Real-Time *In Situ* Studies on Zinc Electrodeposition by the Scanning Tunneling Microscopy and the Computer Simulation

Nobuyuki KOURA* and Sanae TAMURA

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1 INTRODUCTION

The scanning tunneling microscopy (STM) has been shown to be a useful tool for the examination of processes which occur at a solid/liquid interface¹⁾. Usually, the electrochemical and the microscopic measurements have been separately performed. Recently, the real-time and in situ studies of controlled-current electrochemical deposition and dissolution were reported.²⁾ In the meantime, the DLA model³⁾ has been applied for the simulation of a crystal growth of a new phase deposited on an electrode from a solution.^{4,5)}

We have investigated a growth mechanism for the dendritic deposition of zinc by a scanning electron microscopy (SEM) and a computer simulation.^{6,7)} However, actual crystal growth of the deposit which occurs at the electrode / solution interface cannot be directly observed by the SEM. Moreover, the number of atoms simulated by a computer is too small for the SEM to observe the crystal growth. Specifically, the simulated number is $10^4 \sim 10^5$ at most, while the observed number is usually more than $10^9 \sim 10^{13}$. In this paper, by the use of STM, the real-time and in situ studies could be done, moreover, the results were directly compared with those by the computer simulation.

2 EXPERIMENTAL

2.1 STM observation

The STM of a STE-330, Seiko Instruments

Department of Industrial Chemistry,
Faculty of Science and Technology,
Tokyo University of Science,
2641, Yamazaki, Noda, Chiba 278, Japan

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Inc., was used. The working electrode was made of a 10×10 mm HOPG. The electrode surface was renewed by peeling off the top layer of the crystal by means of adhesive tape. The counter electrode was made of a Pt wire surrounding the working electrode. An Ag/AgCl electrode was used for the reference. The STM probes were made of Pt wire (0.3 mm diam.) and covered with a glass layer. They were sharpened by electrochemical etching. The STM was operated at tip bias of 0.275 mV vs. Ag/AgCl. Zinc was galvanostatically deposited at 0.05 mA/cm^2 from a 10 mM ZnSO_4 solution.

2.2 Computer Simulation

In our simulation model, Zinc was galvanostatically deposited, and the zinc atoms corresponded to the current density were deposited at a time. The rate determining step was assumed to be a diffusion of zinc ion. Our simulation model was begun with a three-dimensional square lattice (typically $100 \times 100 \times 100$) where a fraction of the sites corresponding to the concentration of zinc ion were initially occupied with mobile ions at random. It was provided that zinc ions and atoms exist at the lattice and move along the lattice. Following factors were added to the Sander's DLA model³⁾ to expand the simulation model.

- (1) Diffusion by concentration gradient.
- (2) Movement of plural ions at the same time.
- (3) Surface diffusion and crystal nucleation.
- (4) Probability of a nucleus formation for the crystallization.

There are the details of the simulation model in the ref. 7.

In order to conform our simulation model

Fig.1 STM images of an electrode surface after (a)0, (b)10, (c)50, and (d)100 seconds of the electrolysis. A scale of Z axis direction is expanded to 2 times to make clear images.

Fig.2 Simulated images under the same conditions as the STM observation.

to actual electrodeposition processes and to compare the simulation results with STM images, the two-dimensional model^{6,7)} was extended to the three-dimensional model.

3 RESULTS AND DISCUSSION

Figures 1 (a), (b), (c), and (d) show STM images of the electrode surface at various electrolysis times of 0, 10, 50, and 100 seconds. These were continuously observed at the same place. At the early stage of electrodeposition (Fig.1(b)), there are many unevenness of about 1~2nm height on the electrode surface. These unevennesses were assumed to be an early crystal nucleus. After 50 seconds, those nuclei grew into "islands", and a small secondary island formed partially on the islands shown in Fig.1(c). These islands spread two-dimensionally, and covered almost the HOPG electrode surface, and the second crystal layer also grew (Fig.1 (d)).

The results of a computer simulation which was carried out under the similar conditions to the STM observation are shown in Fig.2 (a)-(c). At the early stage (Fig.2(a)), some crystal nuclei(A) were formed in random position on the electrode surface(B). After

50 seconds (Fig.2(b)), these nuclei grew two-dimensionally, and became islands(C), and a second layer of new nuclei(D) was formed on these islands. After 100 seconds (Fig.2 (c)), the first layer covered the electrode surface except for a very small part(E), and the second nuclei grew islands(F) on the first layer. As stated above, the simulated results are very much coincident with the STM observations. Consequently, it appears that our proposed simulation method is correct.

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