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Structural, Surface Morphological and Electrial Properties of Spray Pyrolysis made Cu/Cu_2O Composite films for different Molar Concentration of $Cu(OAc)_2$

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Abstract

Cu/Cu_2O Composites films have been developed at different concentration of copper acetate with0. 3M, 0.35M, 0.4M and 0.45M at 300^0C by spray pyrolysis technique and the effect of concentration on the structural, surface and electrical properties of the films have been investigated. The crystalline structure of the prepared films has been studied using X-ray diffractometer (XRD). The XRD patterns confirmed the presence of cubic structure of Cu and Cu_2O in the films in a reduced atmosphere created by NH_4OH and ethanol. The surface properties have been characterized using Scanning Electron Microscopy (SEM). The surface of the as-deposited films is smooth and comprised of uniformly distributed grains. The resistivity has been investigated by Four probe method for different molar concentrations of copper acetate. The resistivity for the film deposited with the optimized concentration of 0.4M is found to be $4.34X10^{-02}$ Ωcm. From the study it is evident that molar concentration of copper acetate has a strong effect on the structural, surface and electrical properties of Cu/Cu_2O composite films and an optimum molar concentration has been fixed.

Keywords: Spray pyrolysis, Cu/Cu_2O nano composite films, concentration, copper acetate.

Introduction

The Cu-O system has two stable semiconducting oxides: cupric oxide (CuO) and cuprous (Cu_2O). Copper oxide is a multifaceted material having uses in numerous applications in sensor, electrochemical device, solar cell and photovoltaic material and catalytic application because of its p type semi conductivity nature, higher absorption co-efficient, abundant availability, non toxic nature and with a low production cost[1]. Copper oxide films have been deposited using various techniques including to sputtering, chemical vapor deposition (CVD), and spray pyrolysis etc. Referring to the spray pyrolysis technique, assorted parameters like air pressure, deposition rate, substrate temperature, and substrate to nozzle distance (SND) have effect on the physical, electrical and optical properties of the thin films. Owing to its simplicity in the making of the films over a large area and its inexpensiveness, the spray pyrolysis technique is a better suited method among the other methods for the preparation of thin films. Also, it provides an easy path to dope any element, in a ratio of required proportion through the solution medium. This method is convenient for preparing pinhole free, homogenous, smoother thin films[2]. The Cu/Cu_2O nano composite films exhibit a butter combination of mechanical properties and electrical conductivity characteristics. This makes Cu/Cu_2O composites as a good candidate for applications in electrical and electronic industries[3]. In present study the characteristic behavior of Cu/Cu_2O composites have been reported for variation the molar concentration of copper acetate Cu $(CH_3COO)_2.H_2O$.

Material and Methods

Spray Pyrolysis Setup: Cu/Cu_2O Composite films have been deposited on glass substrates by the method of spray pyrolysis technique for different molar concentrations of copper acetate(Cu $(CH_3COO)_2.H_2O$) for 0.3M, 0.35M, 0.4M and 0.45M for a fixed substrate to nozzle distance of 22cm and at constant environment of 300°C. The spray pyrolysis apparatus setup constructed for the deposition of Cu/Cu_2O composite films has been shown a schematically in figure-1.

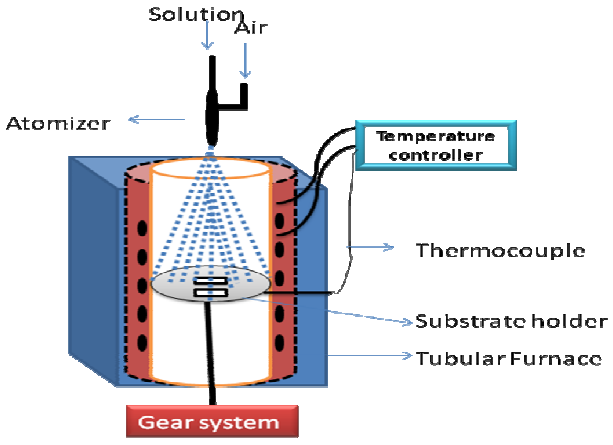

Figure-1
Spray pyrolysis apparatus setup

The main parts of the system setup are i. an atomizer or nebulizer that converts the spray solution to fine droplets and ii. a furnace / reaction chamber for producing pyrolytic action. A similar design has been used by vasu et.al[4]. A tubular vertical cylindrical furnace of diameter 10cm and length of 27.5cm has been fabricated and used as the reaction chamber. With an on build heating coil arrangement powered by AC voltage, a maximum temperature of 600^{o}C has been attained over a uniform cylindrical zone depth of 15cm inside the furnace cavity. A stainless steel plate of diameter 9cm and of thickness 0.7cm has been mounted in the uniform zone of the furnace to serve as the substrate holder. The substrate temperature has been measured using a chromal – alumel thermocouple (placed just below the substrate holder). The temperature of the furnace has been maintained and controlled by a Mars DTC- 203 temperature controller with a temperature sensitivity of 1°C. The spraying of the solution has been carried out using a specially designed atomizer made of glass material. The flow of solution through the tube has been controlled by the stop cock of the burette connected to the inner glass tube of the atomizer which in effect controls the flow of solution through the nozzle.

