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Physico Chemical and Electrical Investigations on Cobalt Enriched Spinel Phased Copper Cobaltite Thin Films

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Abstract

As the ternary oxides of copper cobalt have garnered much attention and have been studied for a wide range of applications, a venture has been carried out in preparing such a compound in thin film form. Spray pyrolysis deposition is undertaken at three different deposition temperatures viz. 250, 300 and 350 °C. From the X- ray diffractograms of copper cobalt oxide films, it was clear that the film was crystalline only at the deposition temperature of 300 ºC and that copper has entered into the lattice only as a dopant as evident from the spinel type cobalt enriched phase $(Cu_{0.3}Co_{0.7})\ Co_2O_4$. XPS studies pinpointed the presence of Cu^{2+} ions and revealed the occurrence of low spin Co^{3+} ions in the octahedral sites and high spin Co^{2+} ions in the tetrahedral oxygen environment. The films were found to have excellent conductivity induced by polaron hopping mechanism. The mixed oxidation states of the cations placed in the octahedral sites are the main contributing factor in the enhancement of electrical conductivity. Film thickness played a key role in determining the electrical properties.

Keywords: *Thin films, X-ray diffraction, XPS, Electrical*

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1. Introduction

Ternary oxides from combination of two transition metals or a transition metal and a post-transition metal have evoked curiosity among researchers due to the enhancement of their properties and better performance in sensor and semiconductor technology. Copper cobaltite spinel with the general formula $Cu_xCo_{3-x}O_4$ is a versatile material known for the catalytic activity towards the oxidation of CO to CO_2, alcohol synthesis, automobile pollution control and oxygen evolution reactions [1-4]. Physicochemical properties of copper-cobalt oxides play an important role in governing electrocatalytic reactions or thermoelectric applications. For spinel electrocatalysts, the mixed oxidation states of the cations placed in the octahedral sites are the main contributing factor in an increase of the electrical conductivity that facilitates the adsorption of oxygen by providing donor-acceptor levels (d-orbitals) for chemisorption, which in turn enhances electrocatalystic activity [5]. On the other hand, it has been well established that the distribution of the mixed cationic valences, which is the key determinant of catalytic activity and other physicochemical properties, is erratic because the distribution is strongly influenced by the preparation method. The spinel-type copper-cobalt oxides tend to form a low crystallized single phase copper-cobalt oxide with a partially inverted spinel structure and minor segregations of new cobalt and/or copper oxide phases, which depend on the Cu/Co ratio in the precursor salt as well as the calcination temperature [6,7]. Diverse synthetic routes have been adopted to prepare spinel copper cobaltites such as chemical coprecipitation [8,9], thermal decomposition [10,11], spray pyrolysis [12,13] and sol gel routes [14]. In this present venture, the spray pyrolysis deposition of copper cobaltite spinels are undertaken at three different deposition temperatures and their physicochemical properties are analysed.

2. Experimental

Copper cobalt oxide thin films were deposited for three different substrate temperatures viz. 250, 300 and 350 °C. The salts of copper acetate (0.05 M) and cobalt acetate (0.15 M) were dissolved in 50% ethanol and 50% distilled water for preparing the starting precursor solution. Utmost care was taken for the cleaning process. Initially the 7.5 x 2.5cm glass substrates were washed in soap solution and rinsed off with deionised water. Then they were soaked in chromium trioxide and heated at 80°C for half an hour following which they were immersed in deionized water. Next the glass plates were rubbed with cotton swab dipped in isopropanol and scrubbed with cotton swab and finally dipped in acetone, dried and packed in air tight packets. The substrate was inserted into a tubular furnace controlled with a SANSEL (Model STC 002) temperature controller. The tubular furnace was 30 cm in height and 12 cm in diameter capable of heating upto 800°C with a current limit of 25 A and a power of 5750 watts. The compressed air from an ELGI compressor, along with the precursor was allowed to enter into the spray nozzle and a fine aerosol was created. Pyrolysis is a form of incineration that chemically decomposes organic materials by heat in the absence of air. Oxides of copper-cobalt were formed by the pyrolytic action on the substrate surface. X-ray diffraction analysis was performed on a X-ray diffractometer (PANalytical- 3040 X'pert Pro) with copper target (λ = 1.5405Å) in θ-2θ scan mode. The chemical composition and binding states of the copper cobalt oxide films deposited at the optimized deposition temperature 300 ℃ was characterized by X-ray photoelectron spectroscopy (XPS) using a PHI 5600ci ESCA spectrometer using monochromated Al- Kα or Mg- Kα X-rays or excitation of photo electrons. The electrical resistivity was measured by the standard two probe set up.

