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# CHIRAL SURFACE FORMATION OF COPPER FILMS BY MAGNETOELECTROCHEMICAL ETCHING

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Formation of a chiral surface was investigated in magnetoelectrochemical etching (MEE). The MEE of copper films was conducted in galvanostatic conditions with various etching currents in a magnetic field of 5 T perpendicular to the electrode surfaces. The MEE film electrodes exhibited a current difference in voltammograms between alanine enantiomers, and such chiral behavior depended on the etching current and magnetic field polarity at the MEE processes.

**Introduction.** It is well known that the MHD effect induces the formation of spiral and helical structures at magnetoelectrodeposition (electrodeposition under magnetic fields) [1–6]. Such chirality induction is one of the most attractive functionality in magnetoelectrolysis. Chiral surfaces of metals and minerals have potentials as chiral catalysts, which could play considerable roles in organic syntheses, pharmaceutical industry and in molecular evolution of biochemical systems. Thus, studies on chiral surface formation are of great significance, and magnetoelectrolysis can be expected to contribute to the development of novel technique for the preparation of chiral surfaces.

We have reported that magnetoelectrodeposition (MED) can produce chiral surfaces of metal films of silver and copper [7–11]. Aogaki and Morimoto proposed that the surface chirality could be induced by the interference of the vertical MHD and micro-MHD vortices arising from the Lorentz force acting on faradaic currents [12, 13]. The MED films exhibited chiral recognition for the enantiomers of several amino acids, glucose and tartaric acid [7–10,14].

The micro-MHD effect was also observed in magnetoelectrochemical etching (MEE) [15] as well as in MED, and thus a similar chiral surface formation can be expected in the MEE processes. Fig. 1 shows a schematic of the micro-MHD and

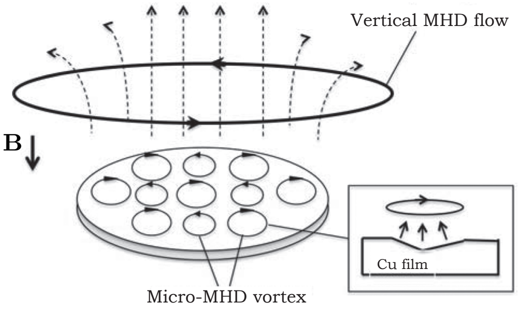

*Fig. 1.* Schematic of the MHD effects in magnetoelectrochemical etching. The magnetic field $B$ is imposed antiparallel to the faradaic current $i$ and perpendicularly to the electrode surface. The inset represents a micro-MHD votex around an etching pit.

vertical MHD vortices to be excited in the MEE processes under magnetic fields perpendicular to electrode surfaces. Electrochemical etching is a non-equilibrium process, and the non-equilibrium fluctuation produces a number of pits on the etching surfaces. The micro-MHD vortices emerge around such pits (see an inset in Fig. 1), and then they form self-organized states on the film surface. The vertical MHD flow emerges around the electrode edge and makes interference on the micro-MHD vortices. Such interference breaks the symmetry of micro-MHD vortices and leads to the chiral surface formation. In this paper, we report the experiments of MEE of Cu films under galvanostatic conditions and the dependence of chirality of the MEE films on the etching currents and magnetic field polarity.

**1. Experimental of magnetoelectrochemical etching.** In the electrochemical experiments, a conventional three-electrode system was employed: a polycrystalline Pt disc working electrode (WE) with a diameter of 1.6 mm, a Cu plate counter electrode (CE), and na Ag|AgCl|3 M (M = mol/dm$^3$) NaCl reference electrode (RE). Before the etching processes, Cu films with a thickness of approximately 300 nm were prepared on the working electrode by electrodeposition in a 50 mM $CuSO_4$ + 0.5 M $H_2SO_4$ aqueous solution in the absence of magnetic field. The etching of Cu films was conducted in the same solution in galvanostatic conditions with various constant currents of 1.0 – 30 mA/cm$^2$ until the film thickness decreased to approximately 150 nm. The passing charges were 0.80 C/cm$^2$ at the electrodeposition and 0.40 C/cm$^2$ at the MEE process. Fig. 2 shows the configuration of the electrochemical cell in magnetic fields at the MEE process. The cell was placed at the bore center in a cryocooled superconducting magnet (Sumitomo Heavy Industries Ltd.), and a magnetic field of 5 T was imposed perpendicularly to the working electrode surface and parallel (+5 T) or antiparallel (–5 T) to the etching currents. In this paper, the MEE films prepared in the magnetic fields of +5 T and –5 T are called +5T-film and –5T-film, respectively.

