Simple Chemical route to Prepared Nanostructured cobalt oxide (Co_3O_4) thin film for semiconductor applications

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Abstract:
At a room temperature Cobalt oxide (Co_3O_4) thin film prepared by simple chemical technique i.e. (SILLAR technique) on the glass substrate, by an aqueous alkaline cobalt chloride source ($CoCl_2$:$6H_2O$) and double distilled water. The as-prepared thin film had observed brown in colour, with thickness is arond 250-270 nm. Further (Co_3O_4) thin film annealed at 200 ^oC up to 2 hour gradualy its colours changed from brown to black. The annealed Co_3O_4 thin film were subjected to structural characterization i.e. XRD diffraction which declared amorphous nature of metal oxide. Electrical characterization were carried by two probe electrical (dc) resistivity set up showed semiconductor behaviors, furthermore optical absorbance & energy band gap of these films were investigated by UV-spectroscopy which are helpful for nanostructure semiconductor electronic applications.

Keywords: Cobalt Oxide, Electrical, SILLAR, Optical, Thin films etc.

1. INTRODUCTION

When we go through the periodic table lots of metal oxide is there found out of that some of the metals shows electric, optical, semiconductor and magnetic property, transition metal like cobalt, manganese or ruthenium had fascinating magnetic properties. Among those transition metal oxides, the cobalt oxide is one of the very good versatile ceramic materials like Cobalt Oxide is a p-type with anti-ferromagnetic oxide semiconductor materials with that lagest Curie temperature, Tc=1396 ^oK. This oxide is chemically identified with its chemical formula Co_3O_4, but in compare with non-stoichiometric. The Cobalt had poor affinity for oxygen than iron but good than nickel.[1] Cobalt oxide had three polymorphs; 1. Monoxide or cobaltous oxide (CoO), 2. Cobaltic oxide (Co_2O_3) and 3. Cobaltosic oxide or cobalt cobaltite (Co_3O_4). Out of that Cobaltous oxide (CoO) is the last product formed, whenever the cobalt compound or other oxides are annealed to sufficiently high temperature as around 1173 ^oK. The pure CoO form is crucial to obtain, its readily takes up oxygen from surrounding even at room temperature to and achieved to a higher oxide state i.e. Cobaltic oxide (Co_2O_3) could be formed, when cobalt compounds are annealed at a low temperature in the presence of inert atmosphere. Cobalt forms two stable oxides state CoO and Co_3O_4.[2,7,8] At room temperatures the Co_3O_4 is a stable normal spinel structure occurs due to their structure and semiconductive behiever of Co_3O_4 its strongly exhibit the well- known applications of cobalt oxide Co_3O_4, also in to the glass industry for colour glasses. The catalytic properties due to reduction of activation energies for chemisorption's of gas molecules and are very useful to gas sensor applications.[3,11] It is also used as on electrochromic material and electrochemical anode in supercapacitors as well as battery. There lot of reports are found in the literature for the preparation of cobalt oxide thin films from various methods such as physical and chemical all individual methods had its own advantages according to its morphology, conductivity and optical property etc.[1-5,9] Through an our environmental condition, precursor solution and reactant, the main target to fabrication and investigation of deposit cobalt oxide Co_3O_4 thin films, so that we had go through SILLAR i.e. Successive Ionic Layer by Layer Adsorptions Reaction technique. This chemical method is a simple and convenient method for the large area deposition at room temperature. In

this paper, we discussed simple chemical approach to fabrication of cobalt oxide Co_3O_4 thin films on to the glass substrates and investigation for structural, optical and electrical properties.[4,5,10]

