D_j}} \sqrt{t}\right) + \frac{n_1 F k_1 k'_3}{i_o} \int_0^t e^{\left(\frac{k_1}{\sqrt{D_1}}\right)^2 \theta} \operatorname{erfc}\left(\frac{k_1}{\sqrt{D_1}} \sqrt{\theta}\right) d\theta, \quad (8)$$

where $i_o = \sum_{i=1}^2 n_i F k_i C_i^o$ and erfc is the complementary error function.

A plot of the normalized current density vs the deposition time is shown in Fig.2. As can be seen, the experimental data can be well described by Eq. (8). Thus, the parameter characterizing the kinetics of electrode reactions, $k_i / \sqrt{D_i}$ is determined from the current density-time curves. Fig.3 gives

$$\sqrt{\frac{D_2}{D_1}} \approx 5 \frac{k_2}{k_1}. \quad (9)$$

This relation is similar to Eq. (1) required for the Turing instability that causes pattern formation. Unfortunately, the experimental values of k_i are unknown. However, since EPMA measurements indicate that the mole fraction of Ag to Sb in the electrodeposits is nearly equal to that in the electrolyte,

we may approximately set $k_1 \approx k_2$. In such a case, Eq. (9) seems to be consistent with a condition required from linear stability analysis of the reaction-diffusion systems. But it is noted that the Ag-Sb electrodeposition system is not equivalent to the activator-inhibitor system. Anyway, the experimental condition for the onset of pattern formation in Ag-Sb electrodeposition is obtained.

3.3 Properties of patterns at the middle stage (180-1320 seconds in Fig.1)

Fig.4 shows the stripe pattern electrodeposited at 480 sec and its Fourier power spectrum. Fig.4 (a) is a typical image observed at the middle stage. It can be seen from Fig.4 (b) that one bright but somewhat blur ring appears and one mode of a wave number exists. This indicates that the stripe patterns have isotropic and periodic properties in real space, i.e., that there exist the rotational symmetry and one wave number characterizing the stripe patterns. If some convection affects the formation of the patterns, some anisotropic pattern such as an array of the dark stripes will appear in real space. In the case, the Fourier power spectrum of the stripe pattern shows bright points or lines. However, at the middle stage, the Fourier power spectrum in this experiment shows only one bright ring. Hence, even if some convection occurs, convection does not affect the formation of the stripe patterns at the middle stage.

3.4 Pattern structure caused by instabilities

In our experiments, left-handed and right-handed spirals of Ag-Sb electrodeposits are formed on substrates at a growth time of 1320 seconds. Fig.5 shows two left-handed spirals, which have the same center site and their phase difference of π . The shape of the spirals is Archimedean best described in polar coordinates (r, θ) ,

$$r = \frac{p(\theta - \theta_0)}{2\pi}, \quad (10)$$

where p is the pitch of the spiral, in this case $p = 16 \mu m$, and $\theta_0 (\leq \theta)$ is the angle of the spiral with respect to a reference axis.

Pattern instabilities that appear in BZ reactions have been reported theoretically and experimentally. It is known that the patterns in BZ reactions break owing to some causes such as the presence of defects¹¹ generating in reactions, Echhaus instability¹⁶ that causes a compression or dilation of patterns and a perturbation by a periodical external force. For example, stripe patterns with dislocations, hexagonal patterns, and breaking of spirals are observed in BZ reactions. However, at present, we have no obvious answer to what causes the pattern instability.

In this experiment, the pattern instabilities are observed at a growth time of 1320 sec as shown in Fig.6. Stripe patterns with dislocations designated as A and hexagonal patterns in the Region B can be seen in Fig.6 (a), which images show intricate mixed patterns. Fig.6 (a) appears that the stripes are higher than the remaining area. However the surface is smooth within a roughness of $0.1\ \mu m$ according to the measurement with the laser scanning confocal microscope. Breaking of a spiral pattern that emits a small spiral is observed in Fig.6 (b). These patterns that indicate the pattern instabilities do not appear at the middle stage. Only stripe pattern shown in Fig.1 (b) and Fig.4 (a) are dominant at the middle stage. Fig.6 (c) shows the Fourier power spectrum of Fig.6 (a) that indicates the presence of two blur points near the origin. This means that there in real space exist the patterns perpendicular to the line that connects the capital letter D to E. In fact, the array of lines can be seen in Fig.6 (a). Hence, the stripe patterns have an anisotropic property in real space in contrast with the stripe patterns formed at a shorter time than 1320 sec.