The MEE Cu films were used as electrodes after the pretreatment of surface oxidization from Cu to CuO, as described in our previous paper [9]. The chiral behaviors of the MEE film electrodes were examined by means of voltammetric measurements of the enantiomers of alanine (an amino acid). The voltammograms were measured in a 20 mM alanine + 0.1 M NaOH aqueous solution with a potential sweep rate of 10 mV/s.

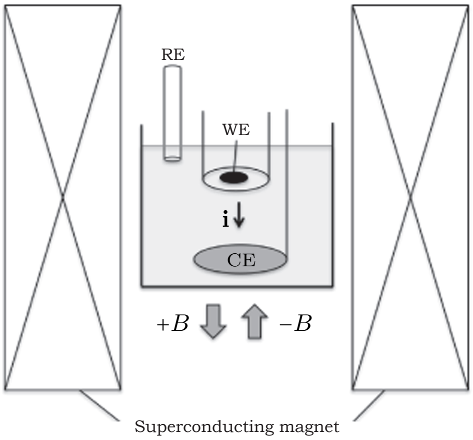

*Fig. 2.* Experiment of magnetoelectrochemical etching with a superconducting magnet. Magnetic fields **B** are applied to parallel (+) or antiparallel (–) to faradaic currents **i** and perpendicular to the working electrode surface. WE: a working electrode, CE: a counter electrode, and RE: a reference electrode.

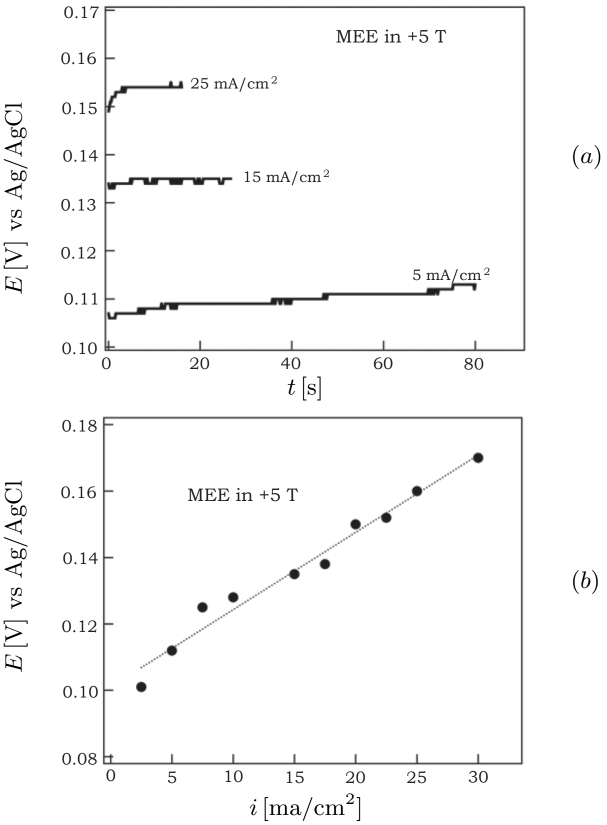

*Fig. 3.* (*a*) Electrode potential $E$ versus the time t during the MEE processes in +5 T at the etching current of 5, 15 and 25 mA/cm$^2$. The passing charge was 0.4 C/cm$^2$. (*b*) The steady potential at the MEE processes versus the etching current. The dotted line is a guide for eyes.

