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GROWTH AND CHARCTERIZATION OF MANGANESE OXIDE (MnO) THIN FILMS DOPED WITH IRON (II) (Fe) - SYNTHESIZED BY CBD METHOD.

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Abstract

Pure and Iron (II) (Fe) doped manganese oxide (MnO) thin films were deposited on glass substrates by chemical bath deposition (CBD) technique using manganese (II) chloride tetra-hydrate ($MnCl_2.4H_2O$), Iron (II) tetraoxosulphate (VI) heptahydrate ($FeSO_4.7H_2O$) and 0.2M aqueous ammonia (NH_4OH) solution. The effect of deposition time on complexed and non-complexed of iron doping on its structural characteristics were investigated. The structural characterization by X-ray diffraction (XRD) showed that manganese oxide (MnO) films diffraction peaks are (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) crystal planes respectively. This is an indication that the films have well-crystallized face centered cubic (FCC) MnO crystal structure. The deposited MnO thin films were found to have a strong preferred orientation along the (111) plane.

Keywords; XRD, Thin films, MnO, synthesized, CBD , complex , Non complex, Fe, Characterisation.

1. INTRODUCTION

A thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness [1]. A familiar application of thin film is the household mirror, which typically has a thin metal coating on the back of a sheet of glass to form a reflective interface [2]. Manganese oxide (MnO) is a transitional material having interesting physical and chemical properties. They can also be prepared each other by varying the temperature and atmosphere (vacuum or air, oxygen, hydrogen etc.,) of the calcinations [3]. Fe doped MnO are prepared in the form of thin films on glass substrate by chemical bath deposition (CBD) technique which produce substance with interesting structural and optical properties worthy of discussion.

MnO and boron doped MnO films can similarly be prepared by different techniques such as radiofrequency sputtering [4]. Solvothermal synthesis [5], hydrothermal method, molecular beam epitaxy [6]. Thermal vacuum evaporation [7]. Successive ionic layer adsorption and reaction (SILAR) [7]. Chemical bath deposition (CBD) [8]., and spray pyrolysis [9]. Manganese oxide (MnO) is a transitional material having interesting physical and chemical properties. It has optoelectronic applications and is often used in electrode materials [10].[11]., electro-chemical capacitors [12],[13]. Rechargeable batteries, sensors [14]., and magneto-electronic devices [15].

The electrode reaction of manganese oxide has been studied during the last two decades for their application in alkaline batteries [16].[17]. Recently, electrochromic properties of manganese oxide thin film have been observed by several authors [18].[19]., an MnO2 was reported as being anodic electrochromic material like hydrated nickel oxide [20]., and that the bleaching is based on the reduction of MnO_2 to MnOOH .[21].[22].[23] and [24]. Similarly, [25] prepared MnO_x (Mn_30_4 or γ-Mn_2O_3) films by electron-beam evaporation, and reported electrochromic properties of the films polarized in 1.0M $LiClO_4$ γ -butyrolactone solution. There objective was to clarify the electrochromism of Mn_3O_4 thin films prepared by chemical vapor deposition (CVD) from manganese (III) acetylacetonate. Preparation conditions and structure of Mn_3O_4 thin films were discussed on the basis of the measurements of the films which were deposited at different substrate temperatures. The optical properties were studied using in situ electrochemical polarization in a spectrophotometer cell.

MnO_2 have higher electrochemical capacity as super-capacitors and the boron dopants were a proficient manner to enhance plus edify the properties of maganese oixide (MnO_2) [26]. Dopants have been utilized on MnO to improve cycling performance and stabilize electrochemically favorable structures [27]. Dopants may be able to improve capacity retention upon cycling if phase transformation is suppressed and volume expansion becomes isotropic and minimized upon lithium insertion [28]. Potassium have been observed to act as a phase-transforming suppressant, but capacity fading and phase conversion have been found to occur at higher current rates [29]. Vanadium-doping on MnO has also been studied recently for a potential pillaring effect in crystalline structures [29]. Most Vanadium-doped compounds for battery applications have been synthesized using hydrothermal and sol-gel techniques [30].

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Cobalt oxide is another exceptional material for super-capacitor electrode, here inclusion of cobalt ions into MnO_2 display a profound enhancement in pseudo-capacitive capacities [31],[32]. [33]., reports that dopping of Cobalt (Co) ions into the structured alkali MnO_2 which displayed a reasonable increment in the condutivity of its eletrodes, and sequel to this research, series of findings have being published on Co-MnO_2 proving en to be a potential super-capacitor electrode [34],[35].

