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Green Synthesis of Cu_xO Nanoscale MOS Capacitors Processed at Low Temperatures

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Abstract:

In this work, we employed two nontoxic green chemistry methods to develop solution-processed copper oxide Cu_xO thin films at low annealing temperature of 200°C. The first aqueous precursor of Cu_xO was prepared by mixing the copper powder with spinach leaves extract, whereas the other solution was formulated using the water-based polyol reduction method of Cu(II) nitrate. The as-prepared precursors were then spun on SiO_2/P^+ Si substrates to form nanoscale Metal-Oxide-Semiconductor (MOS) capacitors by which some valuable information about the Cu_xO semiconductor films and their interfaces with dielectric were acquired. Both fabricated MOS capacitors exhibited p-type polarity with negative flat-band voltages. However, the MOS based on spinach extract- Cu_xO films showed small hysteresis of 100 mV, which could be attributed to its large grain size that sequentially leads to smooth interface and less trap density.

1 Introduction:

Transparency in electronics is an asset that makes it totally possible for these materials to compete with existing silicon materials if high performance can be attained. While several high-performing n-type transparent oxide semiconductors have been demonstrated, equally well performing p-type remains intangible. The copper oxide system (Cu–O) has two stable phases; cubic cuprous oxide (Cu_2O) and monoclinic cupric oxide (CuO). Although, both phases are intrinsically p-conducting, they have unique distinct structural (from cubic to monoclinic), optical (direct and indirect band gaps), and electronic (mobilities, carrier concentrations, band offsets) properties. Cuprous oxide (Cu_2O) in thin-film form is a potentially promising material for transparent electronics technology due to its translucence ($E_g = 2.1\text{-}2.7$ eV) and its native p-conducting which have been attributed to hybridization of Cu 3d states near its valence-band maximum [1, 2]. Cupric oxide (CuO) is also a p-type oxide yet its narrower energy gap ($E_g=1.5\text{-}1.9$ eV) inhibits the material transparency unless it was deposited as a very thin layer [3]. Copper oxide (Cu_xO) thin films have been prepared by several techniques each of them has its own advantages and disadvantages [4-8]. Structural, optical and electrical properties of the deposited films are very dependent on the method used. Recently, there has been a growing trend toward using eco-friendly and organic-free precursors for the sustainable future. This green method of employing plant extracts or water-inducement to prepare Cu_xO precursors has drawn much attention as a simple and viable alternative to chemical procedures and physical methods. Green synthesis of Cu_xO nanoparticles by plants such as *Tridax procumbens* [9], tea leaves [10], *Aegle marmelos* [11] and *Aloe vera* [12] has been reported for antimicrobial [9-12], photocatalytic activities [13] and electrocatalytic materials for the counter electrode in dye sensitized solar cells [14]. Lately, Garlapati et al. [15], Liu et al. [16] and Shan et al. [17] have proved the possibility of fabricating CuO thin film transistors (TFTs) using cupric nitrate with de-ionized (DI) water as solvent and glycerol as a reducing agent. They found

that this polyol reduction method allows the construction of precursor solutes in water without additional additives and it produces films with a smoother surface morphology. However, unlike other metals precursors where the decomposition of the metal salt starts from O₂-rich to O₂-poor oxide with increasing the temperature, CuO precursor was found to decompose directly to metallic copper phase during the drying step at 150°C [17]. High annealing temperature ranges between 400°C [15] and 300°C [16] had to be applied to oxidize the metallic copper and achieve CuO films. However, it has been reported that the rate of copper oxidation under humid conditions can be accelerated significantly in presence of alkali solutions [18, 19]. In such process Cu²⁺ ions are released constantly from the Cu substance into the alkali solutions whereas the naturally dissolved O₂ is reduced. Spinach is known as one of the alkaline powerhouse that has pH level of 6.6 - 7.2 when cooked [20]. Using such natural green alkali solution to transfer copper to copper oxide has not been reported previously in literature to the best of our knowledge.

