Evaluation of Defect Structure in Pulse Plated Trivalent Chromium Layers by Small Angle Neutron Scattering

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Small angle neutron scattering (SANS) was applied to evaluate the defect structure of thin trivalent chromium layers to determine the defect size and distribution without breaking the thin deposits. The deposits were prepared in from a trivalent chromium sulfate bath by various pulsing conditions. Pulse plating with low voltage and current density produces smaller defects in the chromium. The number of nano-size defects less than about 40 nm in size increases with plating voltage at constant current density. From this study, SANS is shown to be a useful technique to evaluate the microstructure of such deposits.

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Introduction

Pulse plating draws an attractive attention as one of effective methods to control microstructure and improve the quality of the chromium deposit, [1]. The pulse-plated chromium deposit is often observed to have refine grains, so called "crack-free structure" with low porosity.[2] However, the so called "crack-free chromium layer" sometimes shows poor corrosion resistance during neutral salt fog spay test. The poor corrosion resistance of the "crack free chromium layer" in the neutral salt fog environment means that the chromium layer has very fine defect or through cracks in the layer. When we think about electro-deposition process whether it uses direct or pulse current, defects are inevitably formed during electro-deposition process because of hydrogen evolution and metallic reduction. Engineering point of view, the evaluation of the defect size and distribution are significantly important because they influence on physical and mechanical properties of the deposited layers. The micro-size defects of the chromium layer such as surface cracks and fine pores have been usually well observed with an optical microscope and scanning electron microscope [4]. One of important things here, their sample preparation methods for the observation with the microscopes are so called a destructive method. The destructive method has several problems such as introducing secondary cracks to the layer and having difficulty to observe exact size of defects. Accordingly, it is necessary to find a non-destructive method to determine real size of defects of the electro-deposited layer. Recently, small angle neutron scanning (SANS) is attractive attention for its potential to analyze multi-phases in atomic scale [5]. The SANS has advantages to quantitatively measure objects with nano-scale in materials such as complex fluids, alloys, precipitates, porous media in fractal structure of ceramics, glasses and biological assembles. Hence, the objectives of this study are to apply small angle neutron scattering to determine defect size and distribution, especially nano-size cracks, of electro-deposited chromium layer and to establish a non-destructive method. Emphasis is on the evaluation of defects of chromium layers with different plating conditions.

1. Experimental Method

Electro-plating was carried out in a glass vessel containing chromium sulfate bath using titanium anode and the AISI 1002 steel cathode. The electroplating of each sample was carried with a regulator (HBS Co. MUP-l00) at the direct current density of 0.4 Acm^{-2} with different pulse voltage at 25 C, respectively. Microstructure of the chromium deposits was observed by field emission scanning electron microscopy (Jeol JSM-6700F). Small angle neutron scattering was carried out in HANARO reactor at Korea Atomic Energy Research Institute. Raw data were analyzed by ILL data treatment code.

2. Results and Discussion

Fig. 1 is typical chromium layer prepared by electro-deposition, which cross section and inside views were observed by optical microscopy and scanning electron microscopy, respectively. This observation is well agreement with previous reports.[1-4] As in Fig. 1, various size and shape of defects are observed on the cross section and inter-grains even for the same specimen. This supports that the crack mouth became bigger by polishing and electro-polishing, and secondary cracks were also introduced. Since the observed cracks of the chromium layers have been originated by hydrogen evolution during electroplating and introduced during a destructive sample preparation such as mechanical cutting and polishing, it is said that the chromium layers have cracks, and the cracks observed by destructive sample preparation do not really show actual shape and size. Accordingly, actual crack size of the chromium layers should be determined by a non-destructive technique such as small angle neutron scattering.

