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Electrochemical Deposition of Stacked Layers of Cu_2O/Cu/Cu_2O and Rendering of Structural Colors

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Cu_2O is a transparent solid with a red color and has a very high refractive index (n~3). Electrochemical reduction of copper-lactate complex from aqueous alkaline solution containing copper, sulfuric, and lactic ions produces thin films of metallic copper and Cu_2O on the electrode. The oxidation state (metallic copper or Cu_2O) and the thickness of the film can be controlled by the electrode potential and the charge. Stacking of Cu_2O and metallic copper films is possible from the same solution using organic additives. We tried to electrodeposit the stacked layers of Cu_2O and metallic copper by applying stepping potential in order to render the structural color, which is much like the structure of a dielectric multilayer mirror. The reflective spectra of the stacked film obtained show interference fringes in the transparent region of > ~450 nm, and they shift according to changes of the incident angle. As a result, the various structural colors can be rendered for the films deposited by consecutive electrochemical deposition of Cu_2O and Cu from the same solution.

Key words: electrochemical, Cu_2O, Cu, layer, color

1.INTRODUCTION

Electrochemistry is one of the attractive techniques for synthesis of layered (structured) materials. Electrochemical methods have several advantages in fabricating nanometer scale materials, including fast and large-area deposition, low temperature processing, precise control of thickness and composition, and the low-cost technique. In fact, it has been demonstrated that superlattices as well as multilayers can be fabricated by deposition or etching processes in the potential or current pulsing method [1-3]. Also recently it has been shown several interesting examples of self-assembled multi-layered structures in the oscillatory electrodepositing systems [4-8]. Such multi-layered structures exhibit negative differential resistance, which suggests the occurrence of a quantum-confined effect of the nanometer scale Cu_2O layers [5].

The emphasis in our study is optical properties of such structured materials [6, 7]. We notice even a single thin film of Cu_2O shows fine interference colors with little dependence on the incident angle due to its high refractive index. The objective of our research is to fabricate stacked structures in the scale of optical wavelength based on transparent Cu_2O in order to obtain the structural colored film.

2.EXPERIMENT

2.1 Setup for electrodeposition

The electrochemical setup is shown in Fig. 1. The deposition was performed in a three-electrode cell with a platinum wire as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. The working electrode was a glassy carbon (GC) disk with a diameter of 18 mm and a thickness of 2 mm purchased from TOKAI Carbon. The color of GC is ebony black, and this facilitates the observation of the structural color of the film.The electrode was polished with 0.3 μm alumina polishing suspension (Baikalox 0.3CR, BAIKOWSKI Corp.) and polishing cloth (MM-431, MARUTO Inc.). After polishing, the substrate was ultrasonically rinsed in water. The disk was then etched with concentrated H_2SO_4, and washed with acetone. The holder for the working electrode had a apperture with a diameter of 15 mm. The electrode was rotated at 500 rpm using the commercial apparatus (PRDE-1,

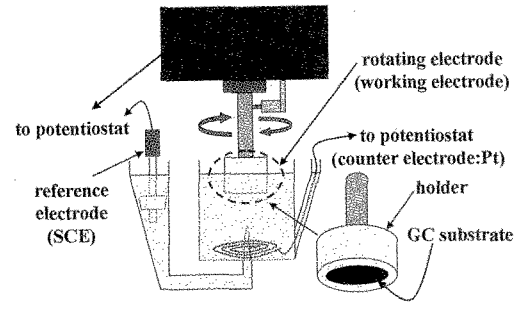

Fig.1 Electrochemical deposition setup. A glassy carbon (GC) substrate was used as a working electrode. A Platinum wire was used as a counter electrode. Saturated calomel electrode (SCE) was used as a reference electorode.

NIKKO KEISOKU). The thickness of films was controled by the total charge passed using a computer. The deposition current was recorded by using digital XY-recoder (DL708, YOKOKAWA).

2.2 Electrodeposition of single Cu_2O films

According to refs. [9-14], an electrolyte solution containing 0.6 mol/L $CuSO_4$ and 3.0 mol/L lactic acid was prepared. The pH of the solution was adjusted with NaOH aqueos solution at 9.5. The solution temperature was maintained at 50±1 °C with a thermostat[12]. The electrodeposition was performed potentiostatically at –400 mV vs. SCE [9-11].