Solution preparation method: The spray solution of various molar concentrations has been prepared by dissolving copper acetate (analytical grade 99.9% purity) in a 100ml solvent mixture of ethanol and ammonium hydroxide taken by the volume ratio of 1:1. Initial trials have been made when ethanol and ammonium hydroxide alone was used for preparing the spray solution but no film formation was observed on the substrate. Hyun suk jung et.al have shown that an addition of diethanolamine (DEA) to the spray solution has enhanced the stability of the films[5]. The amount of DEA in the precursor solution has been progressively increased from 1ml and it was found that well adherent stable films could be obtained when 5ml of the DEA has been added to the solution. The solution has been stirred for 15 minutes at room temperature using a magnetic stirrer. An air pressure of 2 kg/cm^2, a solution flow rate of 5 ml/min and a spray time of 3 minutes have been used for the preparation of Cu/Cu_2O films.

Charactrization Techniques: The structural characteristics of the films have been analyzed with RIGAKU ULTIMA III X-ray diffractometer. The electrical properties of the films have been studied using Four Probe instrument. The study of surface morphology has been carried out using VEGA3 TESCAN scanning electron microscope.

Results and Discussion

Structural Analysis: Figure-2 indicates the XRD patterns for the films deposited with a copper acetate molar Concentration of 0.3M, 0.35M, 0.4M 0.45M mentioned as a,b,c and d respectively. Copper acetate with 0.3M (curve a) gives rise to three peaks of Cu_2O at 2θ equal to 36.16°, 61.12° and 73.68° corresponding to the reflections from (111), (222) and (311) planes respectively. This reveals that Cu_2O is of Cubic structure and in addition also it gives rise to another two peaks of Cu at 2θ equal to 43.3° and 50.3° which corresponds to the reflections from (111) and (200) planes. When the molar concentration increased to 0.35M Cu_2O and the peaks corresponding to (111), (222) and (311) orientations (curve b) the copper peaks corresponding to (111) and (200) orientations got enhanced. When the molar concentration of copper acetate is increased to 0.4M Cu_2O peaks corresponding to (222) orientation is disappears however the intensity of Cu_2O (111) orientations fall. The intensity of (311) Cu_2O orientation as well as the copper peaks corresponding to (111) and (200) orientation got enhanced.

XRD analysis of figure-2 confirms that Cu / Cu_2O composite have been found to be present in the films prepared for the molar concentration of copper acetate of 0.3M and 0.4M. When the molar concentration is increased to 0.45M, the Cu peaks corresponding to (111) and (200) orientation and (311) peaks of Cu_2O are found to be disappearing. A new peak was found to be appearing at 2θ equal to 38.6° and this corresponds to the reflection from (111) orientation of CuO, however the Cu_2O (111) peak got an enhancement. Oxygen from the supplied air and the copper acetate provided the necessary oxidization atmosphere in the hot zone. NH_3 and ethanol decomposition provided the necessary reducing atmosphere in the hot zone[6, 7]. For the spray solution with low molar concentration of 0.3M, the net heat absorbed by the droplet may not be sufficient enough to vaporize the entire droplet, due to fast travel of droplet to the substrate, as a result the precipitation and sublimation has taken place on the substrate. So the reaction appears to be of homogeneous one[8] and the film had low crystallinity (curve a).

When the molar concentration of copper acetate is augmented to 0.35M, the intensities of the peaks of Cu_2O and Cu got enhanced (curve b) which indicates that the crystallinity of crystallites has been improved. The mere existence of crystallinity implies that oxidation and reduced atmosphere appear to have enhanced because of more oxygen got supplied from copper acetate and also by the decomposition of NH_3 and ethanol in the hot zone[6,7]. At this 0.35M concentration might have a reaction transition from homogenous type to heterogeneous type.

Referring to curve c for molar concentration of 0.4M the entire droplet would have evaporated in the hot space above the substrate prior to reaching the surface of the substrate. The aerosol particles precipitate as an amorphous salt and then sublime immediately prior to reach the substrate. The vapor transport to the substrate surface would have resulted in subsequent decomposition/oxidation/reduction which may be a true CVD process. The Cu/Cu_2O composite film with best characteristics has been obtained at this 0.4M spray solution concentration[8]. The increase in molar concentration of copper acetate from 0.35M to 0.4M is found to have the optimum time required for precipitation and sublimation.