**2. Results and discussion.** Fig. 3*a* shows the time dependence of the working electrode potentials during the MEE processes in +5 T at the etching currents of 5, 15 and 25 mA/cm$^2$. The electrode potentials rise at most by 5 mV for several initial seconds and then reach constant values at any etching currents. In such steady states, the micro-MHD vortices and the vertical MHD flow could form a self-organized state [16, 17]. Fig. 3*b* shows plots of the steady potentials against the etching currents. The steady potential increases almost linearly with the increasing etching current, and no potential jump is seen, implying that this anodic process includes only the anodic dissolution reaction of copper metal in this current reagion, without oxygen gas evolution.

Fig. 4 shows voltammograms of L- and D-alanines on the (*a*) 0T-film, (*b*) –5T-film and (c) +5T-film electrodes, where all the MEE films were prepared at an etching current of 20 mA/cm$^2$. Alanine molecules are oxidized on the Cu electrodes around 0.7 V [18], where the voltammogram has a current peak. The voltammograms of alanine enantiomers are coincident with each other on the 0T-film electrode, representing achirality of the film surface. On the other hand, the –5T-film electrode exhibits L-active chirality for the enantiomers; namely, the peak current of L-alanine is greater than that of D-alanine, as shown in Fig. 4*b*. This fact demonstrates that the MEE process induces the surface chirality on the Cu films.

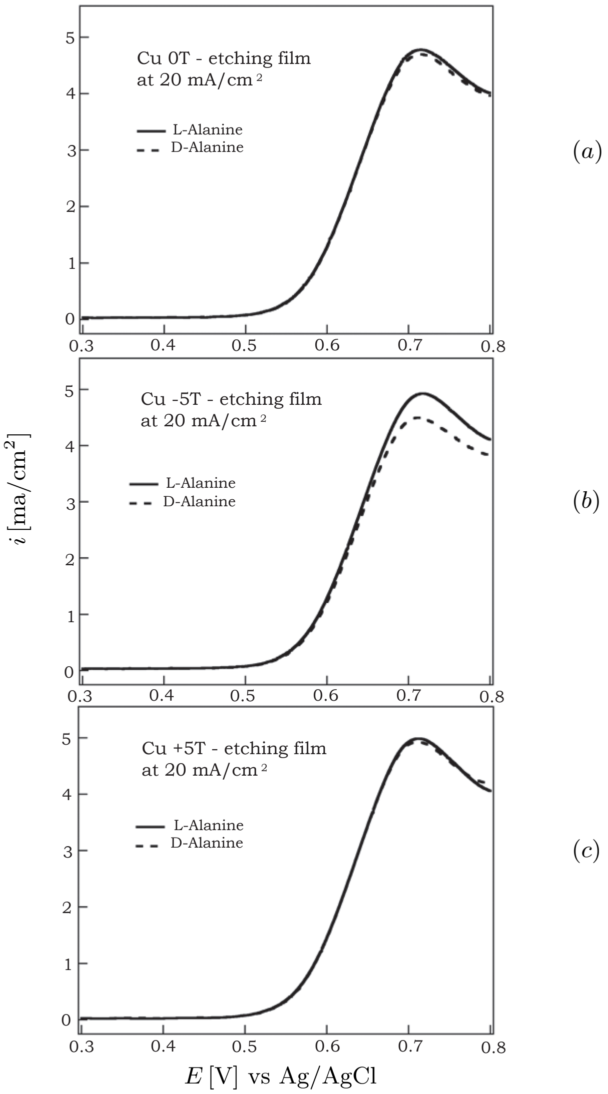

*Fig. 4.* Voltammograms of L- and D-alanines on (*a*) the 0T-film, (*b*) the –5T-film and (*c*) the +5T-film electrodes, where the films were prepared at an etching current of 20 mA/cm$^2$. The potential sweep rate was 10 mV/s.

