Texture and Bandgap Tuning of Phase Pure Cu_2O Thin Films Grown By a Simple Potentiostatic Electrodeposition Technique

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Highly textured phase pure Cu_2O thin films have been grown by a simple electrodeposition technique with varying deposition voltages (-0.3 to -1.0 V). The surface morphology characterized by Scanning Electron Microscopy (SEM) revealed that the deposited thin films coherently carpet the underlying substrate and composed of sharp faceted well-define grains of 0.5 – 1.0 µm sizes. XRD analyses showed that all films are composed of polycrystalline cubic Cu_2O phase only and have average crystalline domain size in the range 30 – 73 nm. The preferred crystalline orientation of phase pure Cu_2O films were found to be changing from (200) to (111) with increasing cathodic voltages and showed highest (111) and (200) crystalline texture coefficient while grown at -1.0 and -0.8 V respectively. Optical bandgap of the as-grown samples were calculated in the range (1.95 – 2.20) eV using UV-Vis Transmission data. The performance of copper oxide films was tested by estimating LED 'ON/OFF' modulated surface photovoltage into a photoelectrochemical cell at a zero bias.

Introduction

Cuprous oxide (Cu_2O) is one of the most desirable p-type semiconducting metal oxides used as absorber materials for ZnO based all-oxide solar cell[1-3] because of its reported direct bandgap (~2.17 eV), a suitable band alignment with n-type ZnO electrodes, and its environmental benign nature[1, 4]. One of the two major difficulties to realize ZnO/Cu_2O based optoelectronic devices are: (1) single phase Cu_2O at low processing temperature to avoid formation of interfacial defects at the ZnO/Cu_2O junction; (2) desired crystallite orientation of cubic Cu_2O phase for achieving heteroepitaxy with hexagonal closed packed ZnO wurtzite structure[1, 4-5]. To this end, Akimoto et al[1] demonstrated that solar cells involving growth sequence of ZnO/Cu_2O exhibited better performance compared to those involving the Cu_2O/ZnO growth sequence and attributed the improved cell performance to the interface with low defects due to the fact of similar atomic structure in ZnO(0001)/Cu_2O(111) stacks. In this direction, we demonstrated that defect-free single crystal like ZnO(0001) NRs could be grown on textured ZnO seeding layers by using hydrothermal method[5] useful for realizing efficient ZnO(0001)/Cu_2O(111) based radial junctions.

Single phase Cu_2O with desired crystallographic orientation can be grown both by physical[1, 4] and wet-chemical techniques[2, 6-8]. Among the wet-chemical techniques, electrodeposition (ED) is simple, economical, and offers good control over large deposition parameters for producing single phase Cu_2O films with controlled texture and thickness[2, 6-7]. Both, 2-electrode galvanostatic[6] and 3-electrode potentiostatic[2, 7] mode ED of Cu_2O thin films were reported. In this study, we report a very simple 2-electrode potentiostatic ED technique for tuning texture and optical bandgap of the single phase Cu_2O films and discussed their physical properties as a function of deposition voltages.

Experimental Methods

Synthesis: The synthesis of single phase cuprous oxide (Cu_2O) thin films was reported details in our previous works[9]. Briefly, the 2-electrode electrodeposition setup is composed of a fluorine doped tin oxide (FTO)-coated glass substrate as working electrode, a graphite rod (dia. ~ 6 mm) as counter electrode, and a Keithley SMU 2450 as dc power supply for applying fixed and stable deposition voltage as shown in Figure 1(a). The plating solutions were prepared by mixing 0.2 M copper sulfate ($CuSO_4$) and 3 M lactic acid ($CH_3CH(OH)COOH$) with a weight ratio of 2:1 dissolved in deionized (DI) water. The pH of this solution was adjusted to ~ 9.5 using a solution of 4 M KOH. The lactic acid served as complexing agent to prevent Cu precipitation when KOH was added to the solution. Prior to deposition, FTO (~20 mm × 12 mm) substrates were cleaned by sequential ultra-sonication into acetone, isopropyl alcohol, and DI water each step for 15 min. and finally blown dried by using a hot-air gun. During deposition, the solution temperature was kept at 60 ^{o}C. The deposition time was set to 40 min. typically, if not mentioned otherwise. A number of thin films were prepared at cathodic voltages of -0.3 V, -0.5 V, -0.7 V, -0.8 V, -0.9 V, -1.0 V, and -2.0 V in order to investigate the physical properties of the as-grown electrodeposited cuprous oxide (ED Cu_2O).