In this study we report a novel and simple green synthesis of Cu₂O thin films, where we used the metallic copper powder with the water of spinach leaves and glycerol. The properties of this precursor solution, and films fabricated based on it, were then compared to the precursor and films prepared by polyol reduction method using Cu(II) nitrate. Films synthesized by both methods were then used to fabricate p-type MOS capacitors.

2 Experimental Details:

2.1 Preparation of Precursor Solutions

- **Preparing Spinach leaves extract**

Fresh and healthy spinach leaves were washed thoroughly with distilled water and dried well. Approximately 20 gm of these leaves were shredded into fine pieces and boiled in 100 ml of distilled water for 1h. After cooling, the extract was filtered through Whatman

filter paper (no.4) to remove any solid particles. The pH of the resulting solution was found to be 6.2.

- **Synthesis of precursor Solution-1**

0.2M of copper powder (Cu, 99.7% purity) was mixed with 10ml of spinach leaves extract for 10 min. In order to improve the solution homogeneity, a small amount of glycerol was added with a ratio of 1:3. The mixture was continuously stirred using a magnetic bar for 1h at 60°C and then left for 24h at room temperature. The pH of the mixture was measured again and turned to be 7.

- **Synthesis of precursor Solution-2**

A 10 ml of copper oxide solution were prepared by dissolving 1M of cupric nitrate $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in 7.5 ml deionized water and 2.5 ml glycerol (3:1 volume ratio). The mixture was stirred for 6 h until a completely homogeneous solution with a pH of 3 was obtained.

2.2 Films Coating and Samples Fabrication

Prior to deposition, heavily doped p-type Si substrates were cleaned ultrasonically in a sequential manner using acetone, isopropyl alcohol and distilled water, respectively. All substrates were subject to an O_2 plasma treatment (12mTorr, 18W) for 6 min to reduce surface hydrophobicity. The solutions were filtered using a 0.45 μm membrane syringe filter and coating was performed using spin coater at a speed of 500 rpm for 5s and then 5000 rpm for 20s. The coated layers were baked on a hotplate at 100°C for 5 min. To obtain an appropriate thickness, the process was repeated for three layers of coating which corresponds to 20 nm and 25 nm for Cu_xO films prepared by Solution-1 and Solution-2, respectively. Finally, all films were annealed in a box furnace at 200°C for 1 hr in air. To fabricate the MOS capacitor, a Si wafer with a 100-nm thermally grown SiO_2 layer was used as the

substrate. After the normal cleaning process the substrates were exposed to UV light for 20 min to improve the surface uniformity. Then, three layers of each Cu_xO precursor solution were then spun on the SiO_2/Si substrate and annealed for 1h at 200°C in air. Finally, 80-nm of Au was evaporated on the surface of the Cu_xO by electron-beam evaporation, in which circled electrodes with different diameters were defined by our local shadow mask.

2.3 Films and Devices Characterization:

Fourier-Transform Infrared (FTIR) measurements were performed to examine the bonding environment of precursor solutions. The structural phase for Cu_xO films were examined by X-ray Diffractometer using $\text{Cu K}\alpha$ ($\lambda=1.5406 \text{ \AA}$) radiation. Chemical compositions and microstructures of the coated layers were investigated by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). Samples for XRD measurements were prepared by coating 10 layers of each film on Si substrates. Samples for TEM analysis were made by putting a drop of as-prepared solution on a carbon coated Cu-grid. Optical transmission was characterized for 3 layers deposited on glass substrate using (UV-Vis) spectrometer. High-frequency (1MHz) capacitance–voltage (C–V) characteristics for MOS capacitors were carried out using Agilent E4980A LCR meter and Cascade probe station. All electrical measurements were measured at room temperature in the dark using a 300-micron-diameter circular electrode.