3. Results and discussions

3.1 Structure of copper cobaltite films

Fig. 1 shows the diffractogram of copper cobalt oxide films deposited at three different temperatures 250, 300 and 350 °C. It is clear that the film is crystalline only at the deposition temperature of 300 ºC and for the other deposition temperatures 250 and 350 ºC. The synthesis of copper cobaltite spinels has been a controversial subject [15]. Contrary to other cobalt based spinels, its preparation has been difficult and the product shows low thermal stability. When heated in air above 400 ºC, it decomposes into copper oxide, oxygen and a cobalt rich spinel phase [16].

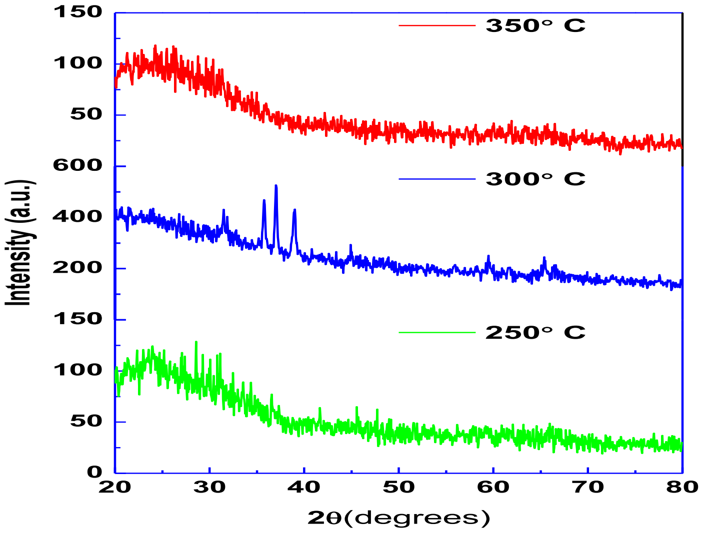

Fig. 1 XRD patterns of copper cobalt oxide

In the present work, all the diffraction peaks matched well with the spinel type cobalt enriched phase ($Cu_{0.3}Co_{0.7}$) Co_2O_4 (JCPDS 25-0270). It is evident that copper has entered into the lattice only as a dopant along with cobalt in the octahedral sites. The location of peaks corresponds to an fcc system with space group Fd3m. As seen, substrate temperature plays a vital role in forming crystalline nature [17]. At a low temperature of 250 ºC, the film is amorphous because the supplied heat energy is not sufficient to form its oxide phase and at a high temperature of 350 ºC, the amorphous nature may be attributed to the fact that the precursor solution gets evaporated even before reaching the hot substrate thus significantly reducing the amount of species available for film formation.

3.2 Cation distribution in copper cobaltite films (XPS)

The XPS survey spectrum (Fig. 2) showcased the peaks corresponding to copper, cobalt and oxygen in the expected binding energy regions. The peaks due to Cu 2p, Co 2p, O1s and O Auger are obviously observed. They are plotted after correction of charging effects using the binding energy of 284.8 eV corresponding to the C 1s peak.