2.3 Electrodeposition of stacked layers of $Cu_2O/Cu/Cu_2O$

We found it is difficult to deposit a thin metallic copper layer on a Cu_2O surface from the alkaline copper-lactate solution described above, since the Cu_2O surface is quite inert. We surveyed several dithiol and diols including 3,6-dithia-1,8-octanediol (DOD), dithiodiglycolic acid (DDG), 1,4-benzenedithiol (BDT), trans-1,2-dithiane-4,5-diol (DTD), and1,5-dithiacyclooctane-3-ol (DTO) in order to find promoters for metallic copper deposition. The concentrations of 20, 100, and 500 μmol/L of each promoter is mixed with the electrolyte solution containing 0.6 mol/L $CuSO_4$ and 3.0 mol/L lactic acid at pH 9.5 and 25±1 °C. The GC substrate with Cu_2O film deposited initially was used. Thickness of the film is 140 nm. Current response measurements from -450 mV to -1000 mV for the solutions containing each promoter were compared with that for the solution without additives. Among these additives, DOD shows the dramatic change of a metallic copper deposition potential. We determined the most appropriate concentration of the promoter to be 18 mmol/L using the solution that 100 μmol/L polyethylene glycol (PEG:WM = 8000), 1 mmol/L NaCl [15-20], and 5 mmol/L Janus Green B (JGB: $C_{30}H_{31}ClN_6$) [15-18] were further incorporated into as a smoother.

The current response of the solution without additives shows a small increase from –900 mV due to the metallic copper deposition and a steep increase from –950 mV. The solution with additives described above shows a lower potential for copper deposition and the gradual current increase at higher potentials. For example, the solution with 500 μmol/L DOD shows a gradual current increase from –700 mV and a slightly large increase from –900 mV. The morphology of the film obtained also changed. Large (>2-3 μm) metallic copper particles were sparsely deposited on a Cu_2O surface from the solution without additives. In case of the solution with DOD, small metal particles (< 1 μm) are deposited densely on Cu_2O.

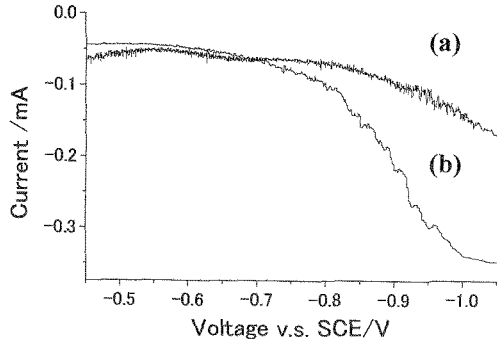

Fig.2. Current response curve upon potential sweep from -0.45 V to -1.05 V applied to the working electrode in electrolyte bath (a) without and (b) with 500 μM of 3,6-dithia-1,8-octanediol (DOD). In addition to DOD, the solution contains the same solutes as described in the experimental section.

2.4 Characterization

Reflection spectra was measured with a UV-Vis. spectrometer with a rotatable stage and an integrating sphere (UV-550, JASCO Corp.). The spectral range was between 840 nm and 240 nm and the incidental angle was changed from 5° to 55°. Atomic force microscopy (AFM) were performed using MFP-3D, Asylum Research Inc, with a cantilever of type bio-tap from Nanoworld Inc.

3.RESULTS and DISCUSSION

3.1. Single Cu_2O films

In Fig. 3, a color photograph of pure Cu_2O single films electrodeposited on GC substrates is shown. The thicknesses of these films are varied using different electrodeposition charge passed. According to the eq. (1), each thickness is designed to be 196, 212, 228, 244, 155, 167, 187 nm for the films from the left to the right, respectively.

$$D = M\sigma / \rho nF \qquad (1)$$

Here, D is thickness, M is formula weight of Cu_2O (143.1 g/mol), σ is charge passed, ρ is density (6.0 g/cm^3), n is number of electrons (2), and F is the Faraday constant (96485 C/equiv.). The diffraction colors are rendered according to the interference of the light reflected at the surface with the one reflected at the backside of the film. The order of the film thicknesses in Fig. 3 is not in the increasing order, since the diffraction is affected by both the refractive index and the absorption coefficient of Cu_2O. As is shown in Fig. 3, the color uniformity seen in the each film indicates that the film is optically flat therefore the diffracted color is pure.

In order to confirm the relation of charge and the actual thickness, atomic force microsopic (AFM) images were measured. A small portion of the film was peeled off for the cross section to be exposed. We determined the thickness of the sample to be 175 nm from eq. (1). Fig. 4 (a) shows the AFM image of the sample. The field of sight is 10 × 10 μm, and the scan rate is 0.5 Hz. Fig. 4 (b) is the section that corresponds to the blue line in the topographic image. The surface roughness is between 10~20 nm, which indicates the film is optically flat. The section analysis shows that

the height of the bump (171 nm) agrees well with the thickness by eq.(1).