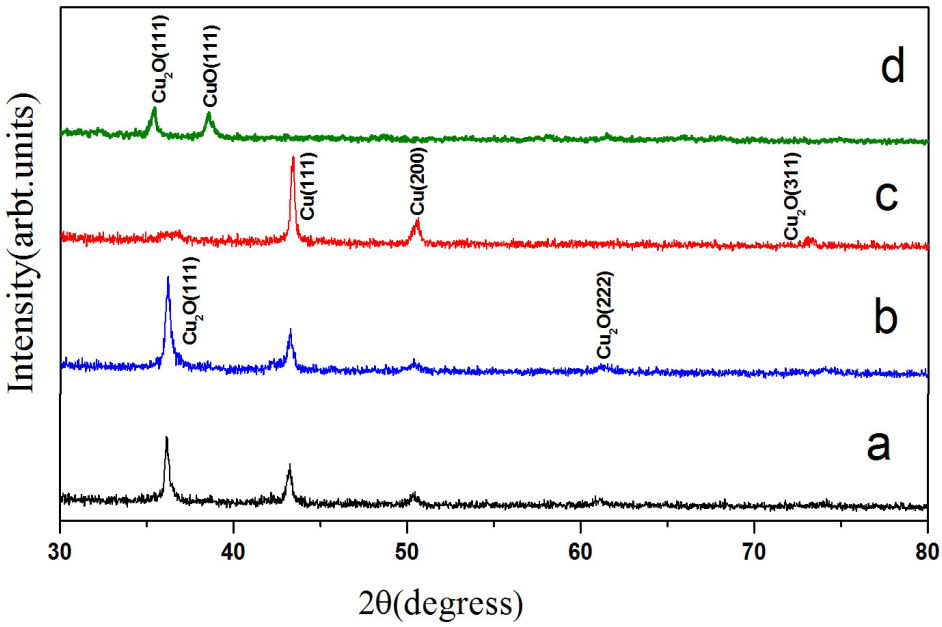

Figure-2
XRD Pattern of Cu/Cu_2O films prepared at Molar Concentration a) 0.3M, (b) 0.35M, (c) 0.4M and (d) 0.45M of Copper acetate.

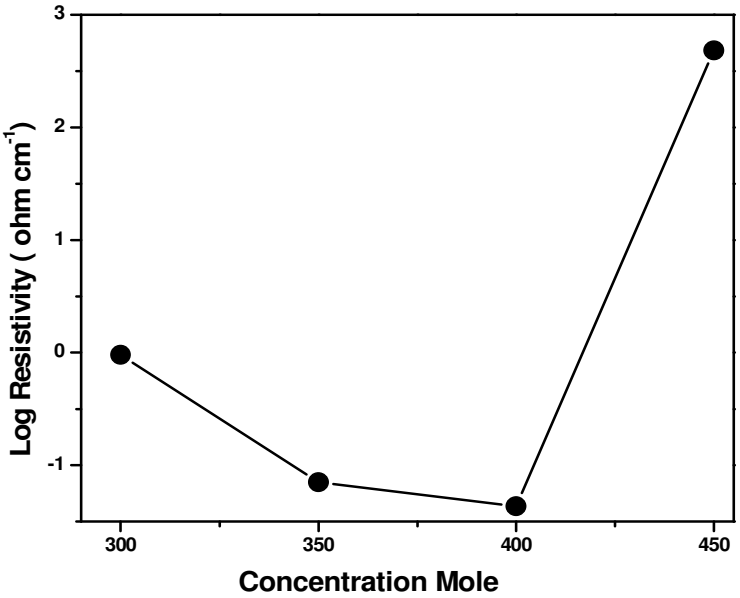

Figure-3
Variation of resistivity of the Cu/Cu_2O films with respect to concentration of Copper acetate