3 Results and Discussion

The formation of Cu_xO precursor solution (Solution-1) from spinach leaf extract was initially monitored by a color change from yellowish green to red-brown after adding the copper powder and stirring. On the other hand, adding 1M of Cu(II) nitrate to the DI water gave the precursor solution (Solution-2) a deep sky blue color. The color of spinach leaf extract, Solution-1, and Solution-2 are shown in inset of **Fig.1**. Chemical bonds of the two

precursor solutions were examined by FTIR spectroscopy and compared to the pristine spinach leaf extract as it is illustrated in **Fig.1(a-c)**. The common broad characteristic frequency of 1637 cm^{-1} perceived in the three solutions referred to the H-O-H bending mode of water [21]. However, the peaks at 1108 and 1041 cm^{-1} , appeared in Solution-1 and Solution-2, can be ascribed to C-O vibration [22] signifying the presence of the glycerol in both precursor solutions. The existence of the nitrate ions in the precursor Solution-2 can be recognized by the asymmetric stretching modes of NO_3^- ions peak at 1338 cm^{-1} [23]. For the film prepared by Solution-1, a broad band at 600 cm^{-1} can clearly be seen in **Fig.1(d)**. This band appeared in the region of oxide vibrations and can be correlated to the Cu-O-Cu stretching vibration [22, 24] indicating the formation of a cubic Cu_2O . On the other hand, the film prepared using Solution-2 shows an absorption peak at 547 cm^{-1} , as illustrated in **Fig.1(e)**, which can be assigned to the presence of Cu-O bond [25] and the formation of monoclinic CuO.

XRD spectra for films synthesized by Solution-1 and Solution-2 and annealed for 1hr at 200°C are shown in **Fig.2(a)**, respectively. The film prepared using Solution-1 exhibited a single peak at 29.8° which can be assigned to the (110) plane of Cu_2O (JCPDS # 74-1230) with an approximate crystallites' size of 40 nm. Such a strong preferred orientation of the (110) plane and the absence of other Cu_2O phases could be correlated to the shape of the nanoparticles formed subsequently by the oxidation of Cu particles. In general nonpolar Cu_2O (110) surfaces have lower free energies than polar Cu_2O (100) surfaces, and it has been proven by density functional theory calculations [26, 27] that, under oxygen-rich conditions, Cu_2O (110) has the lowest surface energy. Such oxygen-rich environment for this film was confirmed by the XPS measurement as we will show shortly. Additionally, it has been reported that selective capping agents can effectively adsorb on the surface and decrease the surface energies [28]. Accordingly, this will lead to precisely tuning the percentages of

different facets of crystals. In particular, Liang et al. [29] found that using oleic acid as a face selective adsorption additive resulted in fully Cu₂O (110) structures. Interestingly, spinach chloroplasts include at least 11 different fatty acids, including oleic acid [30], which, presumably, has played a major role in forming the Cu₂O (110) phase. We presume that the growth mechanism of Cu₂O from Cu particles in the alkaline spinach solution can be described with the same steps presented in [18]. The O₂ in air is dissolved in the solution and then adsorbed on the surface of Cu particles. This O₂ adsorption will oxidize the Cu atoms to Cu²⁺ ions as the following:

Through a very short time the Cu²⁺ ions can be reduced to Cu⁺ ions by neighboring Cu atoms according to the reaction;

Consequently, Cu⁺ ions will react with OH⁻ in the solution to form Cu₂O nucleation sites following this reaction;

In contrast, under the same annealing conditions, when Solution-2 was used the films showed, as in **Fig.2(a)**, four peaks at 2θ values 32.7°, 35.6°, 38.7° and 48.8° which can be correlated to the reflections from (110), ($\bar{1}11$), (111) and ($\bar{2}02$) planes of the monoclinic phase of CuO (JCPDS # 73-6023). The small peak observed at 44.5 belongs to the stage of our XRD system. Both Garlapati et al.[15] and Ao Liu et al.[16] were able to synthesize CuO film using 0.1M of Cu(II) nitrate, yet their annealing temperatures were as high as 400°C and 300°C, respectively. In our case, increasing the molarity of Cu(II)Nitrate to 1M, helped in forming CuO phase at temperature as low as 200°C. It has been reported [25] that in the polyol technique, where the formation of metallic oxide results from a hydrolysis reaction, the concentration of the product is essential for reduction efficiency. Specifically, increasing

the concentration of the starting precursor salt, or reducing the water present in precursor, will slow down the reduction process. All our attempts to use molarity less than 0.5M ended with a pure metallic copper phase after annealing at 200°C. At such low molarities an extra heat budget is needed to oxidize the resulted metallic copper to Cu₂O or CuO.

