Effect of Electrodeposition Conditions on Surface Roughness of Copper Electroformed Replicas

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Abstract

With recent developments in ultraprecision machining methods, the manufacture of devices with sub-10 nm shape accuracy and with surface smoothness at the atomic level has been realized. However, it takes a lot of work and time to fabricate such precise devices. Electroforming, a replication technique using electrodeposition, is expected to be an efficient fabrication process for these devices. In this paper, we report fundamental research on electroform replication of ultra-smooth masters. Smooth float glass substrates that have a root-mean-square surface roughness of 0.1 nm were used as masters. Copper electroformed replicas were fabricated to investigate the relationship between electrodeposition conditions and surface roughness of the replicas. Experimental results indicate that the microstructures of the electroplated films affect the surface roughness of replicas.

Key words: electroforming, electrodeposition, electroplating, replication

1. Introduction

Electroforming is a highly precise replication technique that forms metal parts through electrodeposition. Electroformed replicas are obtained by separating electroplated films with a thickness of hundreds μm to several mm from the masters they are deposited on. Electroforming has been used to fabricate high-precision devices such as x-ray optics1)-3), injection molds4), and MEMS5). In most applications, electroformed replicas have the same accuracy as their masters because the replication accuracy of electroforming is sufficiently high.

With recent developments in ultraprecision machining methods, the precision of masters has increased. For example, quartz glass masters for x-ray optics form a peak-to-valley accuracy of several tens of nm and have a root-mean-square (RMS) surface roughness of a few Å3). Any error in the electroforming process is not negligible, particularly when masters have such high precision. The error is especially affected by the electrodeposition conditions. Previous studies on electroformed x-ray optics found that accuracy in shape replication on the order of several tens of nm in peak-to-valley is achieved under optimized electrodeposition conditions6). However, few studies have been done on the improvement of surface roughness of the electroformed replicas. Nickel electroformed x-ray mirrors had a larger surface roughness than their masters in a previous study7). However, the effects of electrodeposition conditions on the surface roughness of electroformed replicas and its mechanism are not fully understood. In this paper, we report relationships between electrodeposition conditions and the surface roughness of electroformed replicas, and discuss its mechanism in terms of crystalline structure.

2. Experimental apparatus and method

2.1 Fabrication of electroformed replicas

A schematic of the fabrication process of electroformed replicas is shown in Figure 1. Smooth float glass substrates (76 mm × 15 mm × 1.1 mm) were used as masters. First, before electroplating, a thin copper film of less than 1 μm was deposited on the master using electron-beam evaporation, as the master is non-conductive. Next, the master was electroplated with a 50-μm-thick copper layer using the plating apparatus shown in Figure 2. Compositions and operating conditions of the acid copper-plating bath are given in Table 1. The solution was prepared by dissolving copper (II) sulfate pentahydrate (99.5% purity) in dilute sulfuric acid. Oxygen-free copper plates, which had the same width as the masters, were used as anode electrodes. The electroplated film was formed at a constant cathode current density. A part of the

Table 1 Compositions and operating conditions

| Chemical composition | CuSO₄·5H₂O 280 g/L | H₂SO₄ 50 g/L |
|----------------------|--------------------|-------------|
| Anode                | Oxygen-free copper (OFC) plate |
| Temperature          | Room temperature (22 ~ 24°C) |
| Cathode current density | 1, 4, 8, 12, 16, 20 mA/cm² |
| Thickness            | Approx. 50 μm |
electroplated film was separated from the master. The process was repeated at different current densities, 1, 4, 8, 12, 16, and 20 mA/cm², and two replicas were fabricated in each current density.

2.2 Evaluation of surface roughness of masters and replicas

2D surface profiles of the masters and replicas were generated with a scanning white-light interferometric microscope (Newview 700, Zygo). The profiles contained not only roughness elements but also waviness elements. To separate the waviness elements and roughness elements on the profiles, a 2D Gaussian filter with a cut-off frequency of 50 μm was applied. In Figures 3(a), (b), and (c), the profile of a replica formed at the cathode current densities of 1 mA/cm², its waviness profile, and its roughness profile, are shown, respectively. In Figure 4, a surface roughness profile of one of the masters is shown. The masters were extremely smooth; surface roughness was 0.1 nm RMS.

Figure 1: Schematic of the fabrication process of electroformed replicas. (I) A copper thin film was evaporated on a glass substrate as a conductive layer. (II) An electroplated copper film with a thickness of 50 μm was deposited. (III) and (IV) A part of the electroplated film was separated from the glass substrate.

Figure 2: Plating apparatus

Figure 3: (a) Surface profile of a replica formed at the cathode current density of 1 mA/cm², (b) its waviness profile, and (c) its roughness profile.

