Supporting Information

Electrodeposition of Large Area, Angle-Insensitive Multilayered Structural Colors

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S1. Chronopotentiometry Plots

Cu_2O films were electrodeposited on Au/n^+ Si (111) substrates using an alkaline solution (pH ~ 10.9) containing 0.4 M $CuSO_4 \cdot 5H_2O$ and 1.6 M citric acid at T = 50 °C using a current density of j = 0.1 mA/cm^2. The thickness of the Cu_2O layer was tuned to obtain the CMY colors by simply altering the electrodeposition time and the corresponding chronopotentiometry plots for three different thicknesses (20, 40, 60 nm) of Cu_2O is shown in Figure S1. The consistent shape and form of these plots for the three samples indicates a uniform and consistent deposition among the different samples.

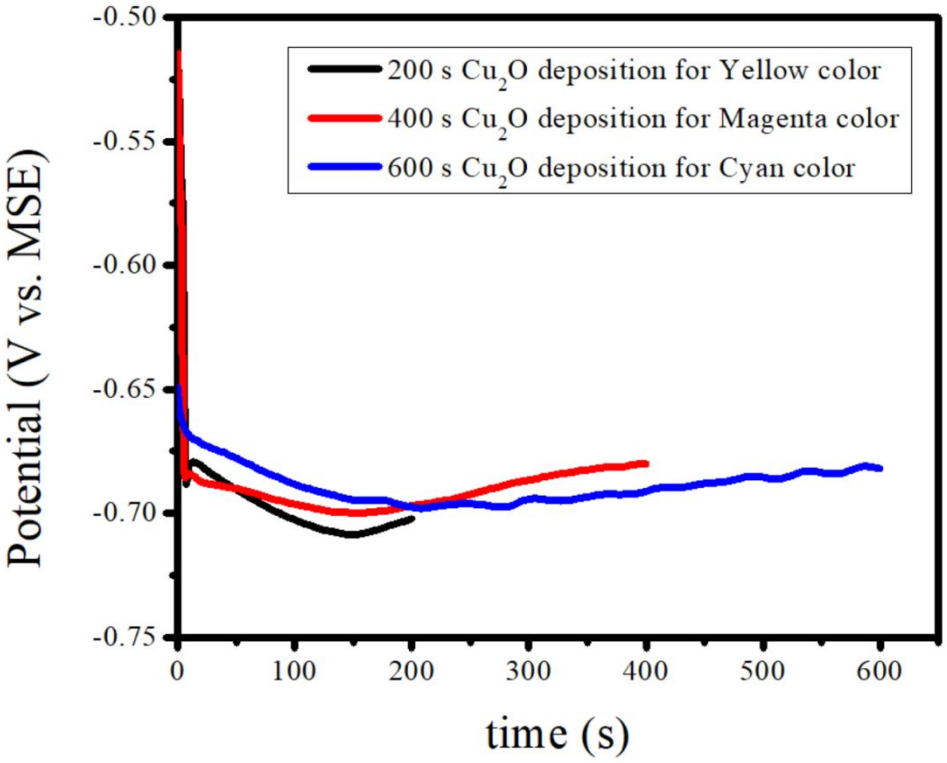

Figure S1. Chronopotentiometry plots of different thicknesses of Cu_2O thin-films electrodeposited on Au/n^+ Si (111) electrodes in an electrolyte containing 0.4 M $CuSO_4 \cdot 5H_2O$ and 1.6 M citric acid at T = 50 °C and using a current density of j = 0.1 mA/cm^2.

The accuracy of the film thickness is a strength of electrodeposition. Specifically, by controlling the total coulombs passed we can control the thickness. The current resolution of the experiment defines the resolution of mass deposition. For example, assuming a current resolution of 5×10^{-4} C s^{-1} for a 1 cm^2 electrode, the mass deposition rate for a $2e^-$ reduction process of Cu_2O is ~ 0.6 nm s^{-1} cm^{-2}.

