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Optical and Electrical Properties of Cu-Based Thin Films by Aerosol Assisted Chemical Vapor Deposition

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Cu-based thin films with doping of Zn and Al were synthesized by aerosol-assisted chemical vapor deposition (AACVD). The AACVD allows simple fabrication method which produced homogenous film when deposited on glass substrates. The structural, optical transmittance and electrical properties of Cu-based thin film with Zn and Al doping were obtained by X-ray diffraction (XRD), UV-Vis spectroscopy and 4-point probe, respectively. XRD results showed peaks for ZnO and $CuAlO_2$ indicating that binary Cu thin film with Zn and Al doping was successfully synthesized by AACVD. The optical band gap of 3.6 and 4.11 eV was obtained for single Cu_2O and ZnO thin film, respectively. The best electrical performance was achieved by single Cu_2O thin film with R_s = 102.8 Ω/sq, however, it was obtained at low T of 28%. The doping of Zn and Al to Cu-based thin film did not improve their electrical and optical properties.

Keywords: AACVD, copper oxide thin films, $CuAlO_2$, transparent conducting film

I. INTRODUCTION

Copper oxide forms two types of oxide: copper (I) oxide (CuO, *tenorite*) and copper (II) oxide (Cu_2O, *cuprite*) which both exhibits *p*-type characteristics of semiconductor with band gap of 2.1 and 1.2 eV, respectively. Conduction of *p*-type semiconductor is attributed to the presence of holes in the valence band due to doping or annealing. Copper oxide shows good electrical and optical properties which is suitable for wide range of applications such as photovoltaic material (Kaur et al., 2017), gas sensor (Navale et al., 2017) and catalytic application (Ren et al., 2015). Copper oxide also has the advantages of low cost, non-toxic and high availability (1000 times abundant than silver).

Previously, copper oxide thin film was deposited on different substrates by various methods such as pulsed magnetron sputtering (Alkoy & Kelly 2005), DC magnetron sputtering (Mugwang'a et al., 2013), thermal evaporation (Navale et al., 2017) and spin coating (Johan et al., 2011). On the other hand, Cu-based nanostructure such as copper nanowires and nanofibers can be obtained by solution-processed (Duong & Kim 2017) and electrospinning (Wu et al., 2010), respectively. Deposition method is important in determining the properties of the materials, thus, we demonstrate the fabrication of Cu-based thin film and metal doping by aerosol-assisted

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chemical vapor deposition (AACVD).

AACVD is a low cost, high deposition rate and facile method, which is uniform and good quality thin film can be obtained (Bakar et al., 2013). There are a few works reported on the Cu-based thin film using AACVD. Previous study has utilized the tube furnace variant of AACVD to synthesize molecular metal organics (MMO) precursors of copper and cobalt mixed metal oxide using heterobimetallic complex consist of *N,N*-dimethylaminoethanol (DMAE), trifluoroacetate (TFA) and tetrahydrofurane (THF) (Hamid et al., 2008). Copper oxide thin films deposited onto glass substrates by AACVD for antimicrobial activity was reported by Hassan et al (2014). Copper oxide and copper gallium oxide was prepared by AACVD using different metal precursor ($Cu(acac)_2$ and $Cu(thd)_2$) and solvents (toluene, dichloromethane, THF) (Knapp et al., 2014). However, these studies were not reporting the electrical and optical properties of Cu-based using AACVD method. So far in literature there there was no attempt to deposit single CuO and binary metal oxide of Al_2O_3 and ZnO as a thin film on borosilicate glass substrates using AACVD setup. So far, binary of $CuAlO_2$ also exhibits *p*-type characteristics was previously synthesized by solution-processed (Chiu & Huang 2012; Tonooka et al., 2002), spray pyrolysis (Singh et al., 2008) and DC sputtering (Banerjee et al., 2003) whereas Zn-doped CuO was synthesized by microwave assisted solvothermal method (Rejith & Krishnan 2013).

Thus, the aim of the present study is to prepare Cu-based thin film via facile approach of AACVD and to determine the structural, electrical and optical properties of these films. The feasibility of AACVD method to synthesize binary film and the doping effect of Zn and Al to the electrical properties of Cu-based thin film is investigated.

