MOCVD OF THIN FILMS OF TRANSPARENT, P-TYPE CONDUCTING $CuCrO_2$ WITH DELAFOSSITE STRUCTURE, USING ACETYLACETONATES OF COPPER AND CHROMIUM AS PRECURSORS

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Most of the useful transparent and conducting oxides, (TCOs), are degenerate, extrinsic, n-type semiconductors. This monopolarity of electrical conduction has restricted their application to only passive components. Design of active optoelectronic devices using these materials entails the development of p-type TCOs with properties comparable to their n-type counterparts. Recently, thin films of transparent $CuMO_2$ (where M is a trivalent cation) type of compounds with delafossite structure have been reported to show p-type conductivity (1) albeit both the transmittance and conductivity of such materials are quite low compared to n-type TCOs such as indium tin oxide (ITO). The most promising one, to date, is the on-axis rf sputtered $CuCrO_2$:Mg thin films (2), with conductivity 220 S cm-1 and transmittance about 30-40 % in the visible range, in films of thickness 270 nm on fused quartz substrates.

In this work, $CuCrO_2$ thin films have been grown on glass and sapphire (11-20) substrates by low-pressure metalorganic chemical vapor deposition (LP-MOCVD) using copper and chromium acetylacetonates, [$Cu(acac)_2$ and $Cr(acac)_3$] as precursors. The X-ray diffraction and selected area electron diffraction patterns confirm that the as deposited films are monophasic $CuCrO_2$ and, irrespective of the substrate type, are polycrystalline with no preferred orientation. The ratio of the copper to chromium in the sample, estimated by energy dispersive X-ray analysis is 1.2:1. Considering the experimental errors in the determination, the slight excess of copper in the sample may be due to the difference in the molar vaporization rates of the $Cu(acac)_2$ and $Cr(acac)_3$ precursors. The Cu $2p_{3/2}$ peak in the X-ray photoelectron spectrum of the film on glass could be resolved into two different peaks of almost equal intensity, corresponding to Cu^+ (932.8 eV) and Cu^{2+} (933.4 eV), respectively. The existence of both Cu^+ and Cu^{2+} in the film may be attributed to the presence of excess oxygen in the $CuCrO_2$ lattice.

The room temperature conductivity, Hall co-efficient, Hall mobility and carrier concentration of the films on glass substrates were estimated to be 0.076 cm^3 C^{-1}, 0.8-3.76 S cm^{-1}, 11.16 cm^2 V^{-1} s^{-1}, and 4.75x10^{17} cm^{-3}, respectively. The Seebeck co-efficient, calculated from the voltage induced by a temperature gradient maintained across the length of the films, was found to be 92.97μV/K. Positive signs of the Hall and the Seebeck coefficients confirmed that the films are p-type conducting. The electrical conduction is thermally activated (Fig.1), with the activation energy estimated to be 74.8 meV and 49.5 meV, for the films on sapphire and glass, respectively. At lower temperatures, ln(conductivity) shows a linear dependence on $1/T^4$, indicating that the conduction in this temperature range is due to variable range polaron hopping.

In the visible range, the film of thickness 390 nm on glass shows a transmittance of 40-50% (Fig.2). The transmittance of the films on sapphire is still higher. The optical bandgaps were estimated from the plots of $(\alpha h\nu)^n$ versus hν, (Fig.3), where α is the absorption coefficient and hν is the photon energy. The direct bandgaps calculated assuming n=2, for the films on glass and sapphire, are 3.13 eV and 3.08 eV respectively.

The nature of electrical conduction in the Cu-delafossites is poorly understood. Substitution of divalent cations for Cr^{3+} has been reported to enhance the conductivity of $CuCrO_2$ (2,3). Further studies are being carried out to understand the p-type conduction in these materials. Success in using MOCVD to obtain TCO thin films of $CuCrO_2$ indicates the possibility of large-scale production of transparent devices.

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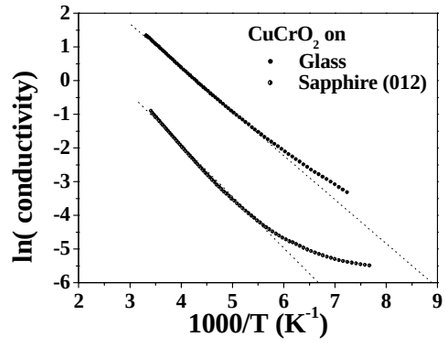

Fig. 1. Arrhenius plots of dc electrical conductivity of the as-deposited $CuCrO_2$ films.

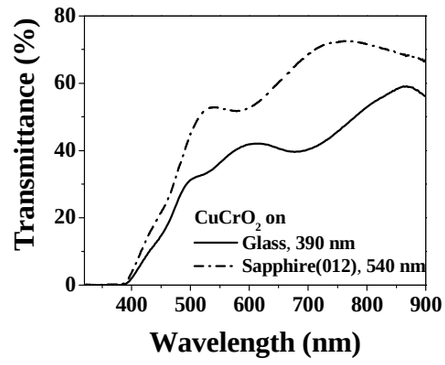

Fig. 2. Optical transmission spectrum of the as-deposited $CuCrO_2$ films.

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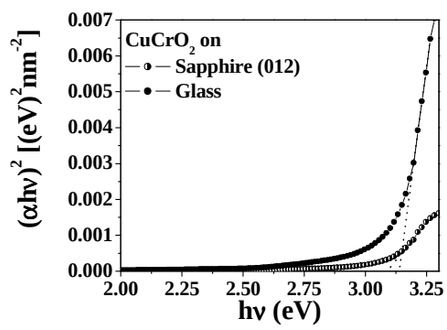

Fig. 3. Plots of $(\alpha h\nu)^2$ versus hν for the as-deposited $CuCrO_2$ films.