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Mixed phase delafossite structured p type $CuFeO_2$/CuO thin film on FTO coated glass and its Schottky diode characteristics

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ABSTRACT

Delafossite structures are of significant importance in the recent context of development of structured and engineered materials because of their natural super lattice structure. The delafossite structured $CuFeO_2$ mixed with crystalline CuO phase has been prepared by the simple chemical method of sol-gel technique on fluorine doped tin oxide (FTO) coated glass substrate. The mixed phase of delafossite structured $CuFeO_2$ with crystalline CuO was appeared on annealing the film at 723 K. The prepared film was characterized with X-ray diffraction measurements, atomic force microscopy, UV–Vis-NIR spectrophotometry and electrical I–V measurements. The optical energy band gap of 2.63 eV was obtained from the UV–Vis-NIR spectrophotometric measurements. On electrical characterization of the film, the (I–V) measurements show a Schottky diode like characteristics.

1. Introduction

The delafossite type crystals are of profound scientific interest because of their p-type conductivity and characteristic structure (space group $R\bar{3}m$) with the general formula ABO_2, where A cations are linearly coordinated with two oxygen ions and the B cations are situated in edge-sharing BO_6 octahedra [1,2]. The layer formed by the A cations is a conducting layer, while BO_6 octahedra forms a nonconductive layer. The special structure of alternative conducting and non-conducting layers formed in delafossites, leads it to have a natural super lattice structure. In such superlattice structure the confinement of carriers in the conducting layer enhances the quantum phenomena giving rise to outstanding physical properties such as field emission, wide optical energy band gap and thermoelectric properties [3,4]. In the recent context of rapid development of materials science there is a growing interest in exploring suitable p-type semiconductor materials, because most of the outstanding inorganic metal oxide semiconductors such as ZnO [5,6], TiO_2 [7], SnO_2 [8], InO [9] and CdO [10,11] are n-type in nature. In the last decade considerable efforts have been devoted to the synthesis of delafossite structured materials such as $CuAlO_2$ [12,13], $CuFeO_2$ [14,15] and $CuBO_2$ [16], however $CuFeO_2$ must receive exceptional interest because of its profound antiferromagnetic properties and multiferroicity [17]. $CuFeO_2$ is a p-type delafossite compound that has relatively higher electrical conductivity compared with other delafossites. Its structure is formed by 2-D layers of the Cu^+ layer and the FeO_6 octahedral-shaped layers which are alternative stacking along with the *c*-axis. Different methods like high temperature solid state reaction [18], hydrothermal process [19] and electrochemical process [20] have been employed to prepare $CuFeO_2$ by different groups. In this communication we have reported the synthesis process of $CuFeO_2$ thin film on fluorine doped tin oxide (FTO) coated glass substrate by a simple chemical method of sol-gel technique. Fluorine doped tin oxide (FTO) has attracted considerable interest as a transparent electrode in optoelectronic devices due to its good conductivity and optical transparency combined with low cost. FTO is commonly used in many optoelectronic devices such as electrodes in various types of solar cells [21–23]. In this work it is shown that, $CuFeO_2$ film forms a heterojunction with FTO film. The metal oxide heterojunction and its bang gap engineering [24,25] are of significant interest to the researchers. Excellent diode characteristics of the prepared $CuFeO_2$ film deposited on FTO coated glass were explored on its I–V measurement. The presence of CuO with delafossite $CuFeO_2$ facilitates it to improve such electrical behavior by introducing defect states and forming a quasi-conduction band. This would make it more significant and functional in finding its applications in various challenges, such as development of solar cell technology,

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transparent electronics and optoelectronic devices due to its functional combination of optical transparency and electrical conductivity. Moreover these materials have been of great interest owing to wide band gap and stability with environment.

2. Experimental details

2.1. Film preparation

$CuFeO_2$ thin films were prepared on FTO coated glass substrate by simple dip coating method followed by post annealing. 0.2 M cupric acetate monohydrate [$Cu(CH_3COO)_2$, H_2O] and 0.2 M Iron (III) Chloride anhydrous [$FeCl_3$] were first dissolved in 50 ml deionised water and magnetically stirred for 1 h until the solution colour become dip brown. At this stage ethylenediamine was added drop wise to the solution and magnetically stirred for 30 min. Then the solution was used to prepare film by single dip coating method on FTO coated glass substrate. The deposited films were then annealed at 723 K in air for 10 h. The deep brown films thus obtained were used for further characterizations.

2.2. Characterization

The prepared film was characterized by X-ray diffraction (XRD) studies using X-ray diffractometer (Bruker, D-8 Advance) with the Cu Kα radiation of wavelength $\lambda = 1.5406$ Å to obtain crystalline phase information. Atomic force microscopic (AFM) measurements (Bruker, MultiMode-8) were done for its morphological investigations. The optical properties were studied through transmittance measurements by UV–Vis-NIR spectrophotometer (Perkin-Elmer Lambda 45 spectrophotometer). The electrical properties were studied by electrical conductivity (I–V) measurements using Agilent, 34972A digital source meter.