II. MATERIALS AND METHODS

Cu-based thin films were deposited from sol-gel solution on the borosilicate glass substrate by AACVD. Borosilicate glass substrates (Borofloat® 33, Schott) were cleaned by standard cleaning procedure of washing with soap; ultrasonic cleaning in acetone and isopropanol each for 15 min; rinsing with deionized water; and drying with N_2 gas flow.

Sol-gel solution was prepared by stirring of metal precursors in solvent of absolute ethanol (99.8%, Normapur AR) for an hour and promptly proceeding to deposition. For single component of metal, metal precursor of copper (I) acetate (97%, Sigma Aldrich), zinc acetate (99.99%, Sigma Aldrich) and aluminium acetate (basic, Sigma Aldrich) were prepared separately whereas for binary component of ZnO/Cu_2O and $CuAlO_2$, the metal precursors were mixed together. A few drops of diethanolamine (≥ 98.0 %, Sigma Aldrich) were added to the mixture to enhance the solubility of metal precursors in the solvent.

The AACVD was carried out in N_2 gas flow with distance between nozzle and borosilicate glass substrate is 10 mm. The thickness of the films was varied by varying the deposition time of 15, 30 and 60 min. Structural, optical and electrical properties of Cu-based thin film by AACVD were determined by X-ray diffraction, UV-Vis and 4-point probe, respectively.

III. RESULTS AND DISCUSSIONS

Single metal oxide thin film of CuO and ZnO; and binary metal oxide of ZnO/Cu_2O and $CuAlO_2$ thin films were successfully fabricated by AACVD. Figure 1 shows the XRD pattern for the CuO, ZnO/Cu_2O and $CuAlO_2$ thin films prepared by AACVD at 400°C. XRD analysis indicated the films were crystalline with different copper phase of Cu_2O, CuO and Cu with highest peak was Cu_2O phase for all samples. The appearance of ZnO and $CuAlO_2$ peaks indicated that the binary metal oxide of ZnO/Cu_2O and $CuAlO_2$ thin films was successfully prepared by AACVD.

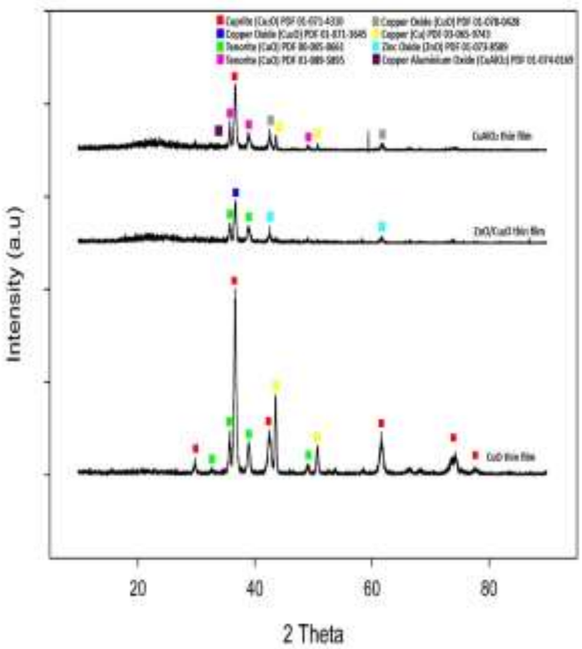

Figure 1. XRD Spectra for Cu-based thin film by AACVD.

Figure 2 shows the optical transmittance for Cu_2O, ZnO, ZnO/Cu_2O and $CuAlO_2$ thin films. ZnO thin film showed high optical transmittance of 100 % (550 nm) whereas Cu_2O thin film showed much lower optical transmittance of 28% (550 nm). The optical transmittance was drastically reduced to 0% transparency for both ZnO/Cu_2O and $CuAlO_2$ thin films. The low transparency of Cu_2O, ZnO/Cu_2O and $CuAlO_2$ is due to the thicker film as the deposition time increased to 1 hour, however, for film deposited at lower deposition time, the R_s is too high (> 10^6 Ω/sq). In Figure 3, the band gap was determined using *Tauc* plot where the band gap of Cu_2O and ZnO thin film was estimated at 3.6 eV and 4.11 eV, respectively.

