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# Self-organization of nanostructured copper filament array by electrochemical deposition

**Mu Wang,* Yan Feng, Guang-Wei Yu, Wen-Ting Gao, Sheng Zhong, Ru-Wen Peng and Nai-ben Ming**

National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, China

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The metal deposits generated by electrochemical deposition usually have a ramified morphology. Much effort has been devoted to understanding how and why the ramified feature is generated, both for the interest of science[1–12] and for the benefit of technology.[13,14] The ramified feature of electrodeposits is often ascribed to the diffusive noise in the interfacial growth.[15] In addition to the random diffusive noise, convection (both natural convection and electroconvection) and electric migration also affect the morphology of the electrodeposits.[16–19] It has been demonstrated that when the electroconvection becomes sufficiently strong the neighbouring deposit branches approach each other, eventually forming a network pattern.[17,20] To suppress the convection, thin cells[18,21] and agarose gel[22] are used in experiments. However, in these cases, very often some uncontrollable factors are introduced that make the situation even more completed.[23]

To solve these problems, we design a unique experimental system with an ultrathin electrolyte layer for electrochemical deposition. In this system the morphology of the electrodeposits has been changed tremendously.[23,24] On a macroscopic scale the copper electrodeposits have finger-like branches, as shown in Fig. 1. The electrodeposits are shiny and grow robustly on the glass substrate. Under the scanning electron microscope one may find that the fingering branch actually consists of many straight filaments with periodic nanostructures, as shown in Fig. 2. The filaments have a considerably lower branching rate. In our experiments we can use either potentiostatic or galvanostatic designs. Similar deposit morphologies are generated for both scenarios. Interestingly, in the potentiostatic mode (where the voltage across the electrodes remains constant) we find that the electric current in the system is oscillating, whereas for the galvanostatic mode (where the current remains constant) the voltage across the electrodes oscillates, as shown in Fig. 3. This type of oscillation is spontaneous. Up to now we have focused on the following questions:

(1) What does the periodic structure on the filaments correspond to? (the distribution of chemical components along the filament).[24]

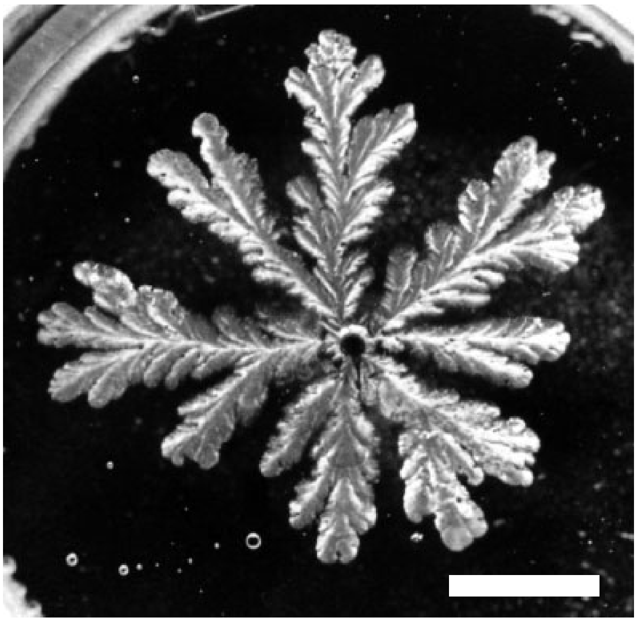

**Figure 1.** The copper electrodeposits generated in the ultrathin electrolyte layer. The deposit grows on the class substrate. The fingering branches can be identified easily. The bar represents 4.0 mm.

(2) How do the periodicity of these nanostructures and the oscillation of the electric signals depend on the experimental conditions?[23]
(3) What are the electric properties of an individual filament with periodic chemical modulation?[25]
(4) What is the mechanism for the formation of the periodic nanostructures on the filaments?[23,26]
(5) Pattern formation and pattern selection during growth of the filaments (unpublished work).

Our studies show that the spontaneous formation of periodic structures on the filaments of the electrodeposits is due to the ultrathin electrolyte layer in our unique experimental system, which restricts mass transfer in the electrolyte layer and hence induces oscillation of the concentration field. The oscillating local concentration of $Cu^{2+}$ triggers an alternating deposition of copper and cuprous oxide.[23,26] The periodicity of the compositional and topographic oscillations depends on the pH of the electrolyte.

Despite the developments mentioned above, however, many questions remain unanswered. The branching rate of

*Correspondence to: Mu Wang, National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, China. E-mail: muwang@nju.edu.cn
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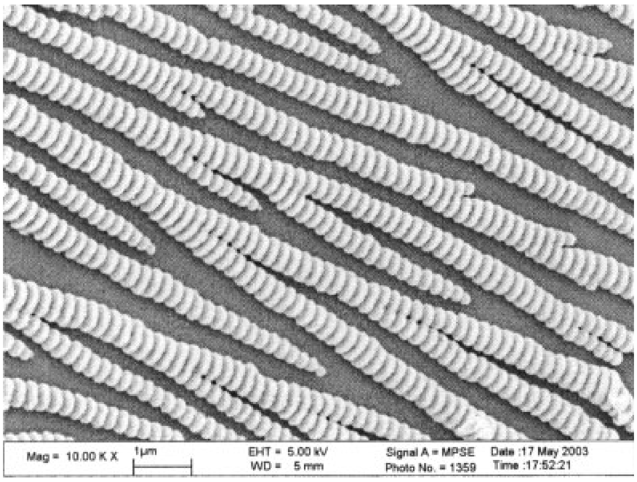


**Figure 2.** Detailed morphology of the copper electrodeposits observed by scanning electron microscopy. The branches are straight and the periodic nanostructures can be identified on the filaments.

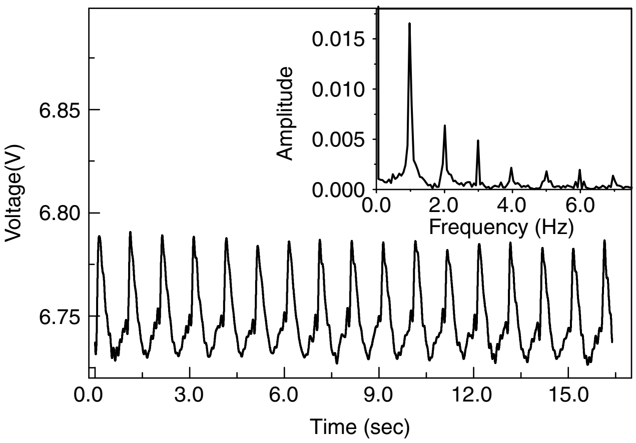


**Figure 3.** In the galvanostatic mode, the voltage across the electrodes oscillates spontaneously. The insert is the Fourier transform of the voltage signal, where strict periodicity can be seen. The oscillation is evident only when the pH of the electrolyte is sufficiently high.

the electrodeposits has indeed been decreased significantly in our case on comparison with previous reports,[1–12] however the branching mechanism remains unclear in the filament growth. To understand the branching mechanism is an essential step for fabricating a regular array of filaments over a large area. Another related problem is the stability of the concentration/temperature fields in front of the growing interface, which may significantly influence the pattern formation and pattern selection in this system. The experiments on these aspects are in progress now.

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