3. Results and discussions

3.1. Structural characterization

The crystal structure of the prepared sample was determined by studying the X-ray diffraction pattern shown in Fig. 1. The structural parameters of $CuFeO_2$ were defined assuming the hexagonal structure with space group $R\overline{3}m$. The calculated lattice constants a = 3.03 Å and c = 17.14 Å at room temperature matched well with the earlier report and JCPDS files [26]. Its structure is formed by 2-D layers of the Cu^+ and the FeO_6 octahedral-shaped layers which are alternative stacking along the c-axis. The Cu^+ cation is linearly bonded with two O^{2-} anions and forms a dumbbell shape [O–Cu–O] parallel to the crystallographic c-axis. The edge sharing of the [FeO_2] forms the FeO_6 octahedral.

The mixed phase formation of $CuFeO_2$ and CuO are observed in the X-ray diffraction pattern. The X-ray diffraction peaks occurred at 2θ = 35.7°40.9° and 55.7° for thin film are assigned to the reflection from $CuFeO_2$ (012), (104) (018) planes and the peaks occurred at 2θ = 33.1° 38.9° and 45.0° are assigned to the reflection from CuO (110), (111) and (400) Miller planes. The inter planner spacing (d_{hkl}) are 2.70 Å, 2.31 Å and 2.01 Å correspond to diffraction planes (110), (111) and (400) respectively. These peaks in the XRD pattern could be indexed with a monoclinic structure of CuO belonging to the space group C2/c. The AFM measurements were carried out in taping mode with single crystal silicon tip. The AFM image of the film is shown in Fig. 2, which shows a nearly uniform distribution of particles over the films. The average particle size is found to be 15 nm. This smaller particle size is due to the mixed phase of $CuFeO_2$ and CuO crystals. The coexistence of dissimilar crystallites induces strain and plays the role in formation of smaller grains.

3.2. Optical properties

In order to study the optical properties of $CuFeO_2$ the optical transmittance of the film was measured and it is shown in Fig. 3. $CuFeO_2$ film shows transmittance from 20% to 70% in the visible range. The transmittance of the $CuFeO_2$ film from 20% to 70% in the visible range is useful for allowing incident photon to reach the junction in designing photovoltaic devices. For transparent electronics this kind of transparent semiconductor materials, particularly metal oxides due to their high stability are of great significance in various applications. The value of the optical band gap can be calculated using the fundamental absorption, which corresponds to electron excitation from the valance band to conduction band.

The valence band in $CuFeO_2$ is formed by Cu 3d and O 2p hybridized orbitals, while the conduction band is predicted by theory to be composed primarily of Fe 3d and O 2p states [27].

As revealed from XRD, the samples are mixtures of $CuFeO_2$ and CuO phases. These physically mixed phases have different band gaps and electronic structures from each other. CuO itself is a p type semiconductor, where the valence band of CuO consists of Cu-3d orbital. The p type conductivity of CuO is considerably low because of the localization of the Cu-3d electron [28]. However in this mixed phase system the presence of CuO become significant in two way, primarily CuO itself behaves as p type semiconductor and secondly the energy levels of CuO plays the role as that of localized impurity states for $CuFeO_2$ leading towards high p type conductivity of $CuFeO_2$, as detailed in Section 3.3. These phase-separated impurities would induce localized in-gap defect states. Such localized gap states are sometimes undesirable for the transparent optoelectronic device applications, but it must find favourability in functionalizing the electrical behavior of semiconductors.

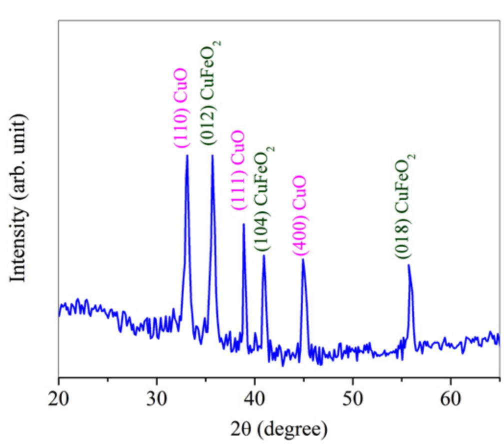

Fig. 1. X-ray diffraction pattern of $CuFeO_2$/CuO thin film.

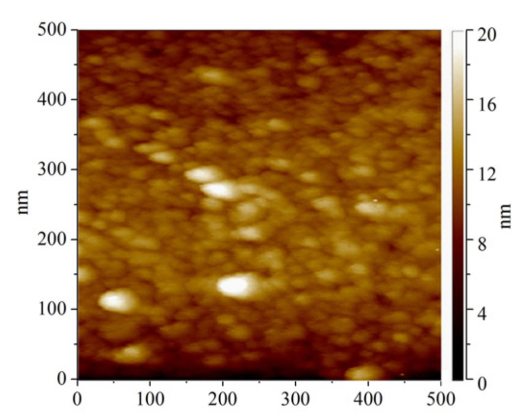

Fig. 2. AFM image of the $CuFeO_2$ thin film.