Characterization: The phase as well as crystalline structure, surface morphology, thickness, and optical properties of the as-grown ED thin films were characterized, respectively, by XRD (GBC scientific; Cu_$K_{\alpha 1}$: λ=1.54062 Å radiation source), SEM (ZEISS EVO18), Stylus profiler (BRUKER DektakXT), UV-VIS-NIR spectrometer (SHIMADZU 2600). The performance of an as-grown ED Cu_2O/FTO electrode was estimated by a homemade surface photovoltage (SPV) measurement setup described elsewhere[8].

Results and Discussions

Figure 1 (b) shows the transient cathodic current during the electrodeposition of copper-oxide thin films at -0.8 V (black curve) and -1.5 V (green curve). The cathodic current at these two different deposition voltages are seen to be quite stable within the deposition span indicating a good and fast growth kinetic[7]. The thicknesses (t) of the copper-oxide films electrodeposited at -1.0 V for 20 min (t~8.08±0.19 µm), 40 min (t~8.08±0.19 µm), and 80 min (t~8.08±0.19 µm) are found to be almost uniform across the wide area of films as evident from Figure 1 (c). The ED films are visibly compact and the thickness of the films was found to be increasing with increasing deposition time as

also evident from the lighter to darker film photographs with longer deposition time given in the inset of Figure 1(c).

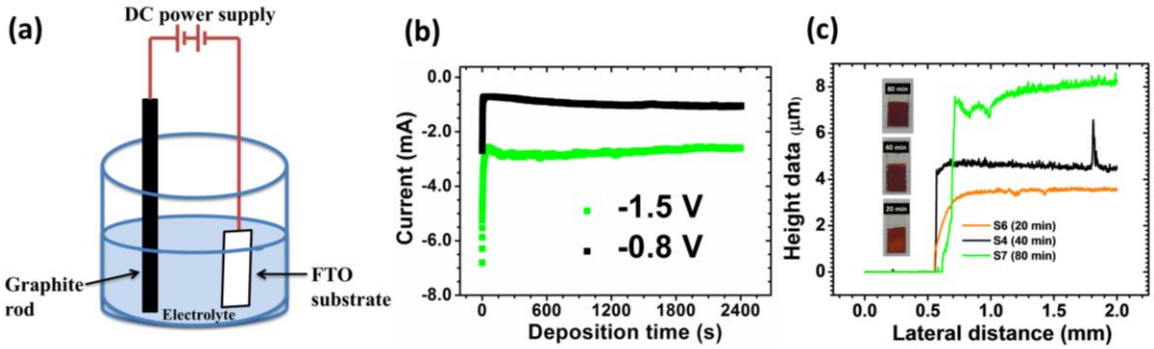

Figure 1. (color online) Schematic depiction of a simple 2-electrode electrodeposition setup (a), cathodic current over elapsed deposition time of Cu_2O on FTO substrate at two fixed deposition voltages (b), variation of film thickness with deposition time 20, 40, and 80 min electrodeposited at -1.0 V (c). The photographs of same samples are shown in the inset of (c).