The patterns observed in this experiment have the same geometrical characteristic as Turing pattern in the reaction-diffusion model. Hence, the patterns formed on Ag-Sb electrodeposits can be considered a kind of Turing pattern formed on the solid surface.

Conclusions

We have investigated into the transient changes in the stripe patterns of Ag-Sb thin films electrodeposited in the aqueous electrolyte. The measurements of the current density for the impulse potential in electrodeposition reveal the experimental condition of the onset of patterns formation,

which can be related to the necessary condition for the Turing instability in reaction-diffusion systems. The changes of patterns in this experiment imply a kind of Turing pattern formed on the solid surface because the hexagonal patterns, stripe patterns with dislocations and the small spiral emitted from the large spiral have the same geometrical characteristic as Turing pattern in reaction-diffusion systems.

ACKNOWLEDGMENT The first author thanks Mr. Hideki Higa in the University of the Ryukyus for the experimental preparations.

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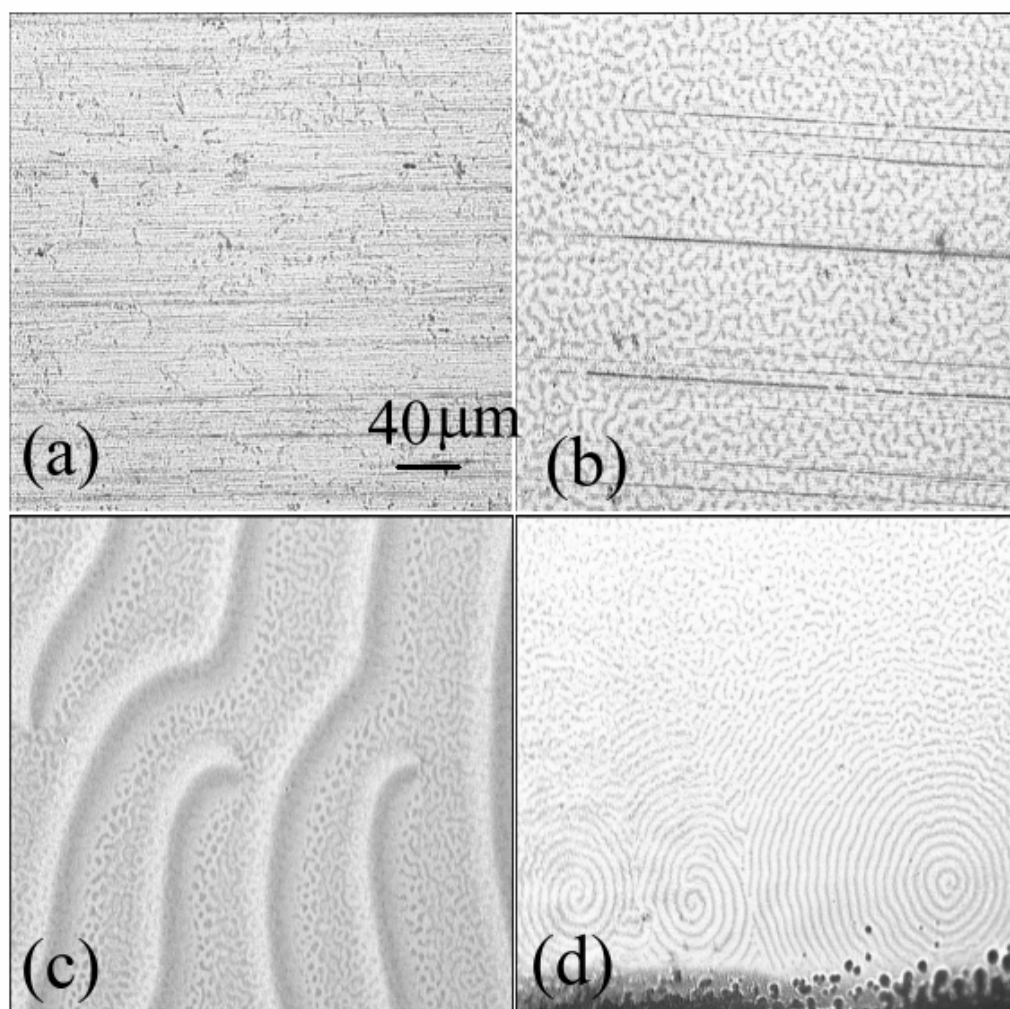


Fig.1 Microscope surface images of Ag-Sb electrodeposits grown at $t=120, 180, 1320$ and 2100 sec (from (a) to (d)) at a potential of 0.8 V and a concentration of APT 6.7 g/l. These images show a change of patterns as the deposition time proceeds.

