Macrostep Growth of Silver Electrodepositing in $AgNO_3$ Aqueous Solution

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INTRODUCTION

The electrodeposition of metal leaf has been focused from the standpoint of pattern formation. However, the number of researches discussing the effect of transport phenomena on the morphological variation is limited, because of the complicated coupling phenomena between electrochemical reaction and induced natural convection. The quantitative measurement on ionic mass transfer rate is indispensable to phenomenologically describe the morphological variation of electrodeposited film. As a reference experiment, the electrodeposition under the pure diffusion field is necessary. In the authors' laboratory, the dendritic growth process of silver in concentrated $AgNO_3$ solution had been in-situ measured with a holographic interferometer and a confocal laser microscope. The effects of current density and $AgNO_3$ concentration on the morphological variation of silver are now examined.

EXPERIMENTAL

A quasi-two-dimensional electrolytic cell, enclosed with two sheets of microscopy slide glass, was manufactured as shown in JEC Vol.145, 1876-1881(1998). Both electrodes were made of 100 μm thick rolled silver foil by the discharge processing. Their lateral faces were used as effective electrodes. This design made it possible to project an image of single dendrite arm along the propagation direction of measurement wave of laser. The cell was horizontally installed. The resolution power is 0.16M $AgNO_3$ per each interference fringe. Most electrolysis was carried out galvanostatically. The relatively higher current densities were selected in order that dendrite arms would appear soon after starting the electrolysis and grow at measurable speeds.

RESULTS and DISCUSSION

Ag^+ ion concentration profile around dendrite arms was visualized by a holographic interferometer. Ag metal uniformly electrodeposited during the initial stage appeared to form a coagulated layer with the critical thickness. Then, several dendrites started to stochastically grow at the surface of coagulated layer after a certain incubation time, which was prolonged with decreasing in the current density and increasing in $AgNO_3$ concentration. At the end of incubation period, the surface concentration of Ag^+ ion was lowered to 90 to 70% of bulk solution. The significant current density convergence to dendrite tips was interferometrically measured, while the primary dendrite grew at a significant speed.

Moreover, the interference fringe pattern among dendrite arms was sometimes fluctuating with time. The existence of fluctuating fine fringe pattern may indicate the induction of localized eddy of electrolyte between primary dendrite arms. Macroscopic natural convection should not be induced in the present electrolytic cell design so long as the duration period is not too long. Thus, the reason why such a localized eddy of electrolyte was induced is still questionable. With the progress of electrodeposition, the concentration gradient is slightly relaxed and the interference fringes start to envelop around the tips of dendrites.

Primary dendrite arm steadily growing is in-situ observed with a confocal microscope. The recorded clear image of surface movement of electrodeposited silver may partly provide a cause of electrolyte eddy. The dynamic movement of giant macrostep or screw dislocation on the silver dendrite arm is successfully recorded. A huge macrostep exceeding over 1 μm high dynamically flows on the lower index plane of silver crystal. It is also influenced by the polarity of electrode. The interesting phenomena of electrolyte fluctuation among the primary dendrite arms may be coupled with such a macrostep movement. The phenomena are not molecular level but mesoscopic. They may also provide the useful information to the shape evolution field.