S2. Issues Related to Electrodeposited Cu

For the electrodeposition of the final top metal layer, the intent was to use the same bath for the Cu_2O electrodeposition and just grow a capping Cu^0 layer on top by increasing the current density to produce Au/Cu_2O/Cu MDM stacks or even Cu/ Cu_2O/Cu MDM stacks. There is precedent for this approach in previous reports of electrodeposition of epitaxial metal-metal oxide layers by pulsed currents.[1-5] However, while Cu^0 layers were readily formed, all samples yielded Cu^0 films that were of poor optical and electrical quality, showing significant lossy character and approximately 100x lower conductivity than thermally evaporated Cu films of similar thickness. Even though energy dispersive *(*EDS) and X-ray diffraction (XRD) spectra showed no detectable impurities and pure Cu character, the optical and electrical properties could not be improved for a film with a thickness below 20 nm. Annealing these Cu films in Ar (g) at T = 200 °C increased the surface roughness of these films (Figure S2), possibly due to the diffusion of entrapped air/solvent in nanoscale voids in the Cu film. Accordingly, electrodeposited Cu thin films were not pursued further using this electrolyte.

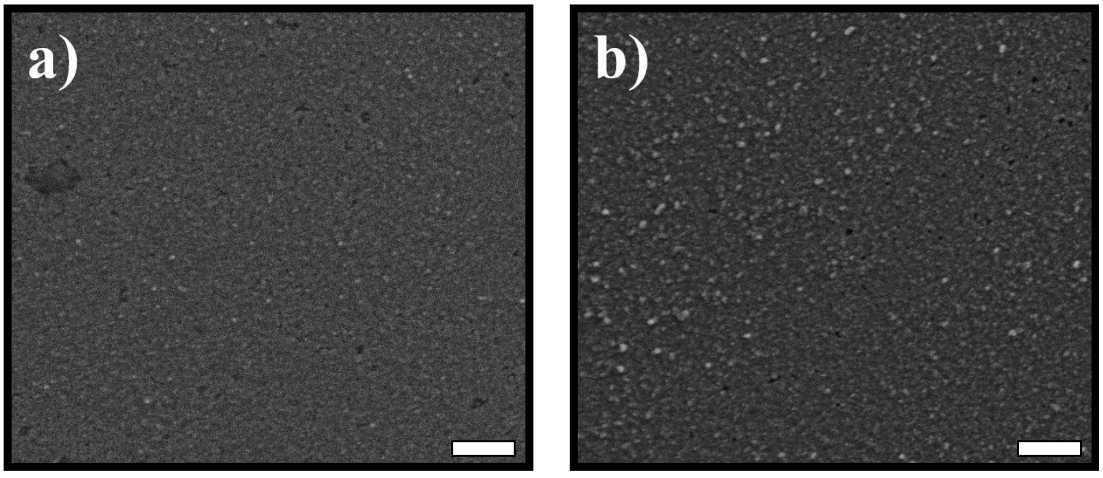

Figure S2. Scanning electron micrographs of a) as-deposited Cu film on a Si substrate b) Cu film annealed in Ar (g) at T = 200 °C for t = 120 s. Scale bar = 2 μm.

S3. Thickness Uniformity of Electrodeposited Films

The uniformity of the electrodeposited films is a major point of this work. Using the yellow colored device as an example, the reflectance spectra at four difference locations of the sample were measured and summarized in the Figure S3. It is evident that these spectra are very similar to each other, which indicates the great uniformity in thickness of each electrodeposited layer. In addition, the uniformity of the observed optical properties (color, reflectance) of the films over macroscopic dimensions (i.e. 6 cm^2 curved spoons) described in the main text is unambiguous proof of the quality and homogeneity of the electrodeposited MDM stacks.

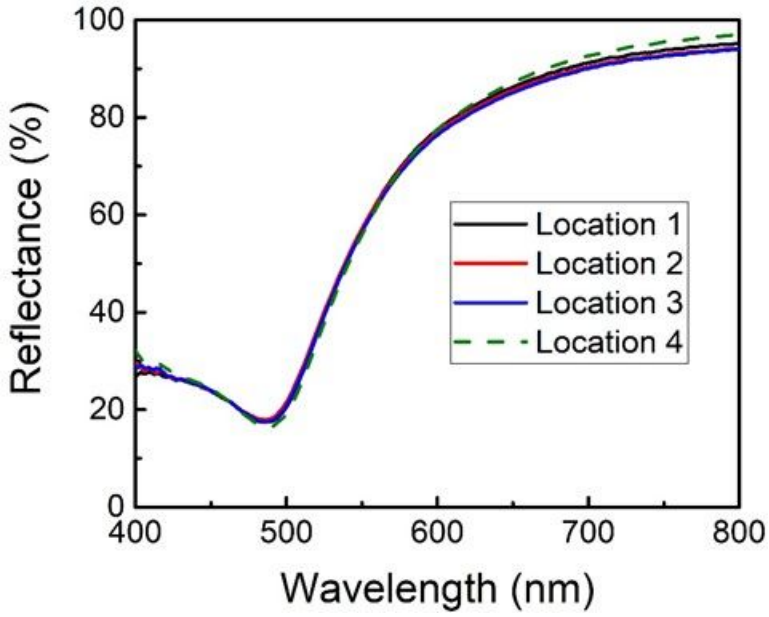

Figure S3. Measured reflectance spectra of yellow colored device at four separate locations.