The surface morphology and microstructure of copper-oxide thin films deposited at -0.3 V (t~0.6±0.1 μm), -0.8 V (t~3.8 ± 0.4 μm), -1.0 V (t~8.0 ± 0.5 μm), and -2.0 V(t~ 46 ± 1 μm) are shown in Figure 2 (a), 2 (b), 2 (c), and 2 (d) respectively where a magnified film area and photographs of the respective samples are included in each figure inset. Clearly, the thicknesses of the ED films were found to be increasing with increasing deposition voltages. Below -0.3 V, no films were observed to be electrodeposited. It is seen from Figure 2 that thin film deposited at -0.3 V is composed of isolated islands composed of grains of octahedral cuboids whereas thin films grown above this deposition voltage were found to be coherently carpet the underlying substrate and composed of sharp faceted well-define grains of 0.5 – 1.0 μm sizes. Both the surface morphology and film thickness of the electrodeposited copper-oxides can be controlled as evident from Figure 2. The pristine copper-oxide films grown by using deposition voltages up to -1.0 V were found to be single phase Cu_2O and those grown at -2.0 V and above (data not shown here) were found to be metallic copper (Cu) with (111) and (200) orientation (see the top panel in Figure 3(a)). Additionally, the surface morphology of metallic Cu revealed that it is composed of spherical shaped grains of dia.~ 1.0 ± 0.3 μm and significantly different from the morphology of Cu_2O thin films as also seen by others[7]. In fact, a coherent photoactive layer with large grains is desirable for light harvesting applications due to the possible reduction of recombination at the grain boundaries.