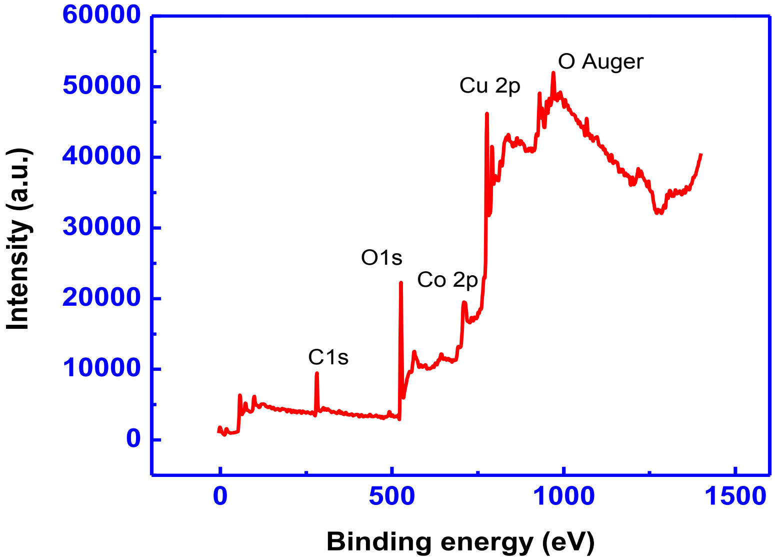

Fig. 2 XPS survey spectrum of copper cobaltite film

The high-resolution spectrum corresponding to Cu 2p is given in Fig. 3. The asymmetric peak at the binding energy value of 933.07 eV is ascribed to Cu $2p_{3/2}$ state. The peaks at 933.07 eV and 952.71 eV can be attributed to the presence of Cu $^{2+}$ ions according to Schon [140] and the appearance of strong satellites indicate Cu^{2+} as in CuO. In addition to the main peak of Cu $2p_{3/2}$, satellite peaks are observed on the high-binding-energy side more than 9 eV (942.36 eV).

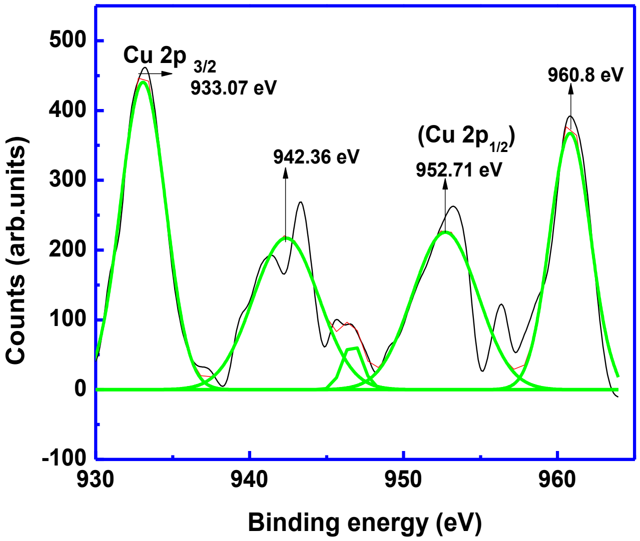

Fig. 3 Copper core level spectrum

The main peak of $2p_{1/2}$ is located at a binding energy that is almost 20 eV higher than that of their $2p_{3/2}$ main peak, which is the characteristic for the formation of CuO. On comparing with previously reported results [18-20], it can be confirmed that Cu^{2+} is the dominant oxidation state of copper in the copper cobaltite films. The Co 2p spectrum of the reference sample is shown in Fig. 4. Apart from the asymmetry, a significant intensity is present in the tail at the high BE side of the Co $2p_{3/2}$ peak of the Co metal. The intensity of the satellite appears to be small at a binding energy value of 778.75 eV.

