Co-Electrodeposition of Au–TiO$_2$ Nanocomposite and the Micro-Mechanical Properties

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Abstract: Strengthening of electrodeposited Au-based materials is achieved by co-electrodeposition with TiO$_2$ nanoparticles dispersed in a sulfide-based gold electrolyte. TiO$_2$ content in the composite film is adjusted by concentration of the TiO$_2$ in the gold electrolyte. Effects of the TiO$_2$ content on surface morphology, crystalline structure and microstructure of the composite film are investigated. Mechanical properties of the Au–TiO$_2$ composite films are evaluated by micro-Vickers hardness and micro-compression tests. The hardness increases from 135 to 207 H$_V$ when the TiO$_2$ content is increased from 0 to 2.72 wt%. Specimens used in the micro-compression test are micro-pillars fabricated from the composite film, and the yield strength reaches 0.84 GPa by incorporating 2.72 wt% TiO$_2$ into the film.

Keywords: co-electrodeposition; Au–TiO$_2$ composite; oxide dispersion strengthening; micro-compression test

1. Introduction

Electrodeposition methods are widely applied in fabrication of micro-components used in miniaturized electronic devices such as microelectromechanical system (MEMS) devices. For instance, the proof mass and micro-springs in a highly-sensitive MEMS accelerometers are prepared by Au electrodeposition [1,2]. Au is used here because performance of a MEMS accelerometer is highly dependent on overall mass of the movable components, while miniaturization of the component is also required. Hence, Au (mass density = 19.32 g/cm$^3$ at 298 K) becomes the ideal material to achieve requirements of high performance and miniaturization at the same time. On the other hand, Au has relatively weak mechanical strengths among materials commonly used in electronics, and this raises a concern on the structure stability of movable micro-structures composed of Au. Strengthening of the electrodeposited Au becomes an important task to ensure high structure stability of the movable micro-structures.

Co-electrodeposition of metal matrix composites (MMCs) is an effective and simple strategy to enhance a specific property of electrodeposited materials. Common reinforcement materials are nanoparticles (NPs) include oxides such as Al$_2$O$_3$ [3], TiO$_2$ [4,5], and Cr$_2$O$_3$ [6], carbides like SiC [7] or graphitic materials like carbon nanofiber [8] and carbon nanotube [9], inorganic particles like phosphorus [10] and polymers like polyaniline [11]. For enhancing mechanical properties of electrodeposited Au while keeping the high mass density, the effects of oxide dispersion
strengthening [12] could be readily applied by incorporating a small amount of oxide NPs into the electrodeposited film.

In this study, TiO$_2$ NPs are introduced into the Au matrix composite by co-electrodeposition. Moreover, in consideration of the sample size effect [13], that is mechanical properties of metallic materials varied along with dimensions of the specimen used in the evaluation, the mechanical properties are evaluated by micro-compression test for application in miniaturized electronic devices.

2. Materials and Methods

Co-Electrodeposition of Au–TiO$_2$ Composite Films

The base electrolyte was a non-cyanide sulfite-based commercial Au plating bath purchased from MATEX·JAPAN Co., Ltd., Shizuoka, Japan. The bath was composed of 18.13 g/L of Au(SO$_3$)$_2$ and additives including ethylenediaminetetraacetic acid (EDTA) and sodium gluconate with pH value of 7.5. 10, 30, and 50 g/L of TiO$_2$ NPs (AEROXIDE$^\text{®}$ TiO$_2$ P25, Evonik, Essen, Germany) were added into the base electrolyte to form Au–TiO$_2$ composite films with different TiO$_2$ contents. Cold-worked Cu plates were masked with polyimide tape into a single side with surface area of 10 × 10 mm$^2$ as the working electrodes. Cu electrodes were treated with 1 M KOH and 1 M HCl for 1 min each at room temperature right before the electrodeposition. The counter electrode was a Pt plate with a total surface area of 40 × 10 mm$^2$, and the reference electrode was Ag/AgCl(sat. KCl). The electrodeposition was conducted at 5 mA/cm$^2$ using a potentiostat (1287A, Solartron, Leicester, UK). The TiO$_2$ contained electrolyte was ultrasonicated for 30 min using a ultrasonicator (VS-100III, AS ONE, Osaka, Japan) right before the deposition to improve the dispersion of TiO$_2$ NPs in the electrolyte. Temperature of the electrolyte was kept at 40$\degree$C during the whole electrodeposition process.