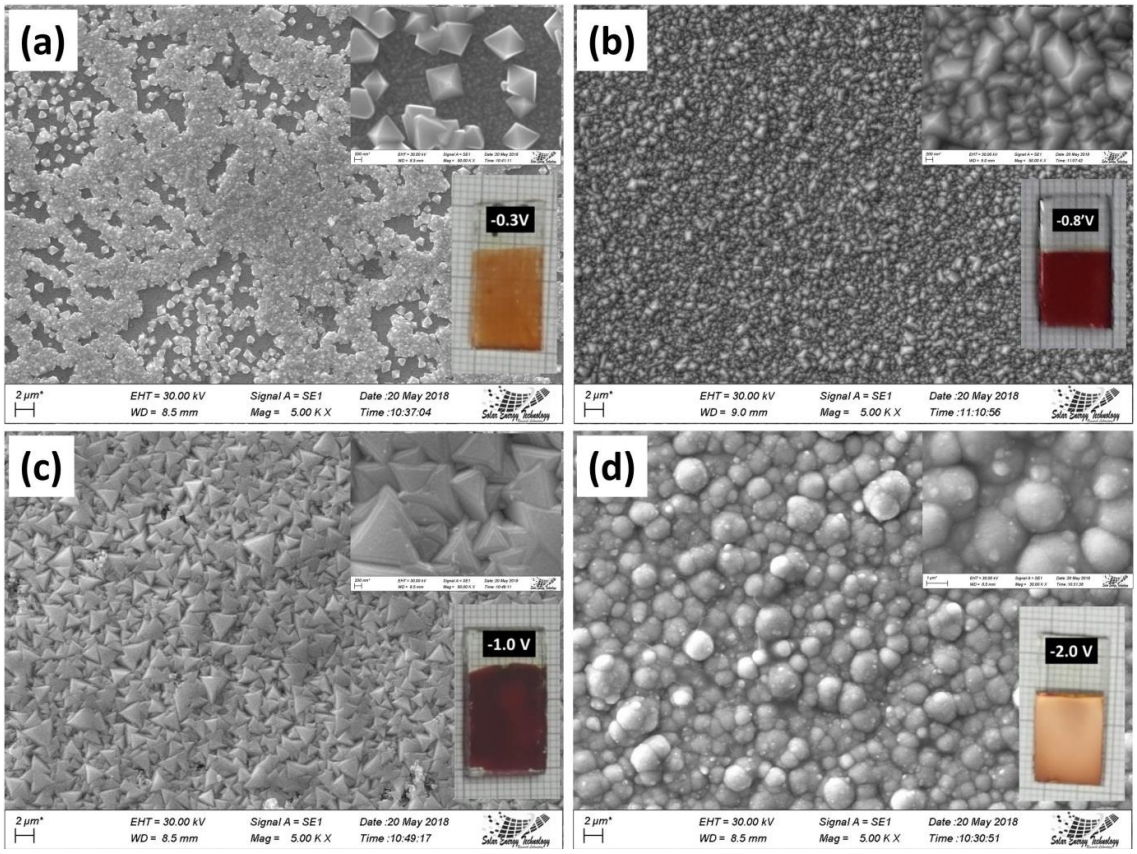

Figure 2. (color online) SEM micrographs and photographs of Cu_2O thin films grown at -0.3 V (a), -0.8V (b), -1.0 V (c), and -2.0 V (d). A zoomed region of the respective sample is given in the each micrograph. Deposition time: 40 min.

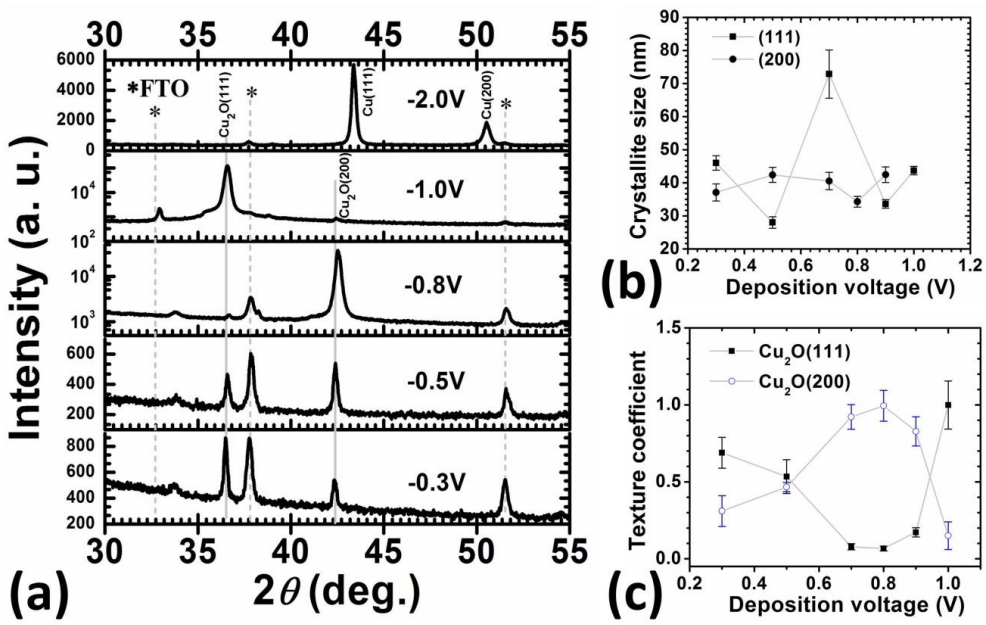

Figure 3. XRD patterns of the electrodeposited thin films grown at -0.3 V to -2.0 V (a). Dependence of crystallite domain size (b) and Texture coefficient (c) on electrodeposition voltage. Deposition time: 40 min.

The XRD patterns of ED thin films at different voltages are shown in Figure 3 (a). FTO substrate diffraction peaks are marked by asterisk. The XRD results confirmed the polycrystalline single phase cubic Cu_2O structure [4, 8] for all samples electrodeposited at -0.3 V to -1.0 V. It is also clear that crystal growth was largely influenced by deposited voltage. The average crystallite domain size were estimated in the range of in the range 30 – 73 nm by applying Scherrer equation[10] to both (111) and (200) planes of the ED Cu_2O (see Figure 3 (b)). The texture coefficient (TC) of the ED Cu_2O were calculated by using modified formula[6]: $TC(111) = \frac{I_{111}}{I_{111}+I_{200}}$ and $TC(200) = \frac{I_{200}}{I_{111}+I_{200}}$ and shown in Figure 3 (c) as a function of deposition voltages. It is clear that the preferred crystalline orientation of phase pure Cu_2O films were found to be changing from (200) to (111) with increasing cathodic voltages and showed highest (111) and (200) crystalline texture coefficient while grown at -1.0 V and -0.8 V respectively.