2. EXPERIMENTAL DETAILS

The Co_3O_4 thin films deposition had carried out on to glass micro-slides of the size 75×25 mm long to width and1 mm thick glass slide. The micro-slides colined by chromic acid, washed with detergent, after that treated with acetone and ultrasonically cleaned with double distilled water. The room temperature deposition took place and to form Cobalt oxide Co_3O_4 films by the cation precursor solution 60 mL, 0.4M $CoCl_2$:$6H_2O$ added in to 25% ammonia solution by drop-wise to maintain pH of the solution up to12 and the anion solution double distilled water mixed with few drops of H_2O_2. This cationic and anionic precursor solutions beakers placed alternately placed in between them, Cleaned micro-slide were dipped in to the cationic solution of cobalt chloride up to 30 s, where has cobalt ions are adsorbed on the surface of micro-slide then by rinsing double distilled we removed weekly bound excess cobalt ions present on surface of micro-slide. Then micro-slide deeped in to anionic solution i.e. double distilled water with H_2O_2 solution up to 20 s where, the pre-adsorbed cobalt ions reacted with oxygen ions on the micro-slide and to formation cobalt oxide Co_3O_4 thin film. To controlled thickness of thin films with the help the of cationic solution and deposition cycles. Thickness of as prepared Co_3O_4 thin film measured by weight difference method, its were heated in furnace up 200 ^oC. then it subjected characterizatin like optical absorption, electrical resistivity measurements, structural and morphological studies.

3. RESULT AND DISCUSSION

3.1 Growth mechanism

In the SILLA technique, a solution were separately placed cationic and anionic between them rinsing water solution because of every deeped micro-slide it prevents ion exchanged solutions and to from homogenous precipitation. The Co_3O_4 thin film deposition process involves the adsorption of cations at the time interacts with anions resulted into occurred nucleation which grows simultaneously with number of cycles. If the concentration of the cobalt chloride solution low below 0.4 M, the film formation rate become slow and when the concentration was high greater 0.4 M, it precipitate done very quickly. Its oxidation of Co^{2+} has to take place in proper rate to form heterogeneous nucleation of cobalt oxide. This whole prosses carried out at room temperature, then concentration of the cobalt chloride solution had to be simillarly lowered to got Co_3O_4 thin films, then its were annealed up to 200 ^oC for 2 hour. The thickness of Co_3O_4 Cobalt oxide films were found 200nm by the help of weight difference method.

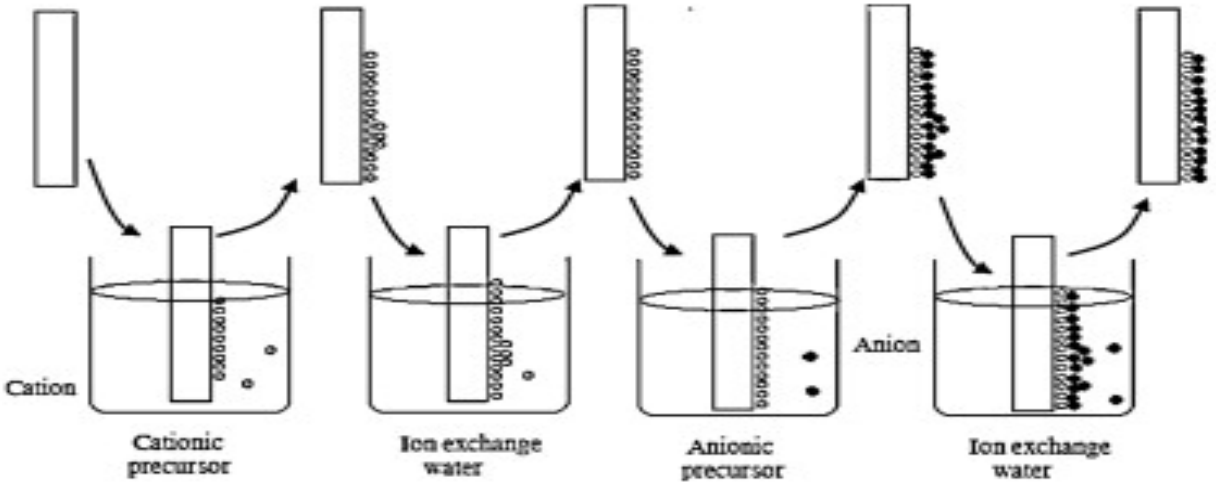

Fig3.1 Shows growth mechanism for formation of Co_3O_4 thin film by SILLAR.