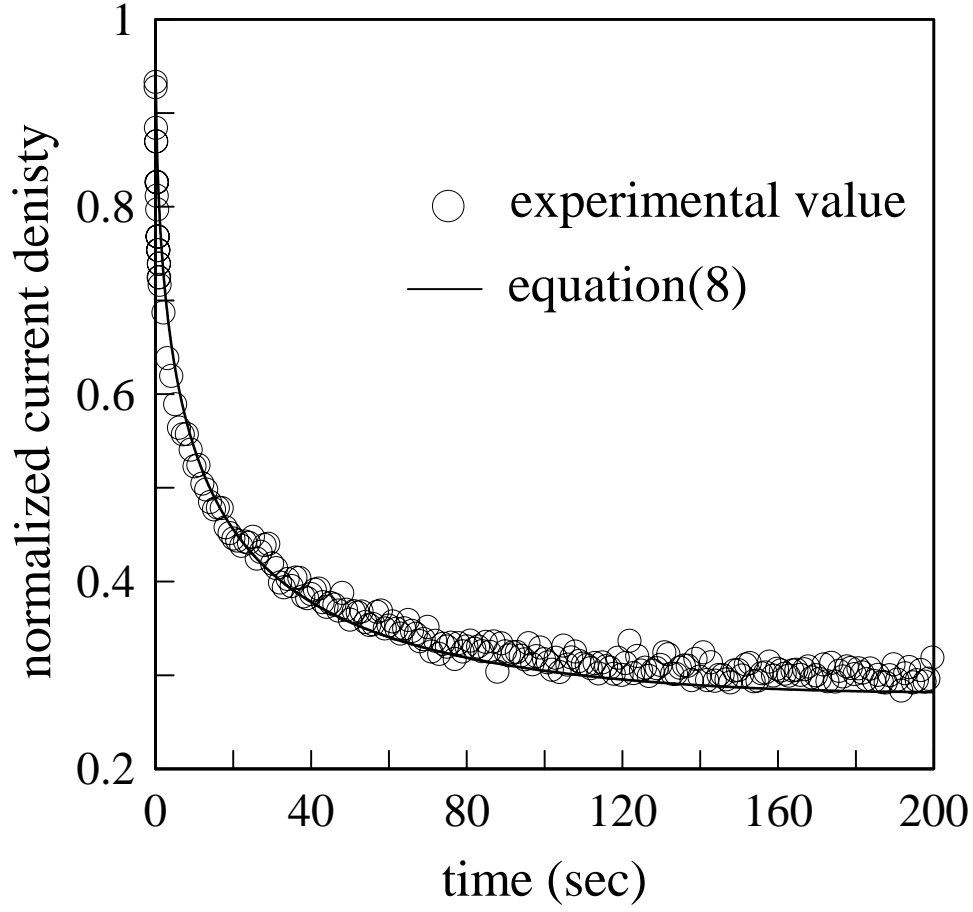


Fig.2 A plot of the normalized current density as a function of the deposition time. The solid line represents the calculated values for $k_1/\sqrt{D_1}=0.2182$, $k_2/\sqrt{D_2}=4.30 \times 10^{-2} \text{ (sec}^{-1/2}\text{)}$ and $k'_3=3.965 \times 10^{-5} \text{ (mol/sec)}$. The circles indicate the experimental values measured at a potential of 0.81 V and a concentration of APT 13.3g/l.