From SEM micrographs and XRD patterns, it is conspicuous that grains/crystals shape are octahedral cuboids of Cu_2O with a strong (111) orientation at -0.3 V deposition voltage (cf. Figure 2 (a), 3 (a) and 3 (c)), which considerably changed to {100} faceted cubic crystal with strong (200) orientation at -0.8 V deposition voltage ((cf. Figure 2 (b), 3 (a) and 3 (c)). Finally, well-defined triangular shaped {111} faceted cubic crystals with highest (111) orientation were observed at -1.0 V deposition voltage (cf. Figure 2 (c), 3 (a) and 3 (c)). The sample deposited at -1.5 V is also exhibited highly (111) orientated Cu_2O (XRD data not shown here).

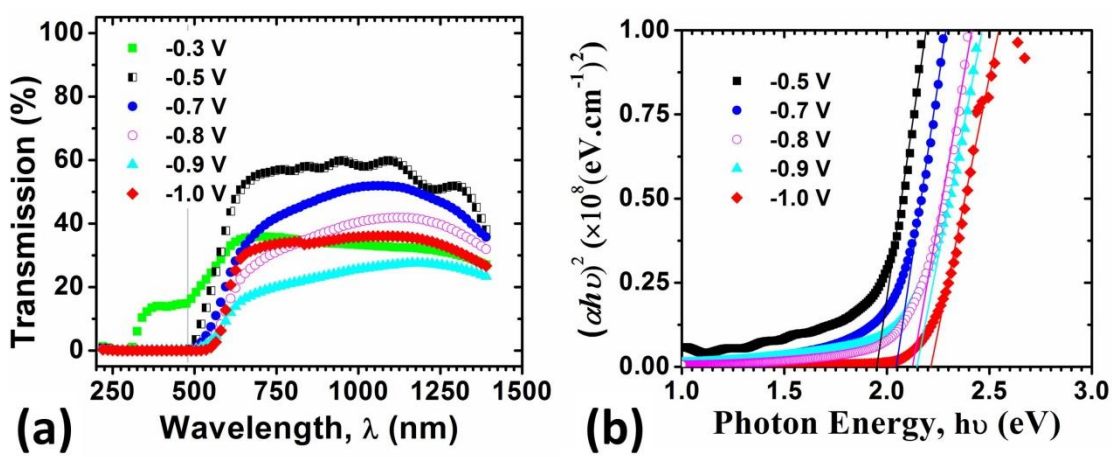

Figure 4. (color online) Normalized optical transmission spectra of Cu_2O films grown on FTO at different deposition potentials (a). Tauc plot for estimating the bandgap of the same samples using transmission data (b).

Figure 4 (a) shows the normalized transmission spectra of ED Cu_2O thin films on FTO substrate as function of deposition voltage. The absorption edge for all ED Cu_2O films is seen at $\lambda \approx 475$ nm, while the feature at $\lambda \approx 300$ nm for films deposited at -0.3 V is due to the incoherent surface morphology exposing the underlying substrate[5] (cf. Figure 2 (a)). The optical bandgap (E_g) of these samples were estimated from the Tauc plot [10] generated by using transmission data and were calculated in the range, E_g = (1.95 – 2.20) eV. The E_g dependence of ED Cu_2O on deposition voltages can be attributed to the variation film thickness and grain size of the films as observed by others[2, 10].

