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Pulse electroplating of ultra-fine grained Au films with high compressive strength

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ABSTRACT

Grain refinement, surface smoothening, and compressive strength enhancement of Au films were achieved by pulse electroplating using non-toxic sulfite-based electrolyte. The estimated grain size of the Au film prepared by pulse electroplating was 10.5 nm, and it was much smaller than the grain size of the Au film prepared by constant-current electroplating, which was 22.8 nm. This can be attributed to the increase in the nucleation rate during the on-time period. The mechanical strength of the Au films in micro-scale was also evaluated. The pulse electroplated Au micro-pillar acquired a high compressive strength of 800 MPa, and it was larger than the constant-current electroplated micro-pillar, which was 600 MPa. The high strength is presumably due to the grain-boundary strengthening known as the Hall–Petch effect. The compression test also revealed that the pulse electroplated Au micro-pillar possesses better ductility and malleability than that fabricated by constant-current electroplating.

1. Introduction

Au materials fabricated by electroplating have been commonly used as contact materials for high reliability circuit boards, electrical connectors, relays, and micro- and nano-scale electronic components for many decades because of their high electrical conductivity, chemical stability, corrosion resistance, and ductility [1–5]. In recent years, Au has become a promising material for use as the movable structures and proof mass in micro-electrical–mechanical system (MEMS) accelerometer devices, because of its high density (19.3×10^3 kg/m^3 at 298 K), which is about 10 times higher than that of silicon (2.33×10^3 kg/m^3 at 298 K) [6]. However, Au is known to be a soft material. The mechanical strength becomes a concern in miniaturization of the MEMS device. Yield stress of bulk Au is reported to be 55–200 MPa [7], and the strength can be increased to 550 MPa when using specimens having sub-micro-dimensions because of the size effect [8]. Decreasing grain size of the Au materials is expected to further enhance the mechanical properties according to the Hall–Petch relationship [9–10].

Pulse electroplating (PE) has been reported to be effective in fabricating Au materials with finer grains, higher uniformity, and lower porosity [11–12]. Also, it is possible to control the composition and the film thickness by regulating the pulse amplitude and width. Most importantly, an increase in the nuclei density could be achieved to obtain electroplated films with finer grains. On the other hand, the Vickers micro-hardness test is the most popular method for evaluating the mechanical properties of electroplated films. However, hardness results are often affected by the substrate. It cannot show the real strength of the electroplated materials, especially for films in micro-/nano-scale. Therefore, it is necessary to evaluate the micro-mechanical strength of Au electroplated films for practical applications in miniaturized devices.

In this study, the Au films prepared by PE with a sulfite-based electrolyte showed fewer defects, lower surface roughness, finer grain size, and denser texture when compared with the Au films prepared by the conventional constant-current electroplating (CE). The micro-mechanical properties of Au micro-pillars fabricated from the Au films prepared by PE and CE were evaluated by micro-compression tests. Some interesting information has been found in a webpage of the Russian Electroplating Society [13] (in Russian), where gold materials are claimed to have mechanical strength higher than 1 GPa. The results presented in the webpage could not be found in any refereed scientific journal, and the method by which the mechanical strength was evaluated is not clear. To the best of our knowledge, this is the first report on the micro-mechanical strength of pure Au materials fabricated by PE. Also, the electroplated pure Au film prepared by PE showed an ultra-high strength of 800 MPa, which is the highest value reported for pure Au in the peer-reviewed literature.

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2. Experimental

The Au electrolyte used in this study was a commercially available sulfite-based electrolyte provided by Matex Japan (Matex Gold NCA). The electrolyte contains 50 g/L of Na_2SO_3, 50 g/L of $(NH_4)_2SO_3$, and 21.63 g/L of $Na_3[Au(SO_3)_2]$ with pH of 8.0 and 5% sodium gluconate. Cu plates and Pt plates were used as the cathode and anode, respectively. For the PE, the pulse current (I_{on}) was 10 mA/cm^2, and the off-time current (I_{off}) was 0 mA/cm^2. The on-time (T_{on}) and the off-time (T_{off}) of the PE were fixed at 10 ms as the optimized parameter. The reaction temperature was 40 °C for both PE and CE. For the CE, the current density was fixed at 5 mA/cm^2, which is the same as the average current density of the PE. A gold film was electroplated using a cyanide-based electrolyte containing 230 g/L of di-ammonium hydrogen citrate, 85 g/L of KCN, and 14.63 g/L of K $[Au(CN)_2]$ with pH of 5.0 also provided by Matex Japan (Matex Gold BOG-10) to serve as the comparison reference. The Au film was electroplated on a Pt substrate. The current density used was 4 mA/cm^2, and the temperature was 60 °C.

After the electroplating, micro-pillars were made from the Au films by focused ion beam (FIB, FB2100, Hitachi) milling. The dimensions of the fabricated pillars were 10 μm × 10 μm × 20 μm. The compression tests were carried out using a test machine specially designed for micro-sized specimens equipped with a flat-ended diamond indenter at a constant displacement of 0.1 μm/s. Observation of the specimens before and after the compression test was conducted using the scanning ion microscope (SIM) equipped with the FIB. The morphology of the Au films was examined by an atomic force microscope (AFM, XE-100, Park System). The crystallographic structures were investigated by an X-ray diffractometer (XRD, Ultima IV, Rigaku). The X-ray was operated at 40 kV and 40 mA. Average grain size was calculated using the Scherrer equation.