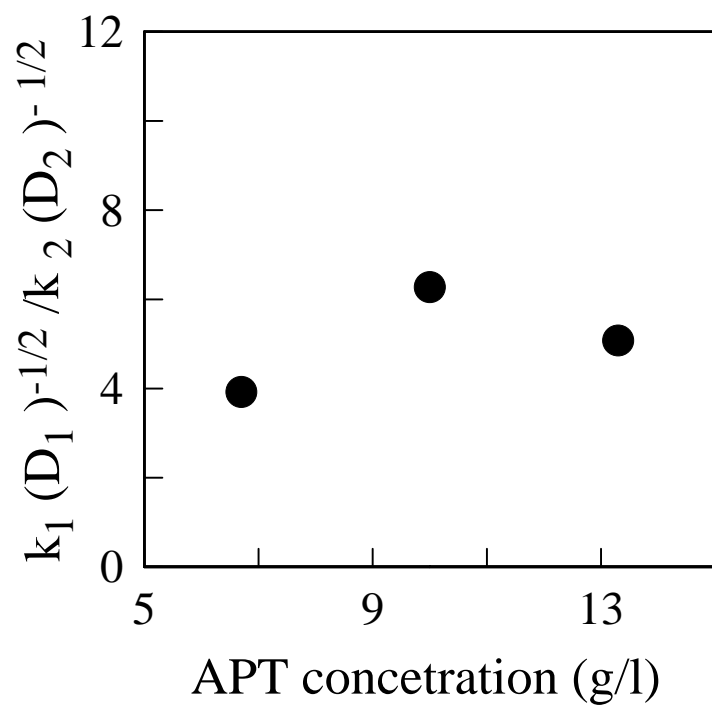


Fig.3 A plot of the ratio of $k_1(D_1)^{-1/2} / k_2(D_2)^{-1/2}$ at three different APT concentrations.

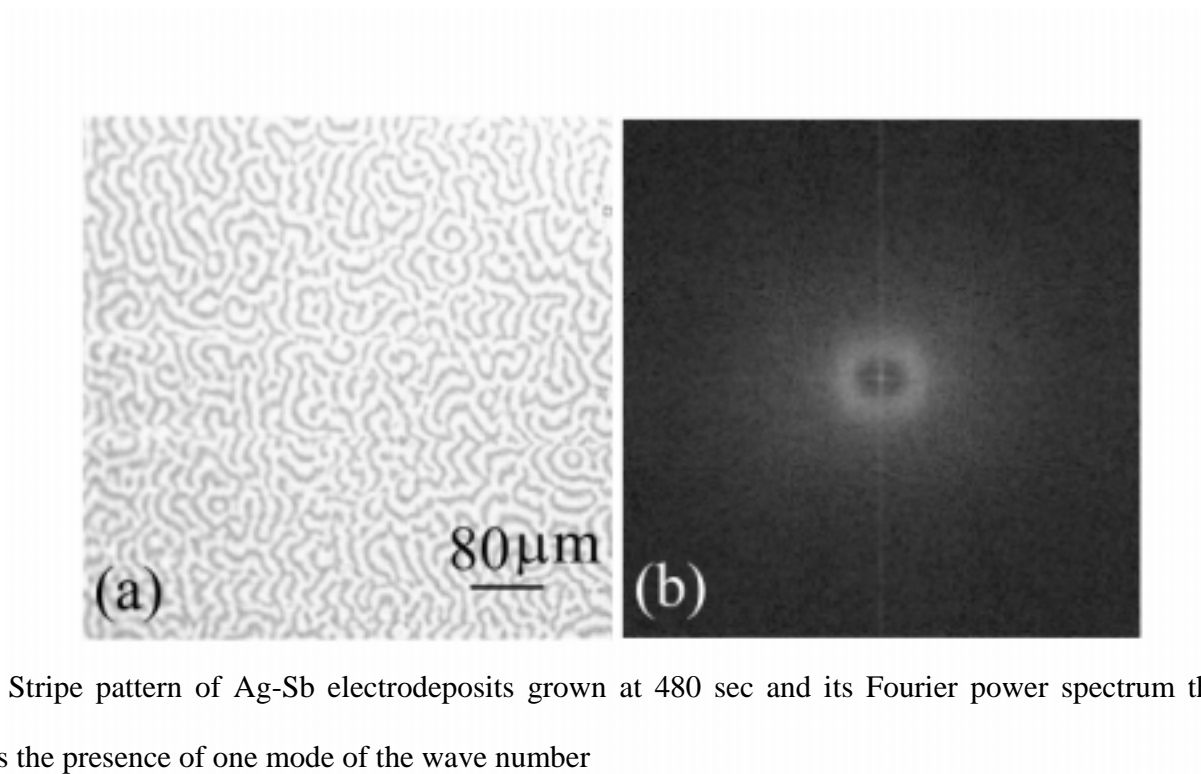


Fig.4 Stripe pattern of Ag-Sb electrodeposits grown at 480 sec and its Fourier power spectrum that shows the presence of one mode of the wave number

