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Comparative study on CuCrO2 bulk and thin film

Abstract-

Copper based delafossites $CuMO_2$ where (M = Al, Cr, Y etc.) has drawn more attention after reporting of transparent conducting oxide (TCO) $CuAlO_2$. CuCrO2 is suitable candidate for optoelectronic devices and as a channel layer in solar cells. Highly stoichiometric polycrystalline $CuCrO_2$ powder was synthesised by sol-gel method and delafossite structure were grown on quartz substrate by solution deposition method. Structural properties were studied of bulk material with X-ray Diffraction. Hall-effect data confirms p-type semiconductor nature of $CuCrO_2$ pallet. Nanocyrstalline thin films exhibits 60-70% transmittance in visible range with direct bandgap around 3.2eV which is in very good agreement with the literature. AFM results shows comparatively smooth surface of the films and indicate an increase in the grain size with increasing annealing temperature.

Introduction:-

The transparent conducting oxides (TCOs) and semiconducting oxides are of particular interest, as they can be transparent yet show metallic-like conductivities.[7] TCOs are widely used in solar cells[16], photodetectors[15], photocatalytic H2 production devices[17], gas sensors[18] and other optoelectronic devices. In photovoltaic and optoelectronic industries more studies were done on n-type TCOs like ZnO, TiO_2 and SnO_2, but there are a fewer reports on p-type TCOs.[3] After the discovery of $CuAlO_2$ by Kawazoe et al in 1997, having delafossite structure with intrinsic p-type semiconductor nature driven more attention to delafossite structures.[5] $CuCrO_2$ is intrinsic p-type semiconductor with delafossite structure along with remarkable optical and electrical properties.[7] There have been many reports on synthesis of CuCrO2 nanoparticles and thin films in last two decades with different methods like sol gel method[9] hydrothermal method[4], Facile and controllable reduction of nanoparitle[14] thin films of CuCrO2 and Mg:$CuCrO_2$ were prepare by PLD technique[2], Magnetron sputtering[1,6] and Spin coating[8,10].

Delafossite compounds belong to a family of ternary oxides with the general formula ABO_2.The structure can be visualized as consisting of two alternate layers: a planar layer of A cation in a triangular pattern and a layer of edge-sharing BO6 octahedra flattened with respect to the c-axis. Depending on the orientation of each layer in stacking, two crystalline forms can exist. By stacking the double layers with alternate A layers oriented 180° relative to each other, the hexagonal 2H type is formed which has P63/mmc space group symmetry. If the double layers are stacked with the A layers oriented in the same direction relative to one another but offset from each other in a three layer sequence, the rhombohedral 3R type is formed that has the space group symmetry of R-3m.[11] In copper based delafossite $CuMO_2$, where M could be post transition metal (Al, Ga, In) or transition metal (Fe, Cr, Cu, Y).

Experimental procedure:-

Copper acetate monohydrate (Cu $(CH3COO)_2 \cdot H2O$) and chromium acetate ($C_6H_9CrO_6$) were dissolved in stoichiometric amount in distilled water, stirred for 2 hours. Citric acid was added as a reduction agent, pH of the solution was maintained to 5 and again stirred for 1 hour than aged for 24 hours.

1. Polycrystalline powder:-

Polycrystalline powder was obtained by sol-gel process by heating the homogeneous solution for several hours on a hot plate at 100°C. Heated solution war first in a green flax form, flaxes were well hand-grinded to make powder, powder was first fired at 500°C for 4hrs in muffle furnace again following the grinding process, and Powder was pressed in hydraulic press at 8000lbs to make a

pallet. A pallet was calcined at 600˚C for 6hrs, the whole process was repeated and pallet was sintered at 750˚C for 8 hrs.

2. Thin films:

Delafossite-CuCrO2 thin films were deposited on quartz substrates via spin-coating method by sol-gel route following the above solution. The solution was spin-coated on quartz plates at 2500 rpm for 30 seconds each, and dried at 150˚C for 10 mins on hot plate to remove water content, organic solvent and unwanted salts. The entire process was repeated for 15 times in order to get desired thickness of the film. Films were then annealed in pre-heated furnace at 650˚C, 700˚C, 750˚C respectively for 1 hour.