Fig. 5 shows the reflection spectra of the film. The thickness of the film is also 175 nm. Each colored trace corresponds to the incident angle of 5°, 15°, 25°, 35°, 45°, and 55°, respectively as is indicated in the figure. The substrate was GC, thus reflection from the bottom of the film is low. Thus overall reflection as low as < 30% is governed by the surface reflection of the film. A very broad and strong reflection peak at around 650 nm is observed. The strength is due to the high refractive index of Cu_2O ($n \sim 3$). This peak shows little shift upon the change of the incidental angle from 5° to 55°, also owing to the high refractive index. Other material shows larger peak shift according to the incidental angle change. For example, in case of quartz (n ~ 1.46@650nm) with thickness of 446 nm, incidental angle change from 5° to 55° causes the diffraction peak shift at 650 nm by 110 nm. Below 550 nm, a bandgap absorption of Cu_2O gradually increases. The reflection peak at 480 nm, however, appears as seen in Fig. 5. This peak is supposed to be an interference fringe since the film is translucent around this wavelength and the optical thickness is not so large. As shown in Fig. 6, this peak becomes weak and moves to shorter wavelength in thiner films.

As shown in the spectra, the color of the film is governed by two components. The one is the wide interference fringe appeared at longer wavelength (>550 nm). The other is weak sharp fringe at around 450-550 nm. As shown in Fig. 3, green, orange, and red colors are due to the broad fringe. A violet and blue color seems to be impure, since the film thickness affects both of the two peaks for thiner films.

3.2 $Cu_2O/Cu/Cu_2O$ stack

Fig. 6 shows photographs of (a) single Cu_2O film, and (b) $Cu_2O/Cu/Cu_2O$ alternated layers. The thickness of the former film is 42 nm. The structure of the latter is Cu_2O (~40 nm) / Cu (~30 nm) / Cu_2O (~40 nm) on a GC substrate. The spectra were measured with incidental angles of 5°, 15°, 25°, 35°, 45°, and 55°. Both of the films showed a blue color, although the tone of the color is different. Figs. 7 and 8 show reflection spectra of the single Cu_2O film and the stacked film, respectively. The single Cu_2O film has broad reflection at 460 nm, and the tail of the peak extends to the very longer wavelength. This is possibly due to the increased reflection from the backside. No interference frings other than the one at 460 nm was observed. This spectra means that the color of the film contains not only blue but also weak green and red. Therefore, the film is whitish and light blue, as is seen in Fig. 6 (a). The stacked film contains Cu_2O layers with the same thickness as the single Cu_2O film. The spectra of the stacked film shows strong blue reflection peak at ~450 nm with a very steep slope at its longer wavelength side. Thus green component is completely missing in the spectra. Due to this sharp peak, the color of the film is more vivid than the previous one as seen in Fig.6 (b) Moreover, the color is very stable when the incidental angle is changed.

4. CONCLUSION

Using electrodeposition from alkaline copper-lactate solution, flat Cu_2O films are obtained. The thickness can be controlled precisely by charge. The film shows a strong interference fringe owing to the high refractive index of Cu_2O. The color is stable on the change of incident angles of light. We found the combination of additives that can deposit a thin Cu metal layer on a Cu_2O surface. Using additives, stacked layers of $Cu_2O/Cu/Cu_2O$ was fabricated. The film with alternated layers shows even more strong and vivid color. Further investigation on deposition of increased numbers of layers with different thickness is in progress.

5. REFERENCES

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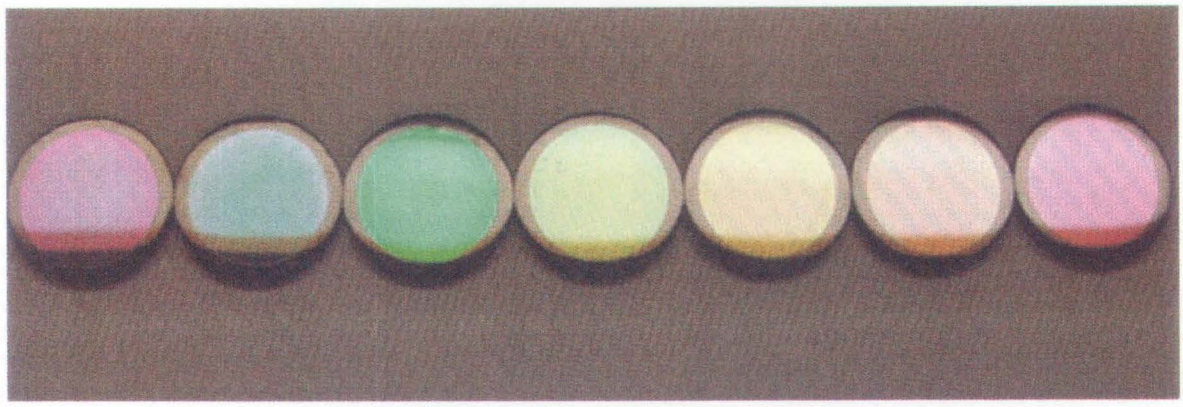

Fig.3 Cu_2O thin films deposited electrochemically from lactate-Cu complex solution. The thickness of each film from the left to the right is 196 nm, 212 nm, 228 nm, 244 nm, 155 nm, 167 nm, and 187 nm, respectively.