3. Results and discussion

Fig. 1 shows the AFM micrographs of the Au films. The Au film fabricated by the cyanide-based electrolyte (CE-Cy-F) had hill-like bumps morphology and the roughest surface, as shown in Fig. 1(a), and the surface roughness (R_a) was 117.09 nm. The Au film prepared by CE with the sulfite-based electrolyte (CE-Su-F) showed irregular small dome-shaped bumps with a height of ca. 0.2–0.25 μm, as shown in Fig. 1(b). On the other hand, the Au film fabricated by PE with the sulfite-based electrolyte (PE-Su-F) had a smooth and defect-free surface, as shown in Fig. 1(c). For the CE-Su-F, the surface roughness was 32.5 nm, whereas it was only 10.7 nm for the PE-Su-F. The smooth surface achieved by PE was attributed to the enhanced desorption of the hydrogen gas bubbles during the off-time of the PE, because the defects are suggested to be caused mainly by the hydrogen gas bubbles during plating.

Fig. 2 shows the XRD patterns of the Au films. All XRD patterns exhibit four peaks corresponding to the (111), (200), (220), and (311) planes of metallic face-centered cubic gold (JCPDS No. 04-0784). The XRD results are similar to the work reported by Bozzini et al. [14]. Unlike the reference CE-Cy-F, the Au films fabricated with the sulfite-based electrolyte showed intense (111) orientation. It was reported that the surface energy of the (111) crystal growth orientation is the lowest when compared with the other crystal orientations such as (100) and (110) planes [15]. Moreover, the XRD peaks of the PE-Su-F were broader than those by the CE. The estimated grain size of the PE-Su-F was 10.5 nm, which was much smaller than the grain size of 22.8 and 17.6 for the CE-Su-F and the CE-Cy-F, respectively. The grain refinement effect can be attributed to the higher pulse current density and nucleation rate during the on-time.

In summary, the AFM micrographs and XRD patterns indicate that smooth and defect-free Au film with an ultra-fine grain size of 10.5 nm can be achieved by the optimized parameters of the PE. The grain size is smaller than the values reported in previous studies [16–18]. For the optimized PE parameters, the pulse current is 10 mA/cm^2 and the off-time current is 0 mA/cm^2. On-time and off-time of the PE are both 10 ms.

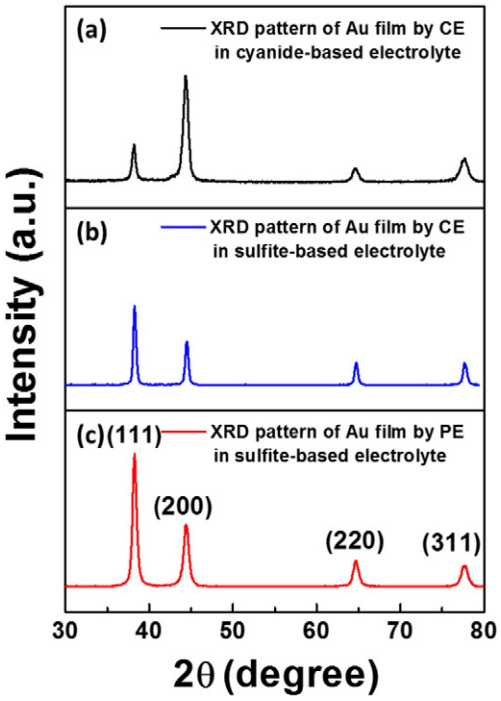

Fig. 2. X-ray diffraction patterns of (a) the Au film prepared by the CE with the cyanide-based electrolyte, (b) the Au film prepared by the CE and (c) the PE with the sulfite-based electrolyte.

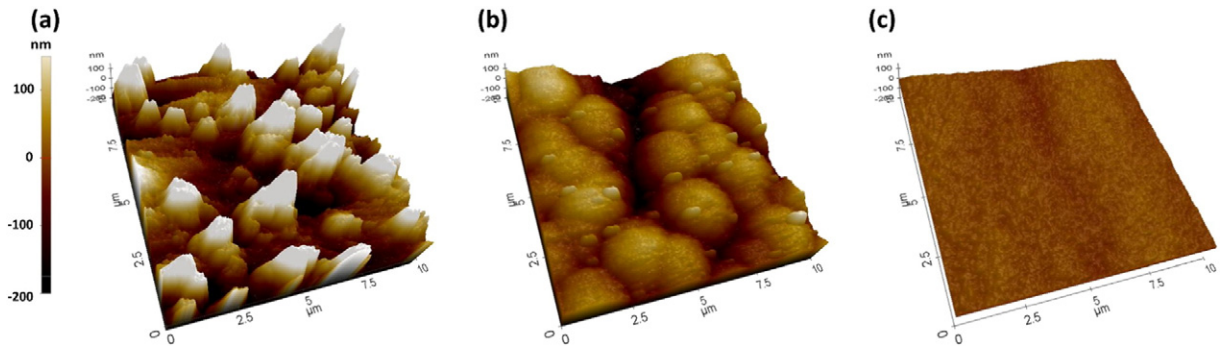

Fig. 1. AFM micrographs of (a) the Au film surface prepared by the CE with the cyanide-based electrolyte, (b) the Au film surface prepared by the CE and (c) the PE with the sulfite-based electrolyte.