## Effect of a Supporting Electrolyte on Crystal Growth of Electrodeposited Ag

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## Introduction

The mechanism of electrocrystallization has been attracting the attention of both scientists and materials engineers. Controlling of the electrochemical metal deposition process is increasingly important because the microelectronics industry requires the microscaled or nanoscaled and highly reliable deposition profile. Ag is electrodeposited in a dendritic manner at high current densities. By adequately changing the experimental conditions different morphology of dendrite can be obtained. In this study, the morphology of Ag dendrite was quantitatively analyzed and coupling phenomena between mass transfer rate and morphology was discussed.

## Experimental

Ag electrodeposition was performed from aqueous AgNO<sub>3</sub> solutions in the presence of HNO<sub>3</sub> using quasi-two-dimensional electrolytic cell placed horizontally. Au disk cathode with 1.0 mm diam. was placed at the center of Ag ring anode with 20 mm in inner diameter, and both electrodes with 100  $\mu$ m thickness were sandwiched with two sheets of slide glass. 3 M AgNO<sub>3</sub> - *x* M HNO<sub>3</sub> ( $0 \le x \le 3$ ) aqueous solutions were used at room temperature. The experiments were carried out galvanostatically at high current densities so that the dendrites would appear soon after the start of electrolysis and grow at measurable speeds.

## **Results and Discussion**

Figure 1 shows the images of Ag dendrites deposited at 1.5 A/cm<sup>2</sup> after 30 seconds passed from the start. 0 M, 1 M, and 3 M HNO<sub>3</sub> was contained in Figure 1 (a), (b), and (c), respectively. It is apparent that the morphology is different depending on the concentration of HNO<sub>3</sub>. Ag was deposited uniformly in (c), particularly. Growth velocity of the longest dendrite seen in Figure 1 was measured, and it is expressed as v in Figure 2. It can be seen that the v value is largely different with t and HNO<sub>3</sub> concentration. v increases very steeply within t = 7.5 sec in (a) and (b), and thereafter, it suddenly decreases. It is due to that the side of the dendrite started to grow in (a). However, only in (b), the other small dendrites also started to grow when vdecreased. It seems that addition of HNO<sub>3</sub> caused suppression of the selective dendrite growth. L is defined as the average length of all the dendrites seen in Figure 1. The drastic increase of L in (b) in spite of rapid decrease of v means that the selective growth was restrained.

The dendrite tips were also observed by SEM, and the crystal growth was examined by in-situ confocal scanning microscopy.