S4. Cyclic Voltammetry

The current-potential characteristics for both an n^+ Si (111) substrate and a stainless-steel spoon immersed in an aqueous solution of 0.1 mM $HAuCl_4 \cdot 3H_2O$, 1mM H_2SO_4, 1 mM KCl, and 100 mM K_2SO_4 are shown in Figure S4. These measurements were performed at T = 35 °C. The hump at E = -0.8 V vs. Ag/AgCl is associated to O_2 reduction. Based on these voltammetric responses, Au electrodeposition on n^+ Si (111) substrates were performed at E = -1.9 V vs. Ag/AgCl.[6] Whereas, Au electrodeposition on stainless-steel spoons was performed at E = -1.4 V vs. Ag/AgCl. This was done to avoid excessive hydrogen evolution reaction.

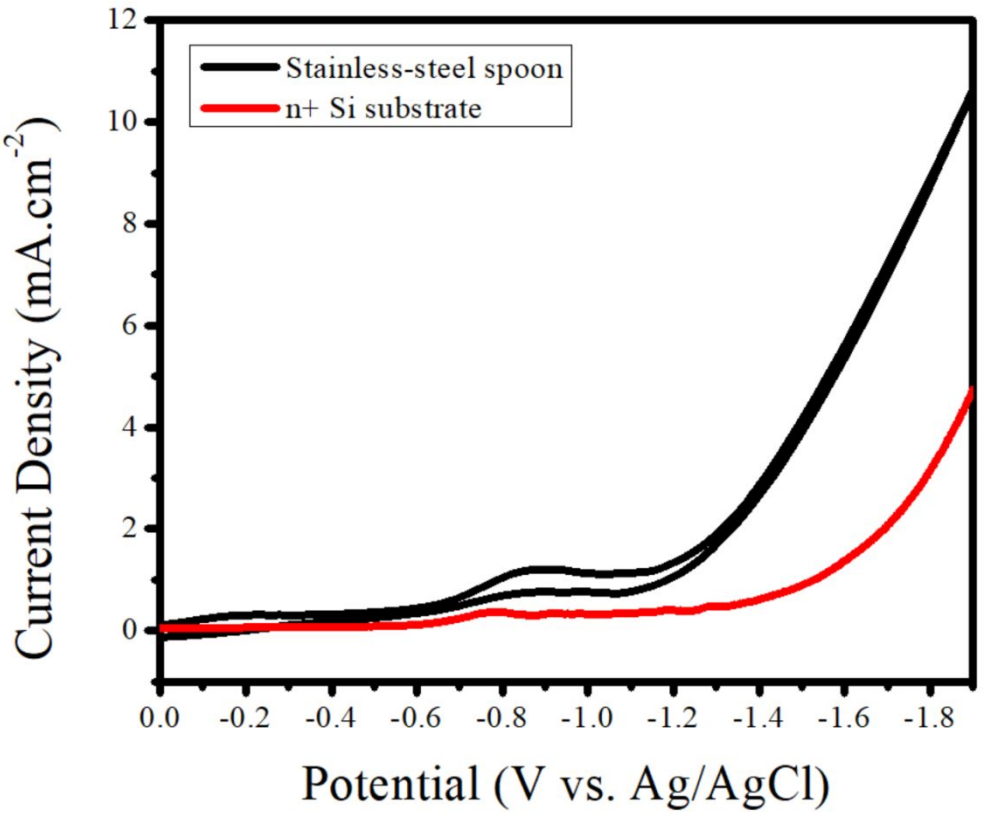

Figure S4. Cyclic Voltammetry response of an n^+ Si (111) electrode and a stainless-steel spoon electrode in 0.1 mM $HAuCl_4 \cdot 3H_2O$, 1mM H_2SO_4, 1 mM KCl, and 100 mM K_2SO_4. Scan rate = 50 mV s^{-1}.

S5. References

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