The chiral sign of MEE films should depend on the magnetic field polarity in the MEE process. The reversal of the magnetic field is expected to lead to the mirror-image chirality of the MEE films. However, Fig. 4*c* shows that the +5T-film electrode does not exhibit D-active chirality, but exhibits achirality. A similar result was obtained at the etching current of 25 mA/cm$^2$, as shown in Fig. 5. The –5T-film electrode exhibited achirality in Fig. 5*a*, and the +5T-film electrode exhibits D-active chirality in Fig. 5*b*.

In the case of magnetoelectrodeposition (MED) of Ag and Cu films, the reversal of the magnetic field polarity induced the mirror-image chirality of the MED films [7–10]. For example, MED +5T-films exhibit L-active chirality, and the –5T-films exhibit D-active one. This is why the direction of vertical MHD flow is determined by the magnetic field direction and the interference of the vertical MHD flow breaks the symmetry of the micro-MHD vortices [13]. However, the

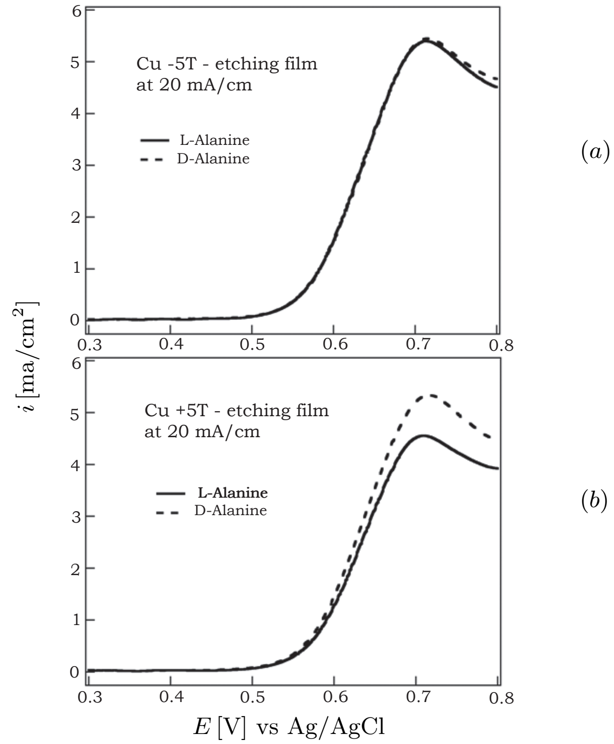

*Fig. 5.* Voltammograms of L- and D-alanines on (*a*) the –5T-film and (*b*) the +5T-film electrodes, where the films were prepared at an etching current of 25 mA/cm$^2$. The potential sweep rate was 10 mV/s.

results in the MEE experiments show that the reversal of the magnetic field direction at the same etching current does not lead to the mirror-image chirality, but lead to achirality.

We examined the etching current dependence of the chirality of MEE 5T-films, and the result is shown in Fig. 6, where enantiomeric excess (*ee*) ratios are plotted versus the etching current for both the (*a*) –5T- and (*b*) +5T-films. The ee ratio in the voltammograms of enantiomers can be defined as $ee = (i_{\mathrm{p}}^{\mathrm{L}} - i_{\mathrm{p}}^{\mathrm{D}})/(i_{\mathrm{p}}^{\mathrm{L}} + i_{\mathrm{p}}^{\mathrm{D}})$, where $i_{\mathrm{p}}^{\mathrm{L}}$ and $i_{\mathrm{p}}^{\mathrm{D}}$ represent the peak currents of L- and D-alanines, respectively. The positive sign of the *ee* ratio means L-activity, and the negative sign means D-activity. In both films, the *ee* ratios are around zero below the etching current of 15 mA/cm$^2$, indicating that the films prepared in this current region exhibit achirality. In the higher current region, the –5T-film exhibits the maximum L-activity at 20 mA/cm$^2$. On the other hand, the +5T-film exhibits the maximum D-activity around 25 mA/cm$^2$.