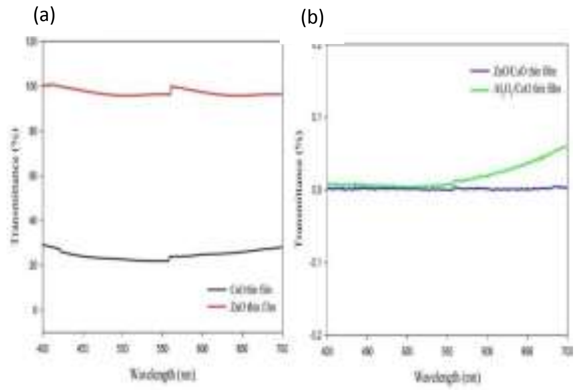

Figure 2. Transmission spectra for (a) single metal oxide of Cu_2O and ZnO; and (b) binary metal oxide of ZnO/Cu_2O and $CuAlO_2$ thin films.

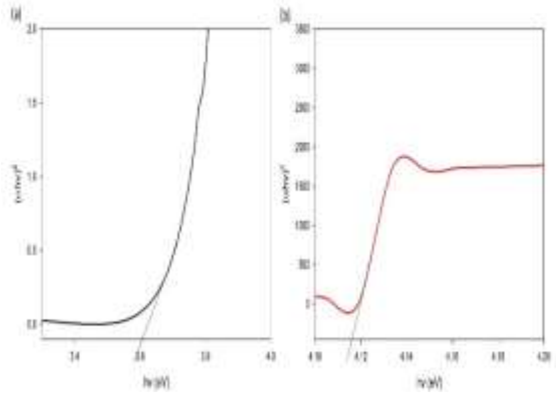

Figure 3. *Tauc* plot of band gap determination for (a) Cu_2O and (b) ZnO thin films.

Electrical properties of Cu_2O, ZnO/Cu_2O and $CuAlO_2$ thin films were summarized in Table 1. The R_s and thickness (t) of the films was obtained by 4-point probe and surface profilometer, respectively. Resistivity (ρ) and conductivity (σ) was determined using the following formula: $\rho = R_s \cdot t$ and $\sigma = 1/\rho$. The best electrical performance of R_s = 102.8 Ω/sq was obtained by single metal oxide of Cu_2O thin film comparable to benchmark TCF performance of (~100 Ω/sq) for other applications such as flat display, however, it has yet to achieve the benchmark of TCF (~10 Ω/sq) for front window of solar cell applications. The binary metal oxide of ZnO/Cu_2O and $CuAlO_2$ thin films have lower electrical performance compared to single Cu_2O thin film. Cu_2O and $CuAlO_2$ thin film synthesized by AACVD showed lower electrical performance compared to thin films synthesized by other methods in previous studies (Alkoy & Kelly 2005; Tonooka et al., 2002).

Table 1. Electrical properties of Cu-based thin film

Thin film type	R_s (Ω/sq)	T (μm)	ρ (Ω.cm)	σ (S/m)
Cu_2O	102.8	1.441	1.481×10^{-1}	6.752
ZnO/Cu_2O	5.31×10^{6}	1.027	1.573×10^{-4}	6.336×10^{-5}
$CuAlO_2$	16.00×10^{6}	1.287	2.060×10^{-4}	4.854×10^{-5}

IV. SUMMARY

Cu-based thin films with metal doping of Al and Zn were successfully fabricated by AACVD and properties of structural, electrical and optical for these films were investigated. XRD analysis showed three different phases of Cu_2O, CuO and Cu were observed for single Cu thin film whereas peaks attributed to ZnO/Cu_2O and $CuAlO_2$ were obtained for binary Cu thin film with doping of Zn and Al indicating the feasibility of AACVD to synthesize the binary film. The best electrical performance was achieved by single Cu_2O thin film with R_s = 102.8 Ω/sq, however, it was obtained at low T of 28%. Thus, due to low T of Cu_2O thin film, it is not suitable to be applied as TCF. In addition, the doping of Al and Zn by AACVD does not improve the electrical and optical properties of the Cu-based thin films. To improve the electrical and optical properties of Cu-based thin films by AACVD, modification to the AACVD parameters, preparation of sol-gel solution and annealing temperature is recommended.

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