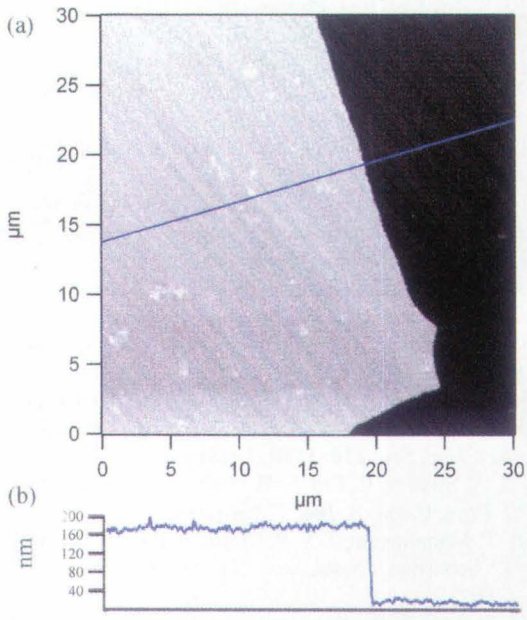

Fig.4 (a) AFM image of a Cu_2O thin film. The field of sight is 10 × 10 μm. A small portion of the film was peeled off for the cross section to be exposed. (b) Cross section that corresponds to the blue line in the topographic image.

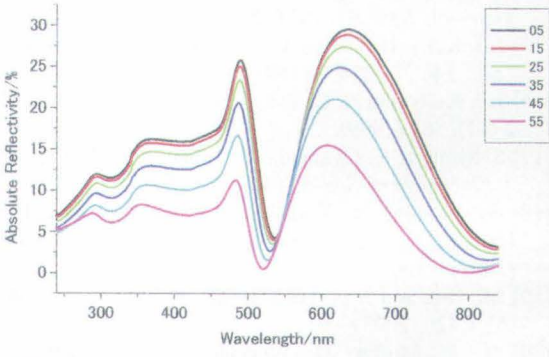

Fig.5 Reflection spectra of a Cu_2O thin film. The thickness of the film is also 175 nm. Incident angle was changed of 5°, 15°, 25°, 35°, 45°, and 55°

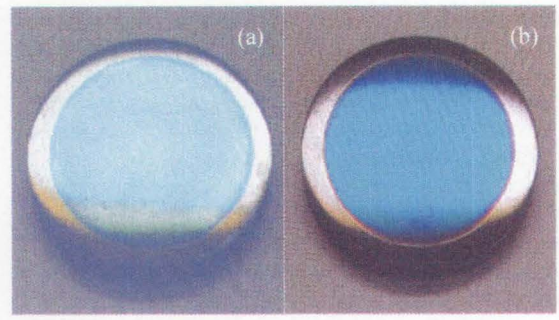

Fig.6 Photographs of (a) a single Cu_2O film and (b) $Cu_2O/Cu/Cu_2O$ alternated layers.

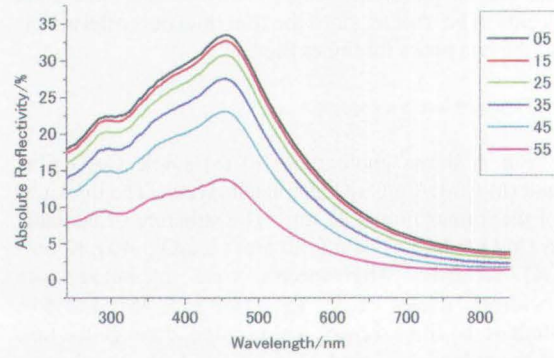

Fig.7 Reflection spectra of Cu_2O single film. The thickness of the film is 42 nm. Incident angles was 5°, 15°, 25°, 35°, 45°, and 55°

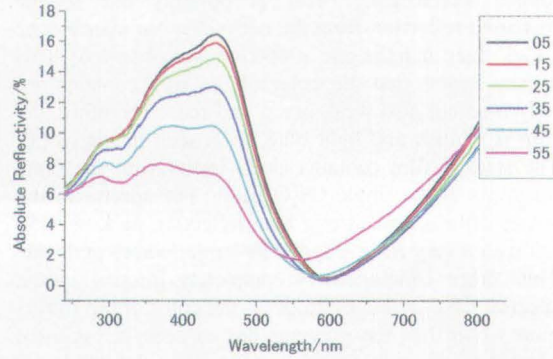

Fig.8 Reflection spectra of multi-layers of Cu_2O (~40 nm) / Cu (~30 nm) / Cu_2O (~40 nm). Incident angles was 5°, 15°, 25°, 35°, 45°, and 55°