Journal of Alloys and Compounds 664 (2016) 682–689

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

# Conduction mechanism in mesoporous hematite thin films using low temperature electrical measurements and theoretical electronic band structure calculations

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ARTICLE INFO

*Article history:*
Received 10 September 2015
Received in revised form
23 December 2015
Accepted 2 January 2016
Available online 5 January 2016

*Keywords:*
Thin film
Mesoporous
Photocurrent
Magnetoresistivity
First principle
Conduction mechanism

ABSTRACT

Low temperature four-probe electrical resistivity and magnetoresistivity measurements in mesoporous hematite thin films imply that the operative conduction mechanism involves impurity band with intrinsic donor defects. The surface morphology revealed the porous nanostructures with necked particle size ranging from 17 nm to 23 nm. Due to the presence of ionized and high magnetic spin configuration of Fe 3d-electrons states in $\alpha$-$Fe_2O_3$, it shows spin magnetic moment per ion 4.17 $\mu$B as described by a Hubbard-type on-site Coulomb repulsion (GGA+U approach), which was found to provide an accurate description of the electronic properties which is good agreement with reported results. It has an estimated band gap about 2.2 eV with enhanced photocurrent (16.73%) properties and could promise photoelectrochemical applications.



## 1. Introduction

It is now well recognized that there is a urgent requirement for alternative and sustainable energy sources as well as various types of energy conversion technologies due to scarcity of fossil fuels [1,2]. Metal oxides play crucial role in a wide range of technological applications like optoelectronic devices, fuel cells and biosensors etc. [3–5]. Among all metal oxides, hematite ($\alpha$-$Fe_2O_3$) has attracted considerable attention due its use in photo electrochemical applications because its earth abundant in the crest and chemical stability in solution under sunlight illumination [6–8]. It has a narrow band gap (1.9–2.2 eV) of n-type semiconductor, low cost, non-toxicity and environment friendliness. It absorbs a good proportion of sunlight and yet has good electrochemical stability. The theoretical predictions shown that hematite photoelectrodes can achieve up to 15% solar-to-hydrogen conversion economically [9]. However, hematite has small optical absorption co-efficient and poor electronic conductivity due to its extremely short hole diffusion length of about 2–4 nm which show increasing recombination rate [10–12]. Several attempts have been made to improve the optical and electrical conductivity through doping [13,14], composite structure [15,16] and to overcome the limitation of small diffusion length, different synthesis approaches have been explored in order to design nanostructured layer [17–20]. The nanostructured porous thin films of hematite as electrodes are currently under extensive investigation, for its important application in solar energy conversion, batteries and sensors. Wu et al. [21] have reported the effect of shape and size control of hematite nanorods on their application in magnetism, Li ion based batteries and gas-sensors. Lin et al. [22] have reported nanonet based hematite hetero-nanostructures for efficient water splitting applications. Ahn et al. [23] have reported the essential conditions of PEC (i) a short diffusion length, (ii) single nanodomain along with growth (110) direction and (iii) high surface area. Until recently few researchers have reported on electrical transport mechanism and activation energy (0.7 eV) in hematite at high temperatures (300–450 °C) [24,25]. Based on the literature survey, there has been no report on resistivity and magnetoresistivity measurements

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http://dx.doi.org/10.1016/j.jallcom.2016.01.019
0925-8388/

on this nanoporous hematite at low temperature region to room temperature *i.e.*, 5–300 K. However, so far only a few reports have explained the density of states (DOS) and the optical bandgap of α-$Fe_2O_3$ theoretically [26,27]. Dazed et al. (2014) and Huda et al. (2010) have calculated the DOS of α-$Fe_2O_3$ using the VASP method under the GGA+U and LSDA + U and their calculated energy gap was 1.7 eV which is much smaller than the experimental results reported [28,29].

The present study focuses on how an increase in the surface area reduces the distance of photo generated charge carriers to travel towards the collection of hematite thin films with mesoporous morphology. This self-assembly structure is introduced by directing polymer and iron oxide precursors. To tailor the optical and electrical properties of these thin films working as an electrode this can be used in the photoelectrochemical cells. Total energy calculations have performed by using density functional theory implemented in Wien2K code, in order to determine the DOS and the optical bandgap of α-$Fe_2O_3$ hematite structure.