3. Characterisation Techniques:

Structural properties of bulk (powder) was characterised by X-ray Diffraction (XRD, PANalytical Expert Pro). Hall-effect data was taken by Hall Effect measurements (HMS-3000, Ecopia Corp.) using four probe method. Optical properties were characterised by UV- spectroscopy (SHIMDZU). Surface topography of films were performed by tapping mode atomic force microscopy (EasyScan 2, Nanosurf).

Result and Discussion:-

1. XRD Analysis:-

Figure1 shows X-ray diffraction spectra of metastable 2H-CuCrO2 polycrystalline powder sintered at 750˚C for 8 hrs. All diffraction peaks are accurately indexed in the XRD spectra. All the peaks are corresponding to single delafossite structure. Lattice parameters were evaluated from XRD and the values were found to be $a=b=$ 2.975 Å and $C=$ 11.400Å, which are matched with standard crystallographic data. (space group: P63/mmc; JCPDS 01-089-0540). Polysynthetic twins are appeared at (1 0 1), (1 0 2) and (0 0 8) in the XRD spectra of fig. 1 are in agreement with previously reported data (Grozescu, 2012). Average crystallite sizes were calculated using Scherrer formula[12]:-

$$D = \frac{\kappa\lambda}{\beta\cos\theta} \quad \text{---(1)}$$

Here D is crystallite size between 43.44nm to 18.96, k is Schrrrers' constant, λ = 1.54059 A ° (Cu- Ka) and **β** is FWHM (full width half maxima).

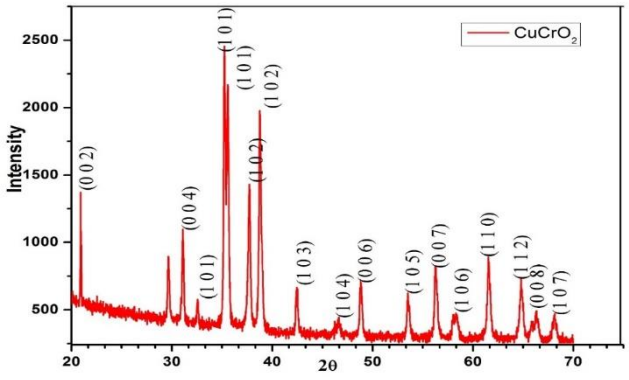

Figure 1 XRD Spectra of 2H - CuCrO2 bulk

2. Hall- effect Measurement :-

Hall-Effect measurements were done using the Van der Pauw geometry at room temperature. For the CuCrO2 pallet annealed at 750ºC, Hall coefficient R_H = 4.13*10^7 cm^2/C was found to be positive, suggesting the hole induced, *p*-type transport. Carrier concentration of a pallet is 1.51*10^{12} /cm^3 and conductivity is σ = 1.898*10^{-3} S/cm, which is comparatively batter than other reports published. These results suggest that Delafossites represent a unique type of ABO2 oxide material which can exhibit a range of electrical properties from insulating to metallic conduction–depending on the composition.[7]