The phases of both films were further confirmed by XPS measurements. As it is illustrated in **Fig.2(b)**, the film made of Solution-1 showed a sharp Cu 2p_{3/2} peak situated at 932.5 eV which corresponds to Cu(I) in Cu₂O phase [31]. While the appearance of a bump at 933.9 eV of the Cu 2p_{3/2} peak and additional satellite peaks between (938-946 eV) for the film fabricated from Solution-2, as shown in **Fig.2(c)**, indicates the existence of Cu(II) in CuO phase [32]. The binding energy of O 1s for both films are presented in **Fig.2(d)**. In case of CuO film, two oxygen components are detected namely the O-Cu at 530.2 eV and the adsorbed oxygen at 531.8 eV. As Cu₂O could attract more oxygen to the surface of the films, the concentration of adsorbed oxygen on Cu₂O film was larger than that on CuO film.

Fig.3 presents the low and high magnification TEM images for Cu₂O and CuO films. The TEM image of Cu₂O film, **Fig.3(a)**, shows that it composes from petal-like structure with an average diameter of 112 to 25 nm. Conversely, **Fig.3(b)** shows the microstructure of CuO film which looks different as the particles were spherical in shape with smaller cluster size and an average diameter of 12 to 6 nm.

Transmission spectra of 20 nm thick Cu₂O film and 25 nm thick CuO film deposited on glass substrates are presented in **Fig.4(a)**. Surprisingly, Cu₂O film showed an average transmittance of 97% in the visible region. The high transparency of the film can be attributed to its thin thickness and the small size of the nanoparticles that compose it. However, the CuO film showed a transmittance between 45% and 75% within the range of 400-700 nm. The optical band gap energy of Cu₂O and CuO can be assessed according to the equation $(\alpha h\nu)^2 = A(h\nu - E_g)$, where A is a constant, α is the absorbance and E_g is the band gap energy.

Fig. 4 (b&c) shows the corresponding curves of $(ah\nu)^2$ vs $h\nu$, for both films, by which the optical band gaps of Cu_2O , and CuO were estimated to be 2.7 and 1.9 eV, respectively.

In order to examine the electric properties of the two green synthesized films, we fabricated two MOS devices by depositing a Cu_xO semiconductor layer on top of a 100 nm SiO_2 which serves as a dielectric (or insulator) layer. Schematic drawing of the MOS prototype is shown in the inset of **Fig.5 (a)**. Typical high frequency (1MHz) C-V curves for the two MOS capacitors are presented in **Fig.5 (a)**. Sweeping in both directions, both samples exhibited P-type polarity with good performance. Small hysteresis voltage around 100 mV was observed in Cu_2O -MOS, which is similar to that reported in [33] for $\text{HfO}_2/\text{SiO}_2$ -stacked gate dielectric. While the CuO -MOS showed a hysteresis of 750mV indicating more charge trapping at $\text{Cu}_x\text{O}/\text{SiO}_2$ interface in the case of sample based on solution-2. Although a 100 nm-thick SiO_2 was used as a gate dielectric, the measured accumulation capacitance (C_{ox}), 23.6 nF/cm² for Cu_2O -MOS and 27.2 nF/cm² for CuO -MOS, turned to be less than the expected 34.5 nF/cm². This slight dropping off could be attributed to an increment in the thickness of the dielectric layer due to the diffusion of O_2 from Cu_xO to SiO_2 layer during the annealing step. The ability of copper oxide to oxidize the underneath layer has been reported before [34, 35] and been justified according to *Ellingham diagram* [36]. Both flat-band voltage V_{fb} and doping concentration N_A can be extracted from the x-intercept and the slope [37] of the plot V vs $1/C^2$, respectively. **Fig.5 (b&c)** represent the aforementioned relation for the two Cu_2O -MOS and CuO -MOS capacitors, respectively. It can be noted that the flat-band voltages V_{fb} for both devices are negative, which suggested that there are significant positive oxide charges in the gate dielectric. The V_{fb} shift of Cu_2O -MOS to the negative direction, indicating that more positive oxide charge could exist due to the increment in the dielectric thickness. The oxide charge density Q_{ox} was estimated according to the relation [33]; $-C_{ox}(V_{fb} - \phi_{ms})/q$, where the ϕ_{ms} is the work function difference between metal (p+ silicon) and