3.2-Structural Study

The structure of annealed Co_3O_4 thin films were studied by X-ray diffraction technique. Fig3.2 shows XRD spectra of annealed Co_3O_4. The graph plotted intensity verses angle 2θ degrees, in that are no one typical peak observed soIt is clear that after annealing distinct diffraction peak was not observed which probably

means that the film consisted of hydrous Co_3O_4 colloidal particles with amorphous in nature XRD hump is cleared that Co_3O_4 thin films amorphous metal structure which is powerful for semiconductoror and nano-electronic application.

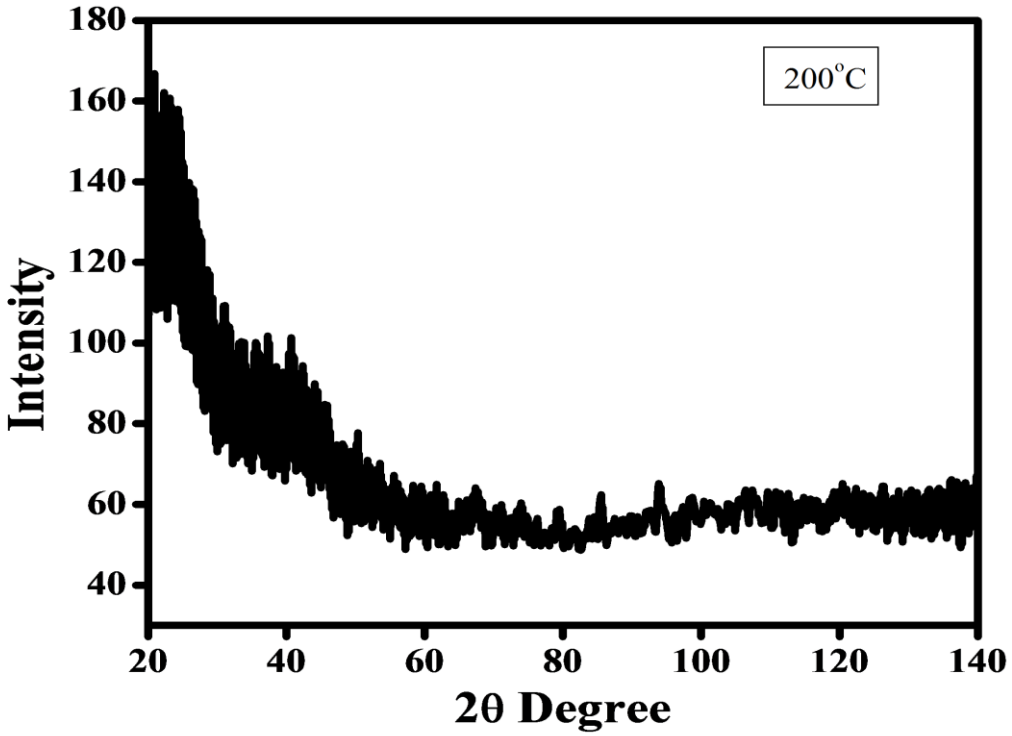

Fig3.2 shows XRD spectra of Co_3O_4 thin film.

3.3 Optical studies

By help of uv-spectrophotometer in the range 300-900 nm we had varied optical absorbance of Co_3O_4 thin film in that fig. 3.3(a) graph plot between absorbance to wavelength, Observed spectra shows that the Co_3O_4 film has vere good absorbance in the near visible region, the range of wavelength 650-750nm shows hump which is sign of photocatyletic activity of the materials. Theoretically optical absorption gives the relationship between the absorption coefficient (α) and the photon energy (hν) to allowed the direct transition.