Figure 4: Surface roughness profile of a master
3. Effect of cathode current densities on surface roughness of electroformed replicas.

Examples of surface roughness profiles of the replicas formed at various cathode current densities are depicted in Figure 5. RMS surface roughness of the replicas was plotted against cathode current density in Figure 6. The replicas had a larger surface roughness than the masters regardless of the cathode current density, and a typical wavelength of roughness was 10 to 30 μm. The replicas formed at cathode current densities of 1 and 4 mA/cm² showed large values of surface roughness (0.8-1.1 nm RMS). Surface roughness of the replicas decreased as the cathode current density increased, and converged to approximately 0.3 nm RMS.

Figure 5: Surface roughness profiles of replicas

Figure 6: RMS surface roughness of replicas. Each point is an average of four measurements.

4. Microstructure of replicas.

Scanning electron microscope (SEM) images of the electroplated copper film of the replicas as a function of the cathode current density are shown in Figure 7. The electroplated film deposited at low cathode current densities (1 and 4 mA/cm²) has a grain size of 20 to 40 μm. The grains decrease in size with increasing cathode current density.

The grain size and a grain distribution were observed in a direction perpendicular to the growth direction via the following steps:
I. The replicas were embedded in epoxy resin cured at room temperature.
II. The embedded replicas were abraded roughly with emery paper.
III. The embedded replicas were polished with alumina slurry (5, 1, and 0.05 μm in diameter).
IV. Etching using 10 wt% ammonium persulfate ((NH₄)₂S₂O₈) solution to highlight.

In Figure 8, cross-section images of the replicas observed with a laser scanning microscope as a function of the cathode current density are shown. The electroplated film deposited at low cathode current densities (1 and 4 mA/cm²) has columnar grains with a size of 10 to 30 μm. The columnar grains decrease and a fine structure smaller than 10 μm in diameter increases with increasing cathode current density. However, even at the maximum current density of 20 mA/cm², coarse grains are still generated.

The microstructure of the electrodeposit is strongly influenced by a balance between a nucleation rate and a crystal growth rate. When the nucleation rate is higher, the average size of the grains will be smaller. Generally, the nucleation rate increases as overpotential increases. In this experiment, a higher cathode current density resulted in a higher overpotential, a higher nucleation rate and a smaller average grain size.

5. Discussion

The experimental results show that the surface roughness of the replicas decrease as the cathode current density increases. We describe a mechanism by which the cathode current density effects a
Figure 7: SEM images of copper electroplated films of replicas

(a) 1 mA/cm$^2$
(b) 4 mA/cm$^2$
(c) 8 mA/cm$^2$
(d) 12 mA/cm$^2$
(e) 16 mA/cm$^2$
(f) 20 mA/cm$^2$

Figure 8: Cross-sectional images of copper electroplated films of replicas

(a) 1 mA/cm$^2$
(b) 4 mA/cm$^2$
(c) 8 mA/cm$^2$
(d) 12 mA/cm$^2$
(e) 16 mA/cm$^2$
(f) 20 mA/cm$^2$
change in surface roughness of the replicas. Generally, residual stresses up to 100 MPa arise in electroplated films. Some residual stresses arise near grain boundary regions. Residual stress in electroplated copper film is known to increase with decreasing grain size\(^6\); in other words, it increases as the total area of the grain boundary increases. The electroplated copper film deposited at low cathode current densities has a columnar structure with a size of 10 to 30 μm. Residual stresses arising near the interface between columnar grains deform the replica in a direction perpendicular to its surface, and as a result, surface roughness of the replicas is larger than that of the masters (Figure 9). The typical wavelength of surface roughness was therefore the same as the size of columnar grains in the experiments. Surface roughness decreased as the cathode current density increased because the columnar grains decreased. However, even at the maximum current density of 20 mA/cm\(^2\), surface roughness of the replicas was still larger than that of the masters. We theorize that the remaining coarse grains caused the roughness of the replicas formed at high cathode current densities.

![Columnar structure](image)

**Figure 9:** Residual stresses that arise near the interface between columnar grains cause roughness of electroformed replicas.

### 6. Conclusion

In this study, we have presented the effect of electrodeposition conditions on the surface roughness of copper electroformed replicas, and proposed a mechanism by which the surface roughness of the replicas can be larger than that of the masters. The surface roughness of the copper electroformed replicas varied depending on the cathode current density, and was 0.3 to 1.1 nm RMS approximately. The typical wavelength of surface roughness of the replicas is 10 to 30 μm, which is in good agreement with the size of the columnar grains observed in the electroplated copper films. The results indicate that residual stresses arising near the interface between the columnar grains deform the replica in a direction perpendicular to its surface, and as a result, the surface roughness of the replicas is larger than that of the masters.

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