Surface morphology of the films was observed with a scanning electron microscope (SEM, S-4300 SE, Hitachi, Tokyo, Japan). The composition was determined by the energy dispersive X-ray analyzer (EDX, EMAX EX-250, Horiba, Kyoto, Japan) equipped in the SEM. The crystal structure was characterized through an X-ray diffractometer (XRD, Ultima IV, Rigaku, Tokyo, Japan).

Mechanical properties of the films were appraised by a micro-Vickers hardness testing machine (HMV-G20s, Shimadzu, Kyoto, Japan) at 50 g of load and micro-compression evaluation using a lab-designed micro-testing system. Specimens used in the micro-compression tests had a cuboidal pillar shape with dimensions of 20 µm in height and 10 × 10 µm$^2$ square cross-section. The focus ion beam system (FIB, FB2100, Hitachi, Tokyo, Japan) was used to fabricate the micro-pillars. The pillar surface was further polished with low current Ga$^+$ beams to allow observation of the microstructure through a scanning ion microscope (SIM) equipped in the FIB.

Micro-compression tests were conducted using a flat-topped indenter with a diameter of 50 µm on the top surface. Load resolution of this equipment was 10 µN, and the displacement resolution was 5 nm. More details of the micro-testing system are reported in a previous study [14]. A constant displacement rate of 0.05 µm/s was used in all micro-compression tests.

3. Results

3.1. Surface Morphology and Crystalline Structure

TiO$_2$ concentration in the film was estimated from the proportion of Ti in the film by the EDX, which Ti signals detected by the EDX were assumed to be contributed by the TiO$_2$ NPs only. From the estimation, TiO$_2$ concentrations in films electrodeposited using the Au base electrolyte containing 0, 10, 30 and 50 g/L of the TiO$_2$ NPs were 0, 1.45, 1.69, and 2.72 wt% TiO$_2$ NPs, respectively. Surface morphology of the films are shown in Figure 1. Condensed structures were observed on surface of the pure Au film. Surfaces of the Au–TiO$_2$ composite films were composed of nodule structures, which were different from that of the pure Au film. The difference is suggested to be originated from the applied potential to the working electrode, since galvanostatic electrodeposition was applied here.
and the electrical conductivity of TiO$_2$ is lower than that of Au, then incorporation of TiO$_2$ into the electrodeposited film would change the applied potential and eventually affect the nucleation of Au on the surface. In addition, TiO$_2$ NPs adsorbed on the surface could also promote heterogeneous nucleation of Au. Hence, nodule structures were observed and size of the nodule visibly reduced due to the promoted Au nucleation.

**Figure 1.** Surface morphology of electrodeposited (a) Au film and Au–TiO$_2$ composite films containing (b) 1.45, (c) 1.69, and (d) 2.72 wt% TiO$_2$.

XRD spectra of the TiO$_2$ NPs, pure Au and Au–TiO$_2$ composite films (2.72 wt% TiO$_2$) are shown in Figure 2. Typical face-centered cubic (FCC) Au characteristic peaks were identified in both Au and Au–TiO$_2$ composite films. The anatase TiO$_2$ (101) peak at $2\theta = 25.1^\circ$ also appeared in XRD patterns of the Au–TiO$_2$ composite film containing 2.72 wt% TiO$_2$ (inset of Figure 2). This result confirmed incorporation of TiO$_2$ NPs into the Au matrix, forming a Au–TiO$_2$ MMCs film. In addition, the peak intensity ratio of FCC-Au (111) peak to other peaks was lower for the Au–TiO$_2$ composite film compared with the pure gold film. This result again revealed the promoted heterogeneous nucleation of Au after adsorption of TiO$_2$ NPs on surface of the working electrode, because (111) orientation is the preferred nucleation orientation for Au and the intensity reduced when the heterogeneous nucleation is promoted.

**Figure 2.** XRD spectra of Au, TiO$_2$ NPs, and the Au–TiO$_2$ composite film. The inset shows zoomed spectra of $2\theta = 20^\circ$ to $30^\circ$. 
Average grain size of Au in the film was evaluated by averaging the weighted grain size values of primary (111) to quaternary (311) X-ray diffraction peaks from the Scherrer equation. The Scherrer equation is defined as follows:

\[ \tau = \frac{K\lambda}{D\cos\theta} \]  

where \( \tau \) is the mean size of the ordered domain, \( K \) is the shape factor, \( \lambda \) is the wave length of incident X-ray beam (approximate to be \( 1.54 \times 10^{-10} \) m), \( D \) is the full width at half maximum of the diffraction peak, and \( \theta \) is the Bragg diffraction angle.