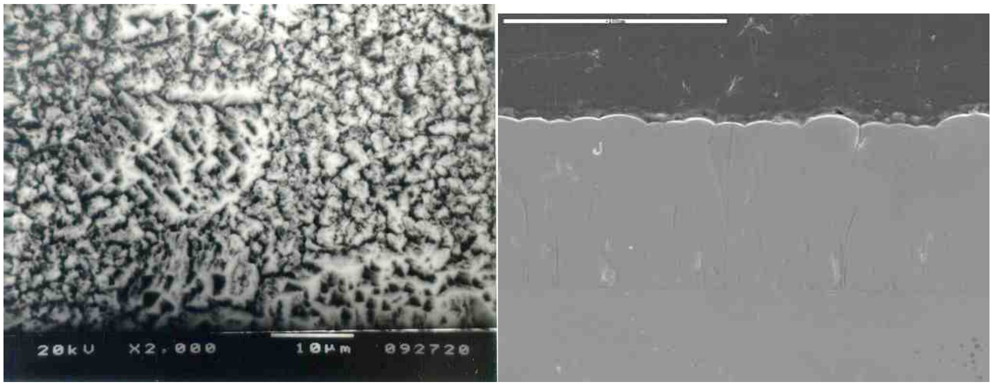

Fig. 1 SEM images of surface and cross section of pulse plated chromium layer

Fig. 2 is the small angle neutron scanning result of the chrome layers formed at direct current density of 0.4 Acm^{-2} and pulse current density of 1.5 Acm^{-2} with plating voltages of 4 V, where absolute cross section and momentum transfer scattering vector are related to relative amount of defect and defect size, respectively. In this study, Porod was used for analyzing the data because the defect size is relatively large. Porod law says that scattering intensity expressed by following equation.[5]

$$\left(\frac{d\Sigma}{d\Omega}\right)(Q) = K_P Q^{-4} \quad \text{------------ (1)}$$

where K_p is expressed by scattering length density (Dr) and specific surface area (S_v).

$$K_p = 2\pi(\Delta\rho)^2 S_v \quad \text{------------- (2)}$$

Defect size can be estimated by using that specific surface area is equal to 3/R with the assumption of spherical shape. As shown in figure 2, defect sizes of trivalent chromium layer are 4.9 µm for direct current plating, 3.3-4.5 µm for pulse plating. It is clear that defect size can be decreased by pulse plating.

Fig. 3 is the small angle neutron scanning result of the chrome layers formed pulse current density of 2.0 Acm^{-2} with plating voltages of 4.5 V. As shown in figure 3, defect sizes of trivalent chromium layer are in the range of 4.6-7.9 µm for the pulse plating. Comparing figure 2 and 3, it is clear that defect size can be decreased by decreasing plating current density and voltage.

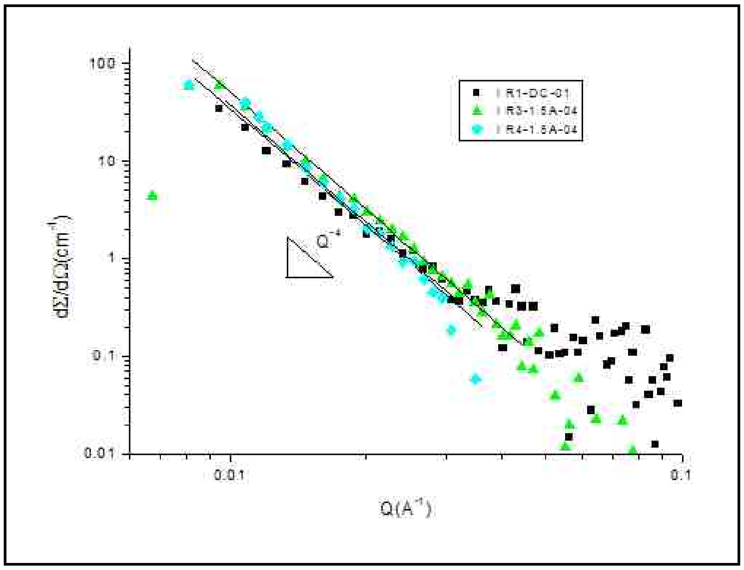

Fig. 2. Effect of Direct and Pulse Current on the Distribution of Defects in Chromium Layers

