Electrodeposited Copper Wire Mesh Formed on Chromium Template, the Formation Mechanism and Application as a Transparent Conductive Film

Kazuo Kondo,∗ Yuichi Ikeda, and Masayuki Yokoi∗
Osaka Prefecture University, Naka-ku, Sakai 599-8531, Japan

Optically transparent and electrically conductive thin films act as a window for light to pass through to the underlying active components of a device while functioning as an electrical conductor.1 In photovoltaic devices, transparent conductive films allow light transmission through the top electrode to the active photovoltaic generating material. In touch panels, they allow light transmission from a display through the capacitance or resistance variation sensor. Both applications require a high visible light transmittance and low sheet resistance to conduct electricity over the panel.

ITO has been the most popular transparent conductive film for over several decades. Vapor deposition or sputtering is generally used for the production of the ITO film,2 however, its production method is expensive and complex. Indium has an unstable supply and this increases the indium cost.3,4 The development of ITO substitutes has been required for the production of the ITO film,2 however, its production method is expensive and complex. The copper wire mesh formation mechanism that preferentially forms along the chromium template crack edges is shown in Fig. 1a B and Fig. 1b D. The copper wire mesh and E is the cracks in the chromium template. The copper wire mesh has been measured by a spectrophotometer (UV-2450, Shimadzu) at the wavelength of 380 to 760 nm. The F-AES is Model 680 by Ulvac-phi operated at a 10 kV acceleration voltage and 10 nA specimen current. 3 kV argon sputtering with the sputtering speed of 3.2 nm/min with every every 1.6 nm depth. (The rough plain effect may have to take into an account since the Ar ion sputtering often causes a surface roughening.)

The LSV of the copper electrodeposition has been measured at the scanning rate of 5 mVs (HZ-300, Hokuto Denko). The working electrode is attached to the rotating disk electrode (Hokuto Denko) and the anode is lead (Nirako Co.). The electrodeposited copper wire mesh has been annealed in air at 150 °C for 5 hrs. The copper wire mesh bath consists of 25 g/L H2SO4 and 200g/l CuSO4 · 5H2O. The current densities are 30 and 50 mA/cm2 for 5 to 150 seconds. The copper wire mesh has been measured by a spectrophotometer (UV-2450, Shimadzu) at the wavelength of 380 to 760 nm. The F-AES is Model 680 by Ulvac-phi operated at a 10 kV acceleration voltage and 10 nA specimen current. 3 kV argon sputtering with the sputtering speed of 3.2 nm/min with every every 1.6 nm depth. (The rough plain effect may have to take into an account since the Ar ion sputtering often causes a surface roughening.)

The LSV of the copper electrodeposition has been measured at the scanning rate of 5 mVs (HZ-300, Hokuto Denko). The working electrode is attached to the rotating disk electrode (Hokuto Denko) and rotated at 100 r.p.m..

Copper wire mesh electrodeposits have been formed along the cracks of an electrodeposited chromium template. By reducing the electrodeposition time, the open area ratio increased and wire width of the copper wire decreased. The electrodeposited copper wire mesh has an 84.0% transmittance, 9.8 μm wire width and 0.187 Ω/□ sheet resistance. These characteristics satisfy some practical use requirements of a transparent conductive film. The copper wire mesh electrodeposits initiate at the crack edges. These initial deposits, which form along the crack edge, combine and then form the copper wire mesh. The copper deposition initiated at sites along the crack edges. As electrodeposition progressed, growth from the initiation sites coalesced to give copper wire formation along the crack edges. It eventually forms a spherical cross section shape along the crack. The initial deposit formation along the crack edge is due to the current incubation removal of the local oxide film preferentially along the chromium template crack edges.

Electrodeposited chromium is well known to form numerous cracks on the deposited surface. If the copper can electrodeposits along these cracks(templates), the electrodeposited copper forms a copper wire mesh. The copper wire mesh formation mechanism that preferentially forms along the chromium template crack edges is clarified. We tried to satisfy the following practical characteristics of copper wire mesh as a touch panel i.e., less than a 10 μm wire width, more than an 80% transmittance and less than a 0.5 Ω/□ sheet resistivity.