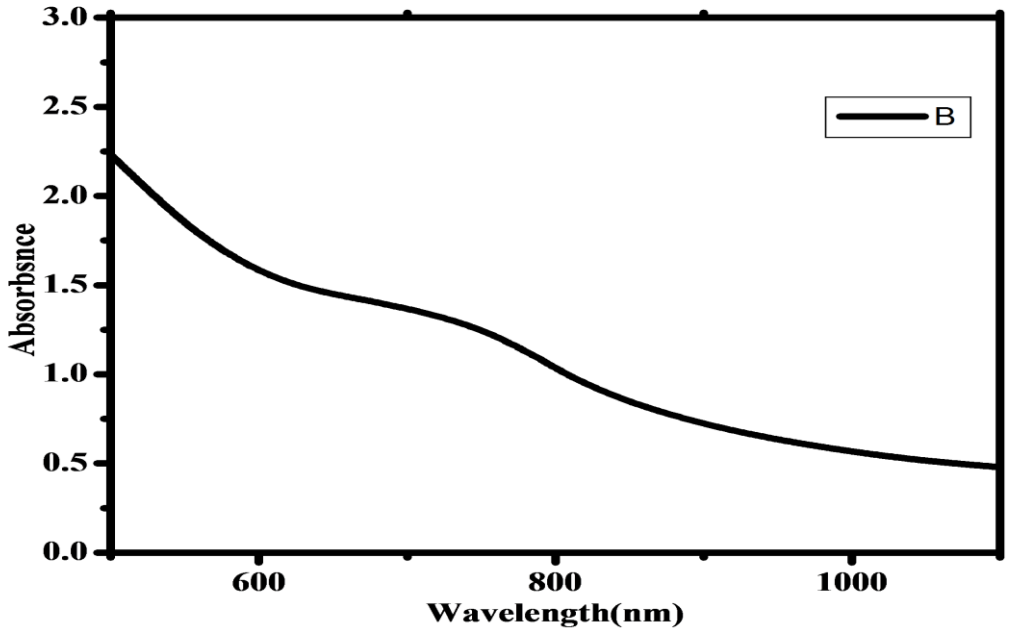

Fig. 3.3(a) The optical absorbance of Co_3O_4 thin film.

From Fig. 3.3(b) we had plot band gap of Co_3O_4 thin film in which we plots the $(\alpha h\nu)^2$ versus $h\nu$ for Co_3O_4 films. With the help of this graph we had estimated band gap energy for Co_3O_4 thin film had foun 1.6 eV which had larger band gap it confirmed that its exhibit's semiconductor behiever this is consistently in the band gap energy of cobalt oxide films reported earlier.[6,9]