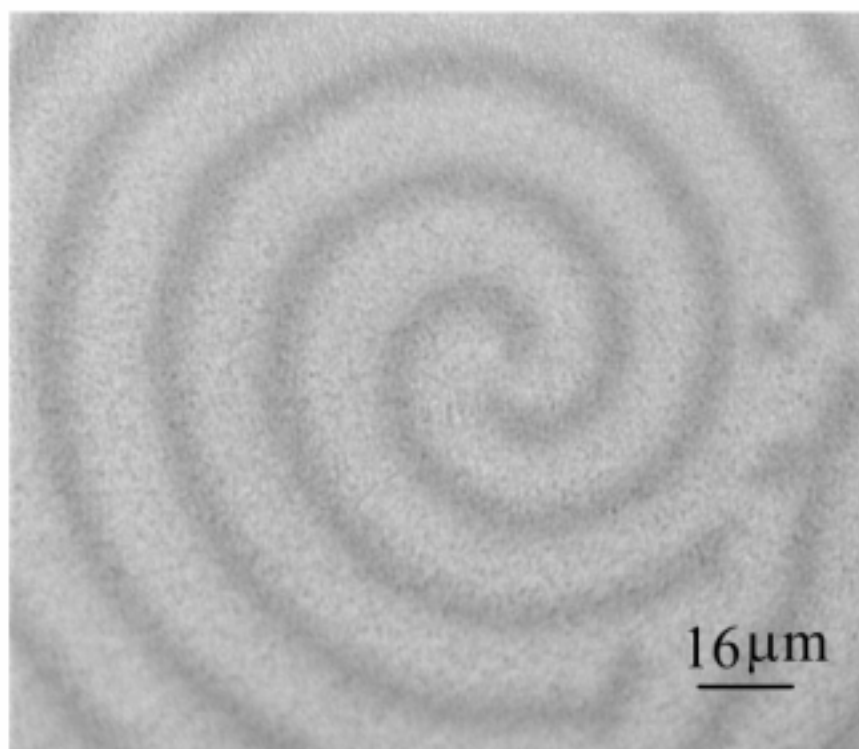


Fig.5 Spiral pattern formed on Ag-Sb electrodeposits at 1320 sec and a concentration of APT 6.7g/l.

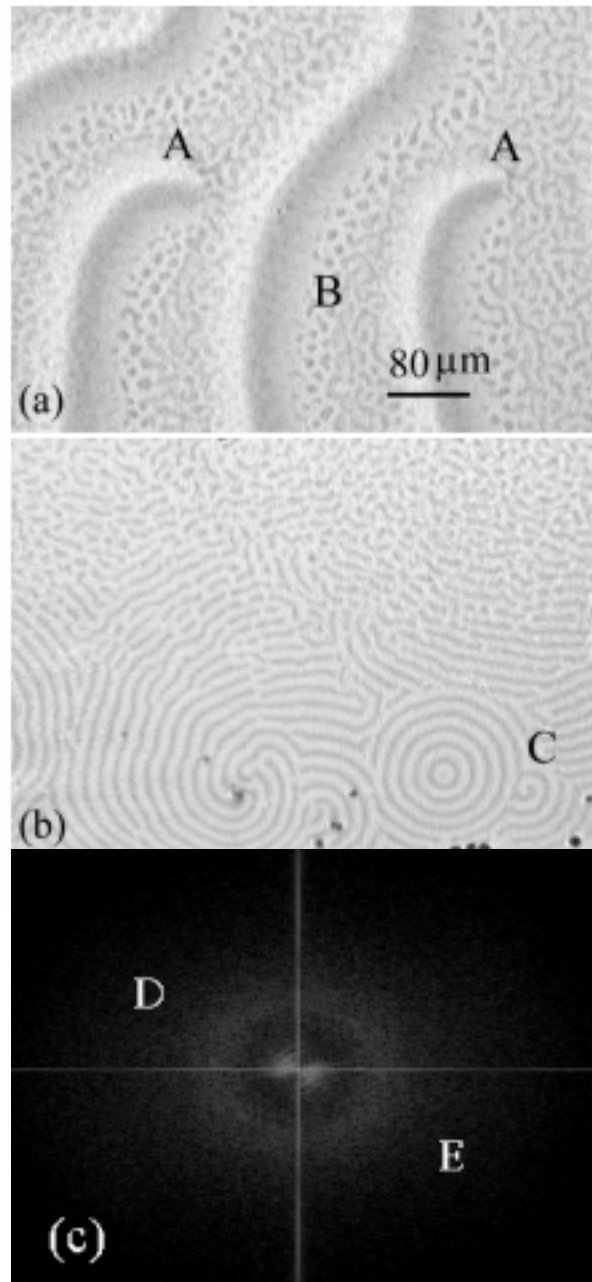


Fig.6 Pattern instability images that emerge on Ag-Sb electrodeposits. (a) stripe patterns with dislocations (denoted by a capital letter A) and hexagonal patterns in the region B at a growth time of 1320 sec. (b) small spiral (denoted by a capital letter C) emitted from the large spiral at a growth time of 2100 sec. (c) Fourier power spectrum of Fig.6 (a) that shows two blur points near the origin.