Experimental

A chromium template bath contains 2.5 g/L H2SO4 and 250 g/L CrO3 (Wako Chemical Co.). The current density is 600 mA/cm2 and the electrodeposition time is 72 minutes. The cathode is SUS-304 (Nirako Co.) and the anode is lead (Nirako Co.). The electrodeposited chromium has been annealed in air at 150 °C for 5 hrs. The copper wire mesh bath consists of 25 g/L H2SO4 and 200g/l CuSO4 · 5H2O. The current densities are 30 and 50 mA/cm2 for 5 to 150 seconds. The anode is copper.

The open area ratio, sheet resistance, transparency and linear scanning voltammetry (LSV) of the copper wire mesh have been measured. The open area ratio of the copper wire mesh has been measured based on the scanning electron microscopy (SEM) image of the copper wire mesh on a chromium template by analysis using image processing software (ImageJ). The sheet resistances of the copper wire mesh removed from the chromium template have been measured by the four probe method (4156CA, Gilent). The transparency of the copper wire mesh has been measured by a spectrophotometer (UV-2450, Shimadzu) at the wavelength of 380 to 760 nm. The FE-AES is Model 680 by Ulvac-phi operated at a 10 kV acceleration voltage and 10 nA specimen current. 3 kV argon sputtering with the sputtering speed of 3.2 nm/min with every every 1.6 nm depth. (The rough plain effect may have to take into an account since the Ar ion sputtering often causes a surface roughening.)

The LSV of the copper electrodeposition has been measured at the scanning rate of 5 mVs (HZ-300, Hokuto Denko). The working electrode is attached to the rotating disk electrode (Hokuto Denko) and rotated at 100 r.p.m..

Results

Figure 1 shows the copper wire mesh and chromium template. Both the wire mesh and template are electrodeposited. Figure 1a is a SEM top view of the copper wire mesh on the chromium template. A is the chromium template and B is the copper wire mesh. A schematic illustration of the copper wire mesh along the cracks of the chromium template is shown in Fig. 1b. C is the chromium template, D is the copper wire mesh and E is the cracks in the chromium template.

On the top of the chromium template, numerous cracks are running over the chromium. The copper electrodeposits seem to preferentially electrodeposits along the cracks of the chromium template and form a copper wire mesh as shown in Fig. 1a B and Fig. 1b D. The copper wire mesh formation mechanism will be described in detail in Figs. 6–9.

Figure 2 shows the relationship between the electrodeposition time and open area ratio. With a shorter electrodeposition time, the open area ratio increases. An electrodeposition time shorter than 75 seconds forms a copper wire mesh with more than an 80% open area ratio. The 80% open area ratio meets the practical use...
Figure 1. SEM top view of copper wire mesh on chromium template (a) and schematic illustration of the copper wire mesh along the cracks of the chromium template (b). A: chromium template, B: copper wire mesh, C: chromium template, D: copper wire mesh, E: cracks in chromium template.

Figure 2. Relationship between electrodeposition time and open area ratio.

Figure 3 shows the relationship between the electrodeposition time and wire width. With a shorter electrodeposition time, the line width decreases. An electrodeposition time shorter than 30 seconds forms a copper wire width of less than 10 μm. The copper wire mesh becomes transparent if the width is less than 10 μm.

Figure 4. Relationship between electrodeposition time and sheet resistance.

Figure 4 shows the relationship between the electrodeposition time and sheet resistance. With a longer electrodeposition time, the sheet resistance decreases. The 30, 75 and 150 second electrodeposition times form sheet resistances less than 0.5 Ω/□ which meet the practical use requirement of the copper wire mesh as a transparent conductive film.