These results indicate that the reversal of the magnetic field polarity induces the opposite chiral sign of MEE films. This fact can be understood by the MHD flow scheme in Fig. 1. Owing to the interference effect of the vertical MHD flow on the micro-MHD vortices, the cyclonic micro-MHD votices becomes stable and the anticyclonic ones becomes unstable. The reversal of the magnetic field polarity causes the reversal of vertical MHD flow and thus changes the direction of stable micro-MHD votices, resulting in opposite surface chirality. A more detailed explanation with an ionic vacancy mecahnism was described by Aogaki in [19].

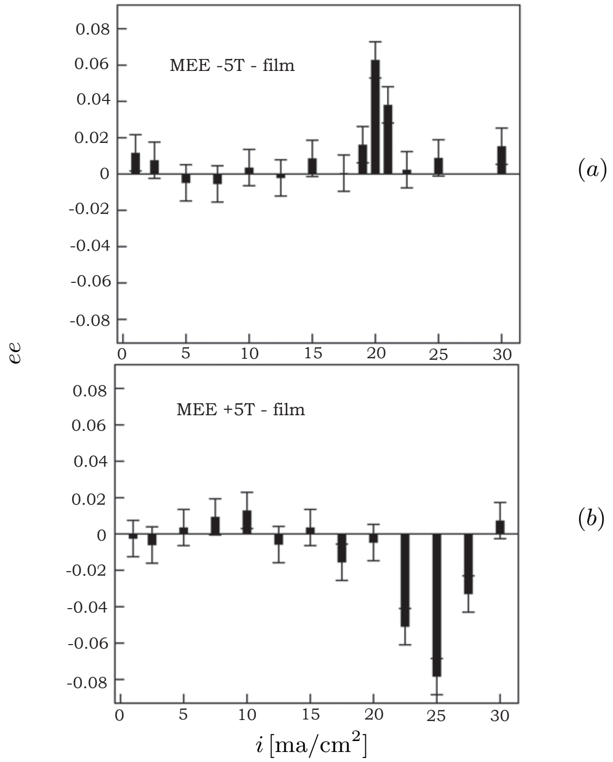

*Fig. 6.* Enantiomeric excess (*ee*) ratios of (*a*) –5T -film and (*b*) +5T-film electrodes versus the etching currents at the MEE processes. The ee ratio in the voltammograms of enantiomers is defined as $ee = (i_p^L - i_p^D)/(i_p^L + i_p^D)$, where $i_p^L$ and $i_p^D$ represent the peak currents of voltammograms of L- and D-alanines, respectively.

Furthermore, it is remarkable that the optimal etching condition for the L-active surfaces is not the same as that for the D-active ones. As a result, the chirality disappears in the MEE films prepared in the reverse magnetic field at the same etching current, as shown in Figs. 4*c* and 5*a*. Such an asymmetric feature in the optimal conditions for L- and D-active surfaces is of great interest in connection with the origin of homochirality in biochemical systems, and it would be a hot issue in the future study.

**3. Conclusion.** We have demonstrated that the MEE process induces chirality on Cu film surfaces and that the surface chirality depends on the etching currents and on the magnetic field polarity. The –5T-film prepared at 20 mA/cm$^2$ exhibits L-activity and the +5T-film prepared at 25 mA/cm$^2$ exhibits D-activity. This result indicates that the optimal etching conditions are different between the L- and D-active film formations.

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## REFERENCES

[1] I. Mogi, S. Okubo, Y. Nakagawa. Dense radial growth of silver metal leaves in a high magnetic field. *J. Phys. Soc. Jpn.*, vol. 60 (1991), pp. 3200–3202.

[2] I. Mogi, M. Kamiko, S. Okubo. Magnetic field effects on fractal morphology in electrochemical deposition. *Physica B*, vol. 211 (1995), pp. 319–322.

