Mechanistic Investigation of Electroless Plating in Micro-/Sub-Micrometer Features

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マイクロ・サブマイクロメートル領域における無電解めっき反応機構の解明

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This study aims to achieve resist-less fine patterning by combining selective surface modification via atmospheric-UV treatment with Pd catalyzation, and to elucidate the underlying reaction mechanisms of electroless plating using both electrochemical measurements and quantum-chemical calculations. The central issues are suppressing lateral growth in the micro- to sub-micrometer regime and systematizing the adsorption and action mechanisms of additives. In electroless systems, the anodic oxidation of the reducing agent and the cathodic reduction of metal ions occur simultaneously at a common interface. On this basis, we develop a measurement- and analysis-based framework describing transitions between rate-limiting regimes and growth dynamics unique to confined features.

As an initial step, we investigated a formaldehyde-based electroless copper bath. Patterning proceeds by selectively modifying the polymer surface with atmospheric UV, adsorbing Pd catalyst, and then forming metallic interconnects by electroless deposition without using a resist. Substrates include polymers such as cyclo-olefin polymer (COP) and liquid-crystal polymer (LCP), and we have successfully formed fine lines down to 1 μm in width (Fig. 1, under 30 μm line). The sulfur-based suppressor 2-mercaptobenzothiazole (2-MBT) is expected, under alkaline conditions, to deprotonate its –SH group and exhibit adsorption affinity toward metal species and Pd active sites, thereby contributing, at trace levels, to the suppression of lateral growth. In practice, we observed suppression of spurious deposition on UV-unexposed areas, improved pattern resolution, and anisotropic growth of the deposit as shown in Fig. 2. However, excessive addition inhibits deposition, so concentration optimization is necessary. We next conducted polarization measurements in the bulk electrolyte of the electroless Cu bath (results in Fig. 3). Using an electrolyte lacking $CuSO_4$, the anodic branch assessed oxidation of the reducing agent HCHO; for the cathodic branch, an electrolyte lacking HCHO assessed Cu reduction. Previously reported anodic polarization showed the reducing-agent oxidation potential shifting nobler, suppressing

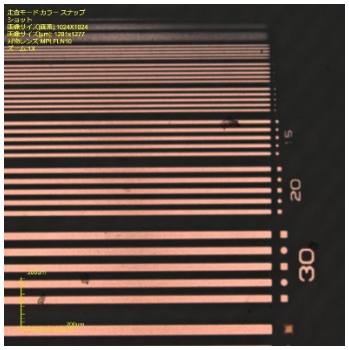

Fig. 1 Fine wiring patterns on COP films by direct patterning

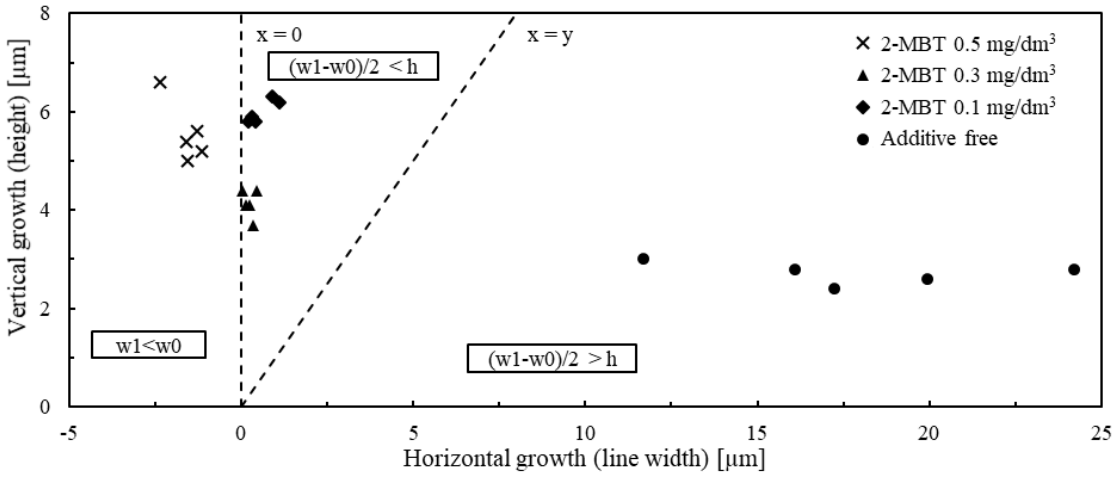

Fig. 2 2-MBT-Controlled Anisotropy in Electrodeposited Growth—Vertical vs. Lateral Comparison, h: height, w1: width after plating, w0: width before plating

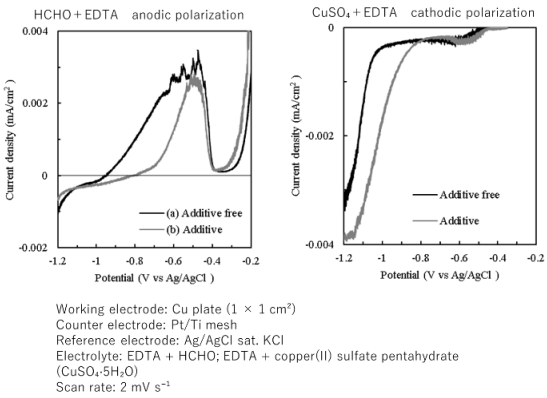

Fig. 3 Effect of 2-MBT additive on anodic and cathodic polarization curves

the overall deposition reaction. In contrast, the cathodic polarization curves indicated promotion of copper deposition. Taken together, addition of 2-MBT exhibited both a “suppressor” effect that enables anisotropic (lateral-growth-suppressed) deposition and an “accelerator” effect that promotes through-thickness growth.

Additive concentration and pH are treated as primary factors. A mechanistic model that integrates Langmuir-type adsorption, mixed-potential theory, and EIS-derived parameters are fitted to the data to clarify the reaction pathways specific to micro-/sub-micrometer features.