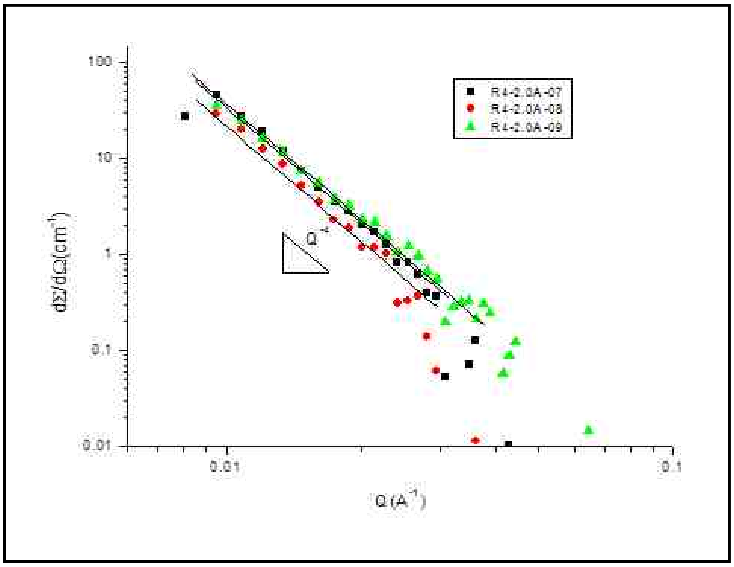

Fig. 3. Effect of Current Density and Voltage on the Distribution of Defects in Chromium Layers

Previous results showed that each defect size is in the range of about 40 nm, which is well agreement with the value evaluated by small angle neutron scanning and observed by field emission scanning electron microscopy.[6, 7] It is interesting to study why so large defect size can be estimated in this study. It should be related to microstructural development during electro-plating process. The effect of electro-plating voltage and current density on the microstructure can be explained by considering the electro-deposition process. The electro-deposition process includes four steps such as charge-transfer reaction, adsorption atom (ad-atom) formation, surface diffusion and growth [6]. The plating voltage and current density are related to ionic reduction rate and ion density in front of electrode. Hydrogen ions besides metallic ions are reduced during charge-transfer reaction and hydrogen gas evolution occurs on the substrate surface. Since the hydrogen gas evolution interferes the ad-atom deposit behavior, fine defects such as nano-size and micro-cracks can be formed. The ad-atoms formed on the substrate surface after the charge-transfer reaction move on the surface to grow by surface diffusion. High surface diffusion rate and low population of ad-atoms, and low over-potentials are factors enhancing the build up of old crystals and finally large grains and nodule are formed, while conversely low surface diffusion rates, high ad-atoms and high over-potentials on the surface enhance the creation of new nucleation and hydrogen gas evolution and relatively fine grains, sometimes so called crack free chrome, are formed [1, 4].

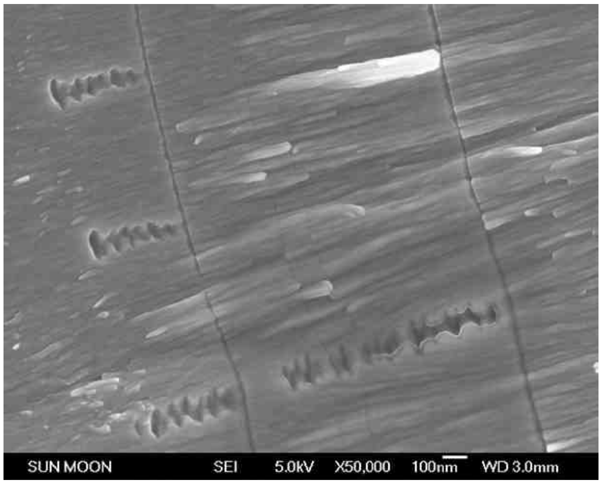

Fig. 4 Calabash Shape Defects in Chromium Layer

Since the defect size originated from hydrogen is related to amount of hydrogen gas trapped in the chromium layer, the defect can be separated or inter-connected. If each defect with about 40 nm gathered and inter-connected together, the defect size becomes larger. Fig. 4 shows the cross sectional view of chromium layer with defects. As shown in Fig. 4, the defect has calabash shape which means that the large defect was formed by inter-connection of small round shape of defect. Hence, it is considered that the result analyzed by Porod law estimates not each small defect but large defect.

Summary

Defect sizes of trivalent chromium layer are 4.9 m for direct current plating, 3.3-7.9 m for the pulse plating, which was decreased with decreasing plating current density and voltage. Calabash shape of defects were observed which supports that the large defect was formed by inter-connection of small round shape of defect. From this study, small angle neutron scattering can well estimate actual size and distribution. This means that SANS is one of useful techniques to evaluate defect size of the deposit.

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