Average grain size of Au in the film without TiO \(_2\) NPs was 20.4 nm while that of the 2.72 wt\% TiO \(_2\) Au–TiO\(_2\) composite film was 16.3 nm. The decrease in the average grain size indicated grain refinement caused by incorporation of the TiO\(_2\) NPs, which demonstrated the effect of promoted Au nucleation when adding TiO\(_2\) NPs into the electrolyte.

Figure 3 shows microstructure of the electrodeposited films from SIM images of the as-fabricated Au–TiO\(_2\) composite micro-pillar. White spots on surface of the micro-pillars illustrated the portion that is TiO\(_2\)-rich (Figure 3b–d). Total amount of the TiO\(_2\)-rich portion increased with an increase in TiO\(_2\) content in the micro-pillar.

![Figure 3](image_url)

**Figure 3.** Scanning ion microscope (SIM) images showing microstructure of the (a) Au micro-pillars and Au–TiO\(_2\) composite micro-pillars containing (b) 1.45, (c) 1.69, and (d) 2.72 wt\% of TiO\(_2\).

### 3.2. Mechanical Properties of Au–TiO\(_2\) Composite

All micro-pillars showed ductile deformation and deformed to a barrel-shape after the micro-compression test. Figure 4 shows SIM images of the 2.72 wt\% TiO\(_2\) Au–TiO\(_2\) composite micro-pillar before and after the micro-compression test. This deformation behavior is typical for micro-pillars composed of polycrystals [15].

Yield strengths (\( \sigma_y \)) of the micro-pillars were obtained from the engineering strain–stress curves shown in Figure 5. Micro-Vickers hardness (HV), \( \sigma_y \), HV to \( \sigma_y \) coefficient (HV/\( \sigma_y \)), and theoretical mass density of the composites are summarized in Table 1. Theoretical mass density of the films was calculated from the TiO\(_2\) NPs content and densities of pure Au and TiO\(_2\). The HV increased from 135 to 207 HV, and the \( \sigma_y \) increased from 0.44 to 0.84 GPa due to its having 2.72 wt\% of TiO\(_2\) in the Au matrix. The strengthening was mostly contributed by the oxide dispersion strengthening. The HV/\( \sigma_y \)’s were all close to three, and the ratio decreased as the \( \sigma_y \) increased. The HV/\( \sigma_y \) is commonly known as the Tabor factor. The value and the decreasing trend observed in this study both corresponded well with the behavior of close-packed structure metals reported in the literature [16]. Mass density of 2.72 wt\% TiO\(_2\) content Au–TiO\(_2\) composite was 98% of that pure Au while the \( \sigma_y \) increased by almost 91%.
In conclusion, the Au–TiO$_2$ composite possesses high strength with high mass density, which is promising for miniaturized electronic devices requiring low Brownian noise with high structure stability.

| Electrolyte | TiO$_2$ Content (wt%) | HV (Hv) | $\sigma_y$ (GPa) | HV/$\sigma_y$ | Mass Density (g/cm$^3$) |
|-------------|----------------------|---------|-----------------|--------------|------------------------|
| 0 g/L TiO$_2$ | -                    | 135     | 0.44            | 3.01         | 19.32                  |
| 10 g/L TiO$_2$ | 1.45                 | 162     | 0.56            | 2.84         | 19.08                  |
| 30 g/L TiO$_2$ | 1.67                 | 176     | 0.63            | 2.74         | 19.05                  |
| 50 g/L TiO$_2$ | 2.72                 | 207     | 0.84            | 2.42         | 18.90                  |

4. Conclusions

In this work, Au–TiO$_2$ composite films were fabricated by the co-electrodeposition method, and the mechanical properties were evaluated by micro-Vickers hardness and micro-compression tests. XRD spectrum of the films indicated grain refinement in the electrodeposited Au after incorporation of TiO$_2$ NPs into the film. Vickers hardness of the Au-based film was enhanced from 135 to 207 Hv by incorporating 2.72 wt% of TiO$_2$ into the film, and yield strength of the micro-pillar reached 0.84 GPa. The yield strength was improved by ~91% and the mass density reduced by only ~2% when compared with those of pure gold. In conclusion, the Au–TiO$_2$ composite possesses high strength with high mass density, which is promising for miniaturized electronic devices requiring low Brownian noise with high structure stability.
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