[3] J.M.D. Coey, G. Hinds, M.E.G. Lyons. Magnetic-filed effects on fractal electrodeposits. *Europhys. Lett.*, vol. 47 (1999), pp. 267–272.

[4] V. Heresanu, R. Ballou, M. Molho. Electrochemical growth of Zn and Fe arborescences under normal magnetic field. *Magnetohydrodynamics*, vol. 39 (2003), no. 4, pp. 461–468.

[5] I. Mogi, M. Kamiko. Pattern formation in magneto-electropolymerization of Pyrrole. *Denki Kagaku (Electrochemistry)*, vol. 64 (1996), pp. 842–844.

[6] W. Duan, S. Kitamura, I. Uechi, A. Katsuki, Y. Tanimoto. Three-dimensional morphological chirality induction using high magnetic fields in membrane tubes prepared by a silicate garden reaction. *J. Phys. Chem. B*, vol. 109 (2005), pp. 13445–13450.

[7] I. Mogi, K. Watanabe. Chiral electrode behavior of magneto-electrodeposited silver films. *ISIJ Int.*, vol. 47 (2007), pp. 585–587.

[8] I. Mogi, K. Watanabe. Magnetoelectrochemical chirality in Ag electrodeposition. *J. Chem. Chem. Eng.*, vol. 4 (11) (2010), pp. 16–22.

[9] I. Mogi, K. Watanabe. Chiral recognition of amino acids by magneto-electrodeposited Cu film electrodes. *Int. J. Electrochem.*, vol. 201 (2011), p. 239637.

[10] I. Mogi, K. Watanabe. Chirality of magnetoelectrodeposited Cu films. *Magnetohydrodynamics*, vol. 48 (2012), no. 2, pp. 251–259.

[11] I. Mogi, R. Morimoto, R. Aogaki, K. Watanabe. Surface chirality induced by rotational electrodeposition in magnetic fields. *Scientific Reports*, vol. 3 (2013), p. 2574.

[12] R. Aogaki. Micro-MHD effect on electrodeposition in the vertical magnetic field. *Magnetohydrodynamics*, vol. 39 (2003), no. 4, pp. 453–460.

[13] R. Aogaki, R. Morimoto. Nonequilibrium fluctuations in micro-MHD effects on electrodeposition. In: *Heat and Mass Transfer: Modeling and Simulation* (Ed. Hossain, M.: InTech, Croatia, 2011), pp. 189–216.

[14] I. Mogi, K. Watanabe.. Enantioselective recognition of tartaric acid on magnetoelectrodeposited copper film electrodes. *Chem. Lett.*, vol. 41 (2012), pp. 1439–1441.

[15] K. Shinohara, K. Hashimoto, R. Aogaki. Magnetic field effect on copper corrosion in nitric acid. *Chem. Lett.*, vol. 31 (2002), pp. 778–779.

[16] I. Mogi, R. Aogaki, R. Morimoto, K. Watanabe. Magnetoelectrodeposition for the chiral surface formation of Cu films. *ECS Trans.*, vol. 45 (12) (2013), pp. 1–8.

[17] I. Mogi, R. Aogaki, R. Morimoto, K. Watanabe. Chirality induced by magnetoelectrolysis. *Acta Physica Polonica A*, vol. 126 (2014), pp. 380–381.

[18] P. Luo, F. Zhang, R.P. Baldwin. Constant potential amperometric detection of underivatized amino acids and peptides at a copper electrode. *Anal. Chem.*, vol. 63 (1991), pp. 1702–1707.

[19] R. Aogaki, R. Morimoto, M. Asanuma, I. Mogi, A. Sugiyama, M. Miura, Y. Oshikiri, Y. Yamauchi. Chiral catalytic activities in magnetoelectrochemical etching. *Proc. the 9th Int. PAMIR Conference on Fundamental and Applied MHD, Thermo Acoustic and Space Technologies* (Riga, Latvia, 2014), vol. 2, pp. 149–153.

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