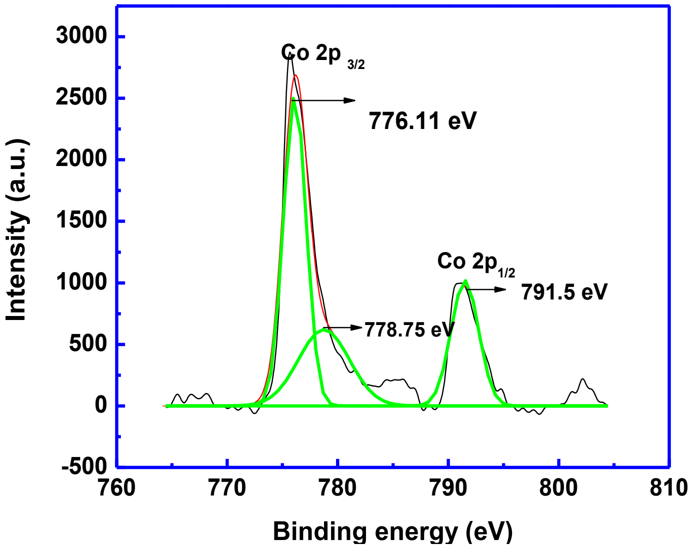

Fig. 4 Cobalt core level spectrum

The cobalt ions are present in different valence and coordination states. Hence there occur peaks due to ionization of both low spin Co^{3+} ions in the octahedral and high spin Co^{2+} ions in the tetrahedral oxygen environment. It exhibits two major peaks with binding energy values of 776.11 and 791.5 eV corresponding to Co $2p_{3/2}$ and Co $2p_{1/2}$ doublet core level peaks. The Co 2p core-level spectra of the high spin (HS) ions contain characteristic multiplet splitting satellite peaks which is due to the presence of unpaired 3d electrons in the valence shells of Co^{3+} ions.

The O 1s level is deconvoluted into two peaks at 528.66 and 530.91 eV as shown in Fig. 5. The O 1s spectrum exhibits a strong peak with a shoulder at the high binding energy side of O 1s peak. The apparent shoulder at the higher energy side of the O 1s main peak is a typical feature of copper−cobalt mixed oxides. The lower binding energy peak at 528.66 eV corresponds to oxygen species in the copper cobaltite spinel phase. The peak at 530.91 eV indicates the presence of O-H adsorbed on the surface of the sample.

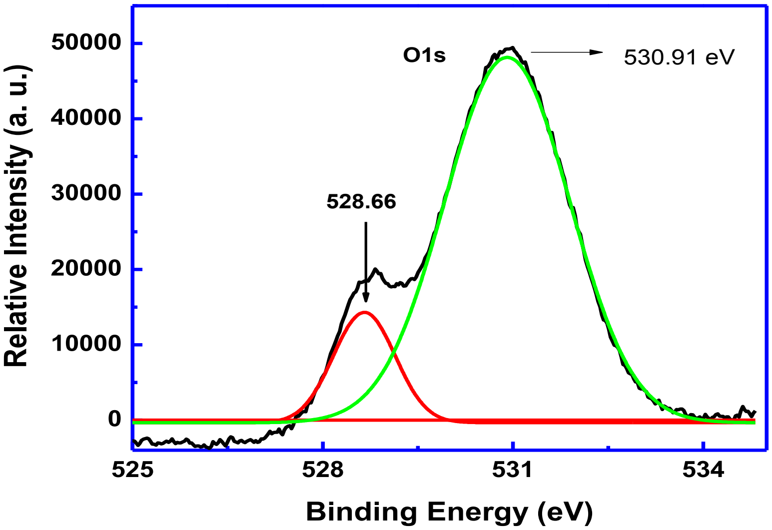

Fig. 5 O1s level spectrum of copper cobaltite film

3.3 Electrical properties of copper cobalt oxide thin films

The temperature dependence of electrical conductivity of the films was studied by two probe set up. Cobaltites of the formula Co_3O_4 adopt a normal spinel crystal structure, which can be envisioned as a fcc packing of oxygen anions with Co (III) filling half the octahedral interstitial sites, and Co (II) filling one-eighth of the tetrahedral sites. The substitution of Co ions by foreign divalent transition metals is known to promote an inhomogeneous distribution of cations and produce a partially inverted spinel structure with foreign and cobalt ions occupying both octahedral and tetrahedral sites, leaving oxygen vacancies. These oxygen vacancies behave as electron donors. Fig .6 shows the variation of resistivity with temperature. The room temperature resistance of the optimized film was found to be 51.39 kΩ. Resistivity decreases with increase in temperature indicating the semiconducting nature of the films.