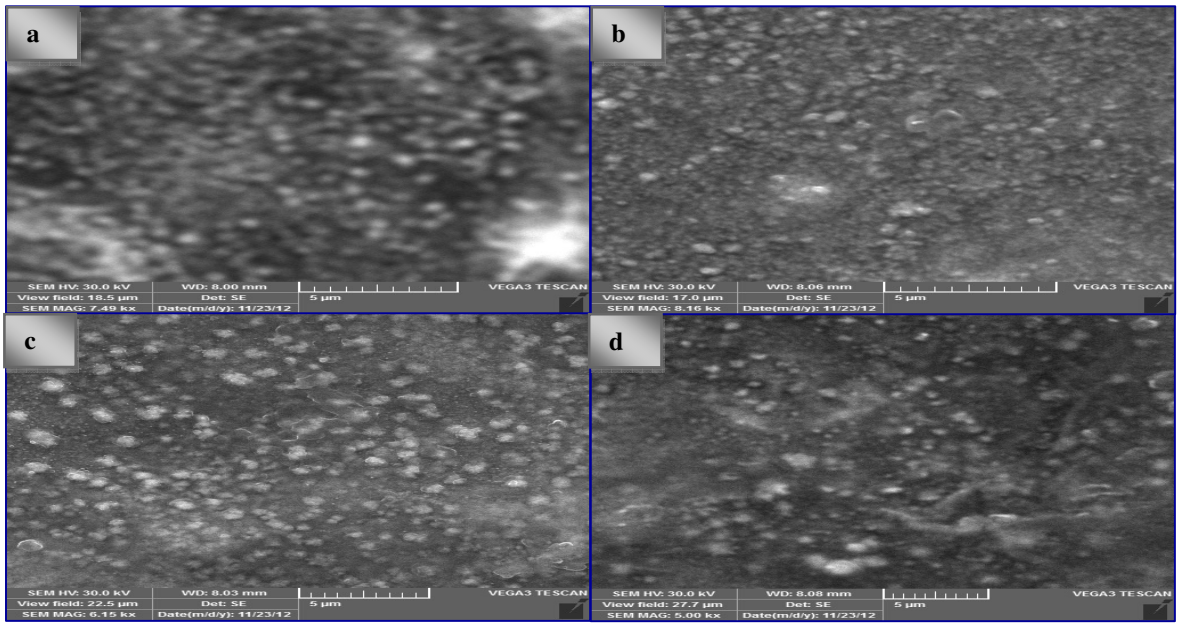

Figure-4
SEM images of Cu/Cu_2O films of molar concentration a) 0.3M, (b) 0.35M, (c) 0.4M and (d) 0.45M of Copper acetate.

When the spray solution concentration has been enhanced to 0.45M (curve d) the prepared film appeared to have only Cu_2O and CuO with poor crystallinity. Poor crystallinity could be attributed to the shortening of the entrainment column length and this would have reduced time available for evaporation, precipitation, and/or sublimation[8]. The droplet would have been evaporated only after reaching the surface of the substrate. Initially the sprayed aerosol particles splash onto the surface of the substrate, followed by precipitation as an amorphous salt and subsequent decomposition/oxidation/reduction. The reaction appeared to be homogeneous again, and also resulted with fogging of the films and this in turn results in relatively poor crystalinity and electrical characteristics (reported in section 3.2)[4, 9].

Electrical properties: The resistivities of Cu/Cu_2O composite films have been measured by Four probe method. The resistivity of Cu/Cu_2O composite films have been found as a function of different molar concentrations of copper acetate of 0.3M, 0.35M, 0.4M and 0.45M and has been reported in figure-3.

Figure 3 shows that the resistivity deceases when the concentration increase from 0.3M. Resistivity reaches its minimum value of $4.34X10^{-02}$ Ωcm for a concentration of 0.4M and these characteristics depreciate on further increase in the concentration. The XRD results also indicate the same trend. The butter electrical characteristics of the film with increase in concentration up to 0.4M may be attributable to the improvement in the crystallinity of the Cu/Cu_2O crystallites while the deterioration in the electrical characteristics of the films beyond a concentration of 0.4M may be attributable to the decrease in crystallinity of crystallites.

Figueiredo et al.[10] has reported that the resistivity of the pure copper film is 3.51×10^{-6} Ω cm, while that of Cu_2O film is 108 Ω cm. The resistivity of the films prepared for the present study with different copper acetate concentration from 0.3M to 0.35M is found to be varying from of 10^{-1} to 10^{-2} Ω cm, which clearly indicates that the films have electrical properties lying in between the values reported by Figueiredo et.al and the films are composed of pure Cu and Cu_2O composite films. The XRD studies (section 3.1) also reveals the same quality of the film. From figure 3 it is further confirmed that the films have a minimum resistivity at a concentration of 0.4M and this concentration is found to be an optimum for preparing Cu/Cu_2O composite films.

Scanning electron microscopy analysis: As in figure 4 shows the SEM images of Cu/Cu_2O composite films for different molar concentrations 0.3M,0.35M,0.4M and 0.45M of copper acetate and are represented as a, b, c and d. The deposited films are found to be smooth and well packed with tiny grains.

From the morphology of the films it is seen that there are no cracks, which indicate that the films are well adherent on the substrates. The grains are clearly visible for the film prepared

with a solution concentration of 0.4M which indicates that this concentration is optimum for making the Cu/Cu_2O composite films.

Conclusion

The study reveals that the molar concentration of copper acetate has an influential role on the structural, electrical and morphological properties of Cu/Cu_2O composites films. A molar concentration of 0.4M has been found to be optimum for preparing these films and at this stage films with the best possible crystallinity, electrical characteristics and surface morphology have been achieved. The change in the type of reaction from homogenous to heterogeneous type and vice-versa with for the specifically chosen variation in concentration seems to be the cause for influencing the film characteristics.

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