## 2. Experimental details

Mesoporous hematite thin films were prepared by following pechini route and spin coating technique [30] schematically depicted in Fig. 1. This method was adopted to form a polymeric precursor solution where the metals uniformly captured in the polymeric chain prison. A hydrocarboxylic acid, Citric acid $C_6H_8O_7$ was dissolved in distilled water, then Iron nitrate nonahydrate Fe $(NO_3)_3.9H_2O$ was added in a molar ratio of 3:1 (Citric acid/Iron nitrate nonahydrate) to the prepared solution under constant stirring and this chelating reaction resulted a light yellow homogeneous transparent solution. Following this step, the addition of Ethylene Glycol to the mixture in a Citric acid/Ethylene Glycol ratio of 60:40 wt % formed soluble polyester in solution. The polymerization reaction was processed by heating the mixture at 90 °C for 2 h until a high viscous dark yellow solution was obtained. This polymerization process result a homogeneous polymer in which Fe ions were uniformly distributed throughout the organic matrix. The resulted solution was aged for 24 h and deposited onto ITO coated glass substrates by spin coating with a rotation speed of 3000 rpm for 30 s. After deposition, the substrate was preheated at 300 °C for 10 min to evaporate the solvents and these deposition processes were repeated for required thickness of the films. Further these thin films annealed at 450 °C and 500 °C for 1 h to obtain a single phase of α-$Fe_2O_3$ hematite structure. During the annealing process polymerization has completely removed at 450 °C for 1hr [31].

The grown films were investigated by X-ray diffractometer (XRD) (Bruker D8 Advance Diffractometer) using monochromatic Cu-$K_{\alpha 1}$ radiation (λ = 1.5406 Å). The surface morphology and surface roughness of the sample were observed using a ZEISS Supra 55 Field Emission Scanning Electron Microscope (FESEM) and Bruker Dimension Icon Atomic Force Microscopy (AFM), respectively. Thickness of the samples was measured by using Bruker Dektek XT Profilometer. Elemental analysis was observed by EDAX. The optical band gap of the sample was characterised from their absorption spectra using Agilent Cary 5000 UV–Vis–NIR double beam spectrophotometer. Resistivity and magnetoresistance measurements were done by standard four probe method using homemade resistivity setup along with cryostat/magnet system from Oxford Instruments, UK in the temperature range of 5–300 K and up to 8T magnetic fields at UGC DAE Consortium for Scientific Research, Indore, India. For in-field measurements magnetic field was applied parallel to current direction. The carrier concentration were determined by Hall measurements (Ecopia HMS-3000) using Van der–Pauw method at room temperature. Current–Voltage measurements were performed by using KEITHLEY 2450 source meter and to determine photo-response behaviour, a solar simulator with illumination intensity of one Sun (AM 1.5, 1 kW $m^{-2}$, NCPRE IIT Bombay) was used as light source for illumination.

## 3. Computational details

In addition to above experimental investigations, first principle calculation for DOS and optical properties (absorption coefficient)

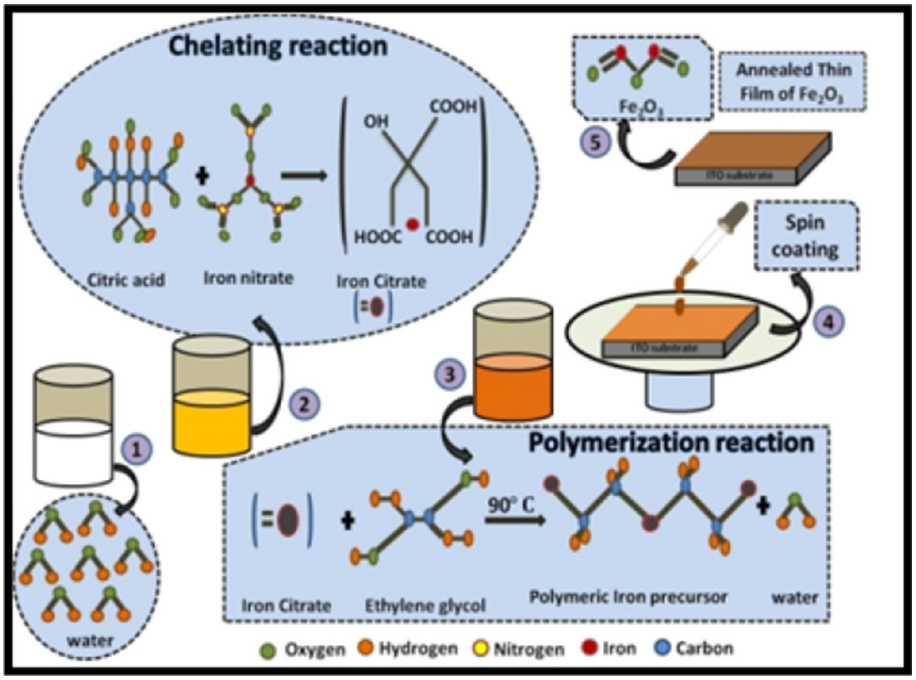


**Fig. 1.** Schematic diagram showing the deposition of mesoporous hematite thin films.