Figure 5 shows the relationship between the light wavelength and transparency. The copper wire mesh has been measured after 30, 75 and 150 seconds electrodeposition times. An electrodeposition time shorter than 30 seconds forms a copper wire mesh with more than an 80% transparency. The 80% transparency meets the practical use requirement of copper wire mesh as a transparent conductive film.

Figure 6a shows an SEM micrograph of a copper wire mesh with a 50 msec electrodeposition time initial. The initial copper wire mesh has been electrodeposited onto a chromium template. A crack in the chromium template runs through the micrograph center. The initial copper wire mesh granular deposit is indicated by the arrow. The initial copper wire mesh preferentially forms at the crack edges.

Figure 6b shows an SEM cross section micrograph of the copper wire mesh. Only 0.49 μm of the copper wire mesh penetrates into the chromium template crack. The copper wire mesh forms a 5.1 μm diameter spherical shape above the chromium template. The copper wire mesh initiates electrodeposition at the crack edges.

Figure 7 shows the LSV measurement of the copper electrodeposition onto the chromium template. No copper electrodeposition current is observed at a potential more noble than +0.11 V vs. SCE.
Furthermore, at 0 to \(-0.14\) V vs. SCE, the copper electrodeposition current is still not observed. This current incubation must be caused by the coverage of an oxide film over the chromium templates. At a potential less than \(-0.14\) V vs. SCE, there is a sudden increase in current. This is because the copper electrodeposition finally resumes.

Figure 8 is the field emission-X ray photoelectron spectroscopy (FE-AES) mapping analysis. a is an SEM image showing that the chromium template has cracks and the initial copper wire mesh granular deposit is located next to the cracks. The No. 1 point is the chromium template and the No. 2 point is the initial copper wire mesh. b is the mapping FE-AES image showing that chromium is at No. 1 point. Copper is at the No. 2 point as indicated in c.

Figure 9 is an FE-AES depth analysis by argon (Ar) ion milling of the No. 1 and No. 2 points, a and b, respectively. The X-axis is the depth and the Y-axis is the atomic concentrations of oxygen, chromium and copper. A large amount of oxygen of several nm depth is detected on the chromium template surface (a, see red arrow). A large amount of oxygen is again detected on the copper wire mesh surface (b). However, if the copper is sputtered and the copper concentration becomes zero (b, see black arrow), there is no oxygen concentration peak. This means that the oxygen along the cracks of the chromium
Conclusions

The copper wire mesh is a less expensive transparent conductive film than ITO. Copper wire mesh electrodeposits have been formed along the cracks of a chromium template. The conclusions of this study are summarized as follows.

1. By reducing the electrodeposition time, the open area ratio increases and wire width of the copper wire mesh decreases.
2. The electrodeposited copper wire mesh has an 84.0% transmittance, 9.8 μm wire width and 0.187 Ω/□ sheet resistance. These characteristics satisfy some practical use requirements of the transparent conductive film.
3. The copper wire mesh electrodeposits initiate at the crack edge. These initial deposits, which form along the crack edge combine and then form a copper wire mesh. It eventually forms a spherical cross section shape along the crack.
4. The initial deposit formation along the crack edge is because the current incubation preferentially removes of the local oxide film along the chromium template crack edges.

References

1. T. Oyama, Kinzoku Hyoumen Gijyutsu, 60616 (2009).
2. Y. Tsuda, Toumei Denkyoku, 2 (2007).
3. R. G. Gordon, MRS Bull, 25, 52 (2000).
4. U. S. Geological survey, Mineral Commodity Summaries Indium, 74 (2011).
5. L. Hu et al., ACS Nano, 4(5), 2955 (2010).
6. D. S. Ghosh et al., Applied Physics Letter, 96, 041109 (2010).
7. J-Y. Lee et al., Nano Letters, 8(2), 689 (2008).
8. http://www.cambridos.com/technology.
9. http://panasonic.co.jp/news/topics/2013/112371.html.
10. Nikkei Electronics, 7-22, P14 (2013).
11. Touch Panel Research Institute, Japan, Private communication.