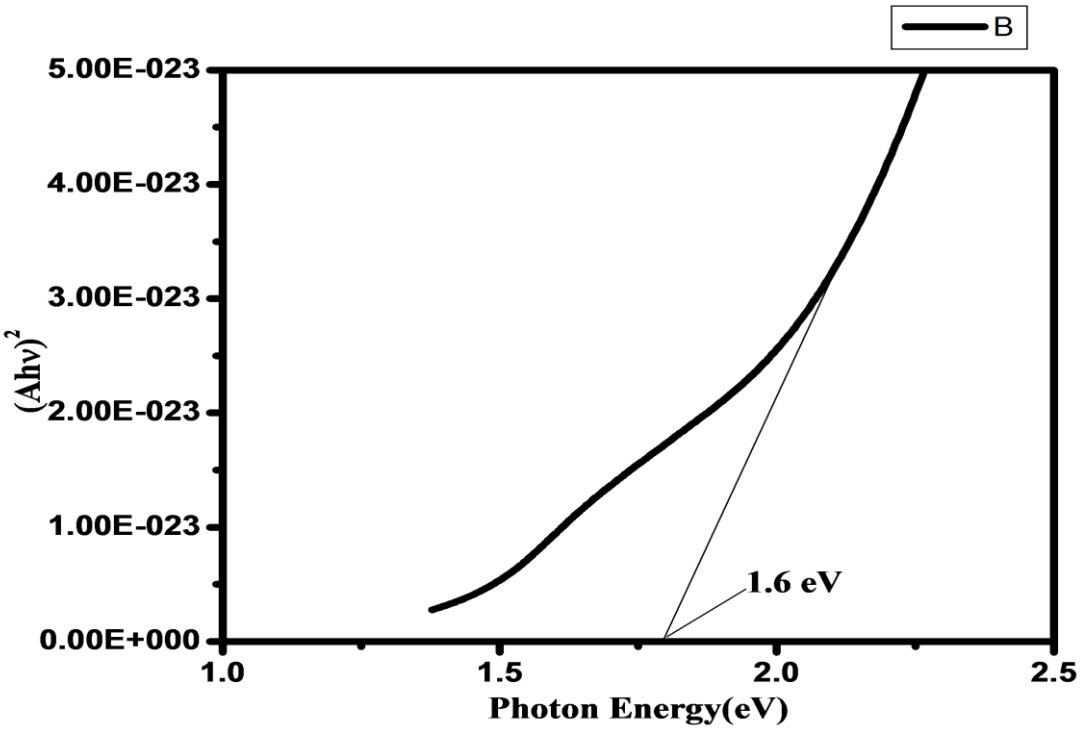

Fig.3.3(b) Band-gap energy of Co_3O_4thin films

3.4 Electrical resistivity studies

The electrical resistivity of Co_3O_4 films was measured by two probe home made resistivity set-up in the temperature range of 150^0- 600^0C Its cleared that Co_3O_4 films exhibits ohamic nature. In the fig 3.4 the graph were plot between electrical resistivity (log ϱ) with temperature (1000/T) in reversible measurements there has no significant difference occurred. It shows the semiconductor behaviour with two different transport mechanisms, the film showed similar trend with no significant change in room temperature resistivity magnitude (104 V cm). where the activation energy found 0.0364 eV , by calculated from the slopes of graphs represents the location of trap levels below the conduction band.

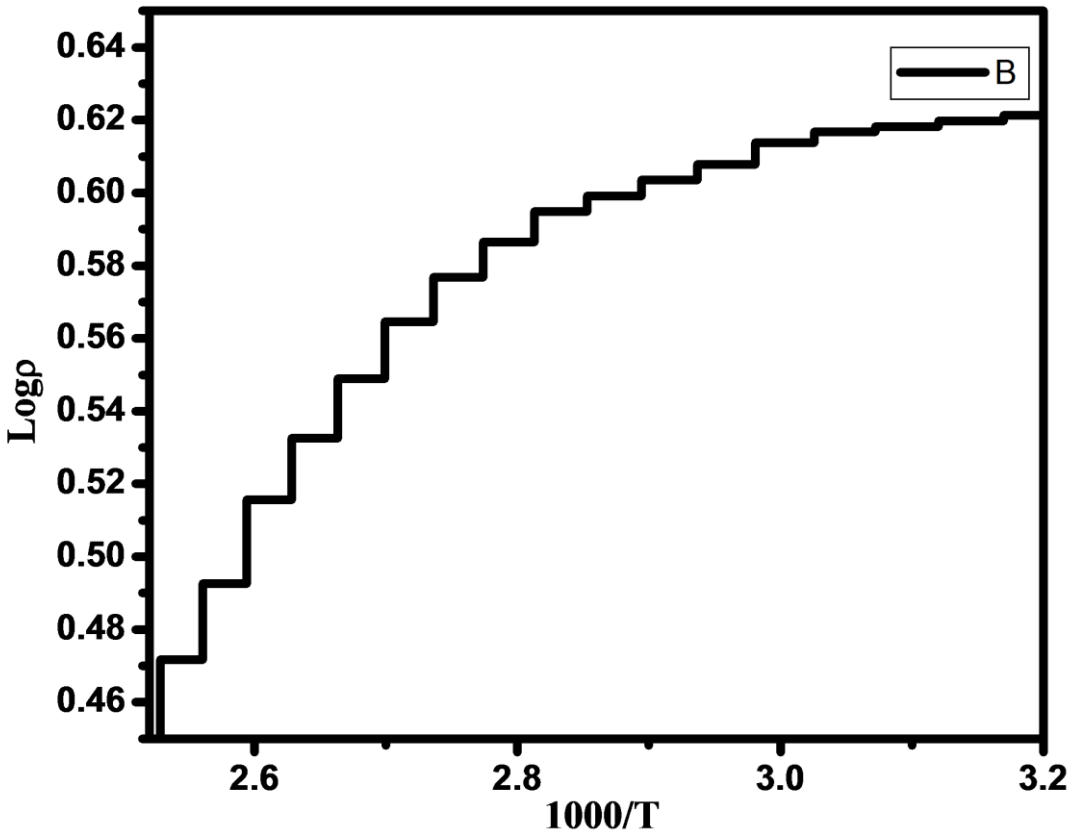

Fig 3.4.The logarithmic electrical resistivity(logρ) variation with reciprocal of temperature(1/t) for cobalt oxide thin films

