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Electrochemical Impedance Spectroscopy to Investigate Electroplating of Metals

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Electrochemical impedance spectroscopy (EIS) is very useful to investigate the quality of electroplating films because the separation of time constants in the impedance spectrum gives the information concerning the film structure. For example, the presence of defects formed in the film can be detected by the curve-fitting of impedance spectrum with the equivalent circuit. In addition to analysis with the equivalent circuit, the elementary steps in electrode/electrolyte interface can be discussed by the simulations of Faraday impedance. The Faraday impedance is concerned with time constants related to elementary steps like adsorption of reaction intermediate and diffusion of reactant. This presentation is composed of following two topics: (a) detection of cracks formed in plating film by curve-fitting with the equivalent circuit, and (b) Faraday impedance to analyze the role of some additives in electrolyte solution for copper electrodeposition.

(a) Detection of cracks formed in plating film by curve-fitting with the equivalent circuit

The Ni-W plating is used as a surface protection of some metals because of the high abrasion resistance and corrosion resistance. Moreover, the Ni-W plating is focused as an alternative surface treatment for the chrome plating with chromate ions. However, the surface state of Ni-W plating changes remarkably depending on the plating condition, and cracks are often generated in the plating film. The detection method of cracks is necessary because the crack may have a significant influence on the corrosion resistance of the plating film. In this section, EIS is applied to detect the cracks formed in Ni-W plating. The Nyquist plots of the electrochemical impedance of Ni-W plated electrode without crack film shows capacitive loop whose diameters is huge. The impedance of Ni-W plating film with cracks shows small two capacitive loops. These results indicate that the presence of cracks can be discriminated by the measurement of the impedance. In addition, the influence of the cracks on protection property is discussed theoretically by assuming the equivalent circuits.

(b) Faraday impedance to analyze the role of some additives in electrolyte solution for copper electrodeposition

Many kinds of additives are included in electroplating bath of copper because the additives have important roles as accelerator, brightener and leveler. It is necessary to clarify the contributions of additives to elementary reactions in electrodeposition. EIS is able to discriminate several time constants involved in electrode reactions. In this section, impedance spectra of copper in various electrolytes were measured. For example, Nyquist plots of electrochemical impedance Z of copper in electrolyte solution containing chloride ions showed some semicircles. The capacitive semicircle in high frequency range was related to the time constant of charge transfer resistance and electric double layer capacitance. On the other hand, the inductive semicircle in low frequency range corresponds to Faradaic impedance regarding the adsorbed intermediate formed by the reaction of copper and chloride ion. The simulations for the electrochemical impedance were performed in order to obtain the kinetics parameters of each elementary step and the roles of some additives were discussed.