3. Optical Property of $CuCrO_2$ Films :-

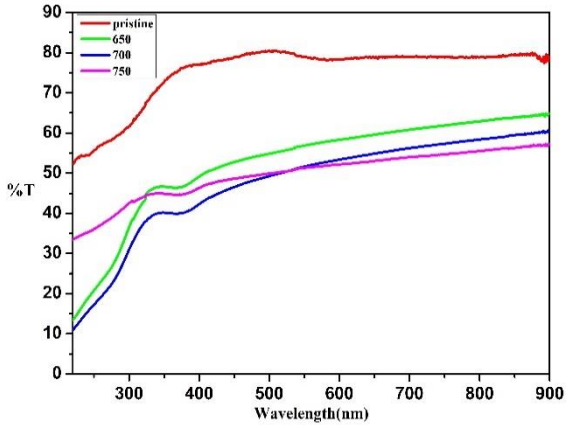

Figure 2Transmittance Spectra

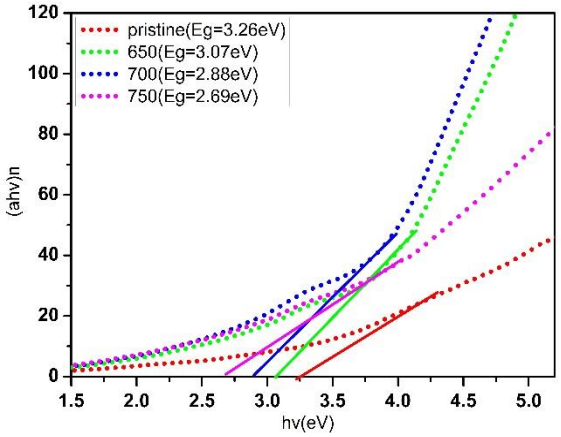

Figure 3 Bandgap Graph

Figure.2 and Figure.3 shows transmittance spectra and direct bandgap graph of post- annealed films, respectively. As films were annealed at higher temperature, transmittance decreases in ultra-violate and visible region from around 80% to 60%, as well as direct optical bandgap of the films from 3.4eV to 2.8eV. The observed absorption edge occurred at approximately 350 nm and the optical transmittance is in the range of 35% to 75%.

4. Surface Topography of Films:-

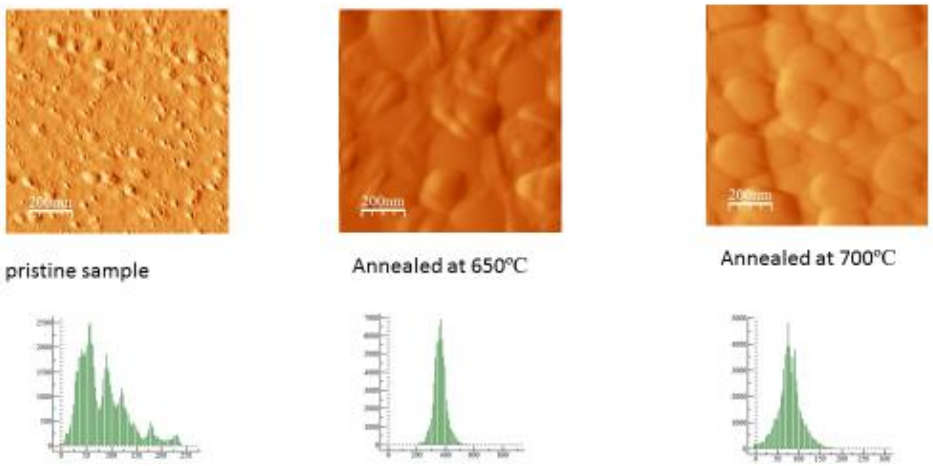

Figure 4 Surface topography and roughness analysis of thin films

Morphological study of thin films was done by using Atomic Force Microscopy (AFM). The AFM data of fig. 4 shows smooth surface and nano-crystalline morphology of pristine and annealed films at different temperature. As the annealing temperature increases grain-size of the films are improved. From the histograms corresponding to the each AFM image gives grain size distributions. The RMS Roughness were calculated from the AFM images and were found to decrease with increasing temperature. It shows increment in annealing temperature results into smoother surface of CuCrO2 thin films. Result shows homogeneous and mono-dispersed grain distribution in the 700˚C annealed film, with average grain size of 16.802nm estimated from the AFM data.

Conclusion:-

P-type $CuCrO_2$ polycrystalline powder was successfully synthesised by sol-gel method. CuCrO2 thin films were effectively deposited on Quartz substrates, and annealed in pre-heated muffle furnace. Delaffosite structure with hexagonal symmetry is confirmed with X-ray diffraction data which is in very good agreement with standard crystallographic data on bulk CuCrO2. Hall- data of pallet exhibits p-type semiconductor nature of bulk. Conductivity of pallet is found to be better than the literature reports. Optical properties were studied by UV-Vis. Spectroscopy. The observed transmittance of T= 60% to 80% is suitable for TCO applications.

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