Thickness has a profound effect in electrical properties. Fuchs and Sondheimer theory suggests that conductivity is increased with increase in film thickness due to the factor of mean free path. In thick films, the mean free path is long and thus collisions are reduced thus enhancing the conductivity. The film deposited at 250 °C has the maximum thickness of 1.69 µm and thus it has the least value of resistivity than the film deposited at 300°C and 350°C whose thicknesses are 1.14 and 1.05 µm respectively. In copper cobaltite, the cobalt ions are present in two different oxidation states Co^{2+} and Co^{3+}. The conduction mechanisms may be due to polaron hopping. In this polaron conduction mechanism, mobility is small because of the relatively deep potential well in which the localized carrier sits. However, conductivity in small polaron materials is often very good so the carrier densities can be high to offset the lower mobility [21]. In the present study, film deposited at 250 ^{0}C has higher conductivity and therefore polaron hoping is predominant that modifies spin states of the cations. For the region in which the electrical conductivity increases with increase of temperature, the well known dependence of semiconductor electrical conductivity on temperature is considered. Activation energy is the minimum amount of energy that is required to activate atoms or molecules to a condition in which they can undergo chemical transformation or physical transport. From the constructed Arrhenius plot the activation energy of each thin film sample has been evaluated. It is evident that the activation energy increases with decreasing film thickness. The activation energy of copper cobaltite films are found to be in the range of 0.19 - 0.33 eV. The film deposited at 250 °C has the maximum thickness of 1.69 µm and therefore it has the least value of activation energy of 0.19 eV. The film deposited at 300 °C has the activation energy of 0.28 eV. The film deposited at 350 ^{0}C has the maximum activation energy of 0.33 eV. Decrease in crystallinity of this film is already confirmed through the XRD analysis. Due to disorder in the lattice, charge carriers are scattered in all directions and therefore requires more energy to hop into the conduction band.

4. Conclusion

Spray pyrolysis deposition of copper cobalt oxide thin films have been prepared at three different deposition temperatures viz. 250, 300 and 350 °C from the salts of copper acetate and cobalt acetate dissolved in 50% ethanol and 50% distilled water. From the X- ray diffractograms of copper cobalt oxide films, it was clear that the film was crystalline only at the deposition temperature of 300 ºC and the obtained peaks matched well with the spinel type cobalt enriched phase $(Cu_{0.3}Co_{0.7})\ Co_2O_4$. XPS analysis revealed peaks corresponding to Cu 2p, Co 2p, O 1s. The main peak of Cu $2p_{1/2}$ is located at a binding energy that is almost 20 eV higher than that Cu $2p_{3/2}$ main peak which is the characteristic for the presence of Cu^{2+} as in CuO. The cobalt core level spectrum exhibited two major peaks with binding energy values of 776.11 and 791.5 eV corresponding to Co $2p_{3/2}$ and Co $2p_{1/2}$ doublet core level peaks. Hence the occurrence of both low spin Co^{3+} ions in the octahedral sites and high spin Co^{2+} ions in the tetrahedral oxygen environment was pinpointed. The O 1s spectrum exhibited a strong peak with a shoulder at the high binding energy side is a typical feature of copper-cobalt mixed oxides. Thickness was found to have a profound effect in the electrical properties. The film deposited at 250 °C had the maximum thickness of 1.69 µm had the maximum conductivity due to the factor of mean free path. In copper cobaltite, the cobalt ions are present in two different oxidation states Co^{2+} and Co^{3+} and so the conduction mechanism was ascribed to polaron hopping.

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