3.5 I-V characteristics study

One of characteristics is I-V which were shows basic idea about semiconductor nature of materials from Fig.3.5 shows the I-V characteristics ploted current in micro ammeters to Voltage in volts graph s from the graph its cleared that Co_3O_4 films exhibets ohmic nature, with the current from 0.4×10^{-10} µA to 2.1×10^{-10}µA Therefore the conductivity lies in between semiconductor to insulator region.

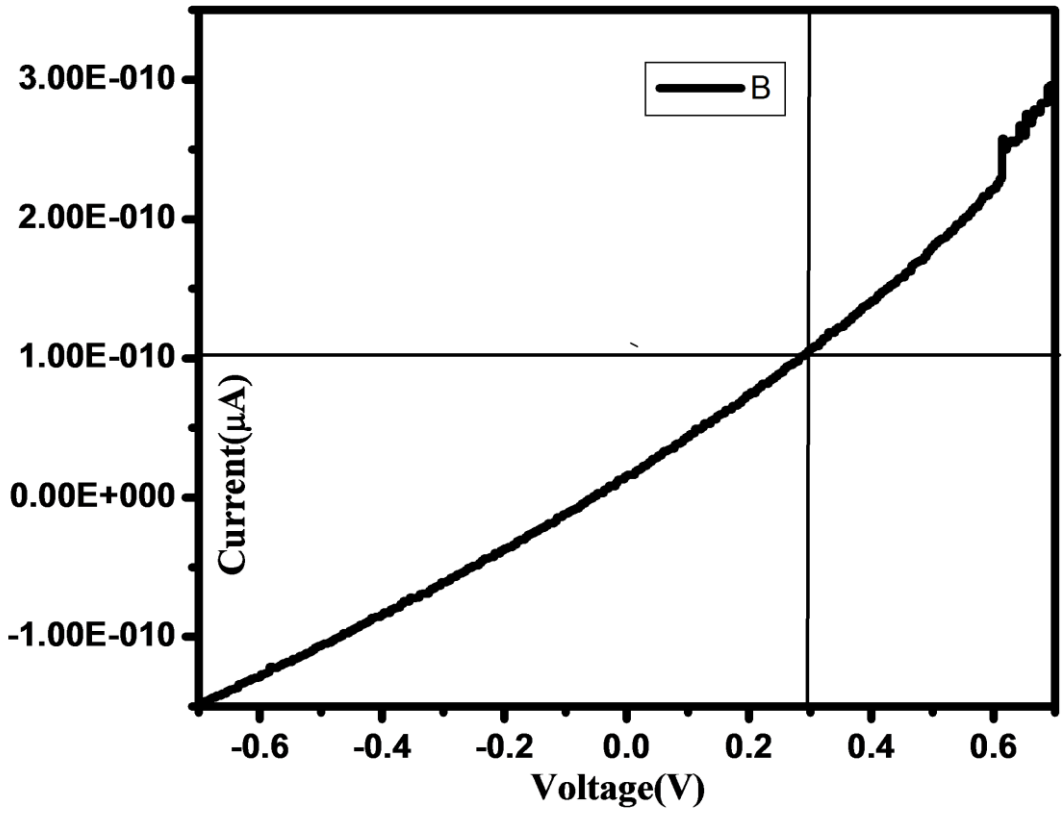

Fig. 3.5 representation of I-V characteristics of Cobalt oxide thin Film.

4. CONCLUSION

The Co_3O_4 thin films were successfully deposited on glass by simple & economic SILAR technique. The thickness had found to be 200 nm which is investigated by Weight difference method. Amorphous nature found by XRD pattern of the films. Optical study shows two optical transitions occurred with band gap energy is 1.6 eV. Electrical resistivity shows semiconductor nature of the films with decreased in activation energy. Ohmic nature was observed of the films by I-V study

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