semiconductor (Cu_xO)), C_{ox} is the accumulation capacitance, and V_{fb} is the flat-band voltage. The oxide charge density for Cu_2O -MOS found to be $2.16 \times 10^{12} \text{ cm}^{-2}$ which is higher than $1.86 \times 10^{12} \text{ cm}^{-2}$ that related to the MOS based on CuO as expected. A summary of the measured parameters for both Cu_2O -MOS and CuO -MOS are summarized in **Table 1**.

Table 1. The most important parameters of the two $\text{Au/Cu}_x\text{O/SiO}_2$ capacitors, all annealed at 200°C for 1h in air.

	N_A (cm^{-3})	V_{fb} (V)	V_t (V)	Hys. (mV)	Q_{ox} (cm^{-2})
Cu_2O -MOS	2.01×10^{17}	-13.9	-10.04	100	2.16×10^{12}
CuO -MOS	1.45×10^{17}	-10.26	-7.05	750	1.86×10^{12}

4 Conclusion

Cu_2O and CuO thin films were obtained by adopting a free-solvent, green synthesis approach at a temperature as low as 200°C . Both films were used to fabricate MOS capacitors which exhibited p-type polarity with good performance and hysteresis voltages in the range of 100mV-750mV. We believe that the simplicity of the process, together with the low growth temperature, will contribute to the optimization of solution processed p-type oxide-based devices and its future in printed devices.

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7 Figures Captions:

Fig.1. FTIR spectra for (a) pristine spinach leaves extract, (b) Spinach solution after the addition of 0.2M copper powder and glycerol (Solution-1), (c) 1M of Cupric nitrate dissolving in deionized water and glycerol (Solution-2), (d) films prepared by Solution-1 and (e) films prepared by Solution-2.

Fig.2. (a) XRD spectra of Cu_xO thin films prepared by both solutions. XPS for Cu_xO films produced by (b) Solution-1, (c) Solution-2 and (c) the O 1s for both films.

Fig.3. Low and high magnification TEM images for (a) Cu_2O and (b) CuO films.

Fig.4. (a) Uv-vis transmittance spectra of 3-layers of Cu_2O and CuO films deposited on glass substrate, and relation between $(\alpha h\nu)^2$ and $h\nu$ using (b) Cu_2O and (c) CuO films. Insets show the transparency of each film.

Fig.5. (a) C-V curves of the two MOS capacitors fabricated using Cu_2O and CuO films. The MOS schematic structure is shown in the inset. The plot of $1/C^2$ versus V and the linear fit (dot line) used for the calculation of flat-band voltage for (b) Cu_2O -based MOS and (c) CuO -based MOS .

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Highlights:

- We used a green solvent-free method to develop cuprous oxide (Cu_2O) by mixing the copper powder with spinach leaf extract at low annealing temperature (200°C).
- We used another green solvent-free method to develop cupric oxide (CuO) using the water-based polyol reduction method of Cu(II) nitrate at low annealing temperature (200°C).
- The as-prepared precursors were then spun on SiO_2/P^+ Si substrates to form nanoscale p-type Metal-Oxide-Semiconductor (MOS) capacitors.
- Cu_2O -based MOS showed small hysteresis of 100 mV, which indicating the less trap density exist in the case of using spinach leaf extract.