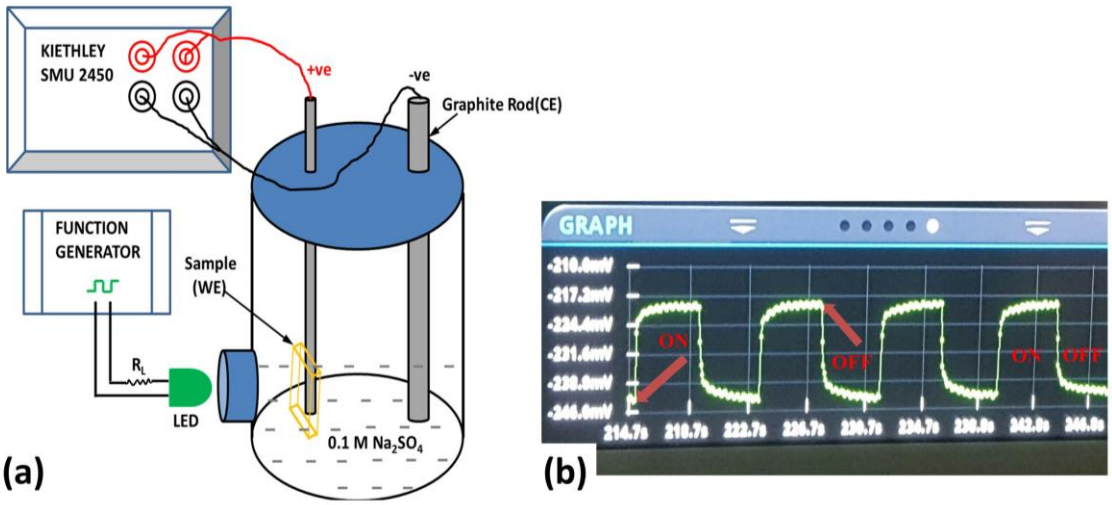

Figure 5. (color online) Schematic depiction of a surface photovoltage measurement setup (a). A low power green LED 'ON/OFF'(~0.1 Hz) modulated transient surface photovoltage of a typical electrodeposited Cu_2O(111)/FTO electrode measured at zero bias voltage (b). Average photovoltage, V_{oc} ~ 30 ± 2 mV.

<u>Performance of an ED Cu_2O(111)/FTO photoelectrode:</u> The type of conductivity as well as the performance of a typical ED Cu_2O(111) film was investigated by monitoring transient surface Photovoltage (SPV) under periodic illumination of a green LED as shown in Figure 5. The positive value of V_{oc} confirms the p-type conductivity of photoactive Cu_2O layer and indicating that photogenerated minority carriers are electrons[8]. Notice that SPV measurement in Figure 5(b) also reveals a rapid and stable photoresponse of the ED Cu_2O(111) in aqueous electrolyte within the investigated time frame (see Figure 5 (b)), suggesting a good stability as well as compactness of the electrode. The open-circuit voltage (V_{oc}) of this film was measured to be V_{oc} ~ 30 ± 2 mV which might be reasonably good to integrate them into ZnO/Cu_2O based solar cell[2]. Further experimental investigations are currently in progress to elucidate the effect crystallite orientation and exposed faceted surface of the ED Cu_2O thin films for their possible integration atop the vertically aligned (0001) ZnO NRs grown on oriented ZnO seeding layers by different method[11].

Conclusions

In summary, we successfully synthesized highly textured phase pure Cu_2O using a simple electrodeposition (ED) technique with varying deposition voltages (-0.3 to -1.0 V) using FTO substrates as working electrodes and a carbon rod as counter electrode immersed in an alkaline aqueous electrolyte held at ~60 ^{0}C. The surface morphology, texture, and thicknesses of the ED Cu_2O films can be controlled by varying deposition voltages and time as evident from the SEM, XRD, and stylus surface profiler results. XRD analyses further showed that the preferred crystalline orientation of phase pure Cu_2O films can be tuned from (200) to (111) with increasing cathodic voltages and showed highest (111) and (200) crystalline texture coefficient while electrodeposited at -1.0 and -0.8 V respectively. The estimated optical bandgap of the as-grown ED Cu_2O films were found in the range (2.00 – 2.20) eV and the variation of the optical bandgap could be attributed to the variation of the film thickness. The performance of ED

$Cu_2O(111)$ films was tested by estimating LED 'ON/OFF' modulated surface photovoltage into a photoelectrochemical cell at a zero bias and was found to be reasonable to integrate them into optoelectronic devices.

Acknowledgments

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