Research on vanadium-doped manganese oxides is cathode materials for rechargeable lithium batteries was carried by [36]. X-ray diffraction patterns for pure amorphous manganese oxide, vanadium doped (V-doped) manganese oxide, and V-doped manganese oxide heated at 400 °C for 24 h in air showed a very weakly layer-like, amorphous structure. XRD taken after the V-doped manganese oxides which were heated for 24 hours at 400 °C showed no evidence of crystallization.

Eelectrochromic characteristics of manganese oxide slim films arranged by chemical vapour depositton (CVD)was studied by [37]. The x-ray photoelectron spectroscopy (XPS) measurements showed that the atomic ratios O/Mn were 1.4 for the manganese oxide films prepared at substrate temperatures 250ºC and 300ºC and 1.7 for the film prepared at 400ºC. At +3.0 V, a decrease in optical transmittance throughout the visible wavelength spectrum is observed. This decrease in optical transmittance (30% to 50 % at 550 nm) finds a practical application as an anodic electrochromic material in combination with a cathodic electrochromic material like tungsten oxide for window applications. The x-ray diffraction patterns of the Mn_3O_4 films deposited on a borosilicate glass substrate showed substrate temperatures of 250ºC, 300 ºC, and 400ºC respectively. The Mn_3O_4 film deposited at 250ºC is amorphous, while the peaks appeared for the films deposited at 300ºC and 400ºC displayed that the flims were made up of crystalites plus a predominant tetragonal structure (hausmannite).

MnO2 thin flims arranged via non-aqueous solgel procesing: Prefrential formation of birnessite was studied by [38]. The XRD result showed approximate 7Å (7×10^{-10}m) interlayer distances which mearnt that of birnessite-kind manganese oxides were present plus the enhanced spacing affiliated with bigger alkalli metal catoins are intandem with previous findings involving artificial birnessites. XRD peak intensisties were 2-5 times higher when compared with films made from a spin coat. Inclusional coatings didn't give extra aggrandizement to film quality.

Structural and optical investigation of manganese oxide thin films by spray pyrolysis technique was studied by [39]. The XRD result which showed the diffraction pattern as exhibiting peaks at 2θ=36.5587˚, d=2.4579Å; 2θ=38.1193, d=2.3608Å; 2θ=56.03˚, d=1.6398Å; 2θ=68.5735, d=1.3712Å and 2θ=73.7512˚, d=1.2836Å were identified to be (111), (200), (220), (311), (222) planes having cubic structure with lattice parameter a=4.36084Å. The presence of shift in few zeniths is because of inside strain living in the crystallites due to unproportionate display of the ingredients. The optical property showed that the film deposited at 400ºC shows 10% increase in transmittance compared to the deposit at 350ºC. This increase in transmittance is due to decrease in the thickness of the film as substrate temperature increases from 350ºC to 400ºC.

A study on hydrothermal synthesis of boron-doped MnO_2 and her decolorization attributes carried out by [40]. The XRD style with zeniths located at 2θ =12.6º,17.8º, 28.5º,37.3º ,41.8º,49.7º, and 60.0º , matched well with the main tyles of α-MnO_2 (JCPDS 44-0141).And showed no major variation for the XRD peak with further increase in the boron dopant. Besides, the peaks belonging to borate impurities are not detected. This present study is on growth and characterisation of Manganese Oxide thin film doped with iron (11) – synthesized by CBD Technique. The crystal nature and peception of the MnO films were studied using an X-ray diffraction (XRD) method using an X-ray diffractometer plus radiation (Ni filtered CuKα) of wavelength λ = 1.5418 Å.

2. METHODOLOGY

Preparation of glass substrates

The glass substrates (micro slide-25.4 mm wide × 76.2 mm lengths and 1mm-1.2mm thick) were washed in detergent rinsed with distilled water and soaked in concentrated hydrochloric (HCl) acid (to degrease the substrates from any possible stains) for 72 hours. Thereafter, they were removed from the concentrated hydrochloric (HCl) acid, rinsed with distilled water and cleaned with cotton wool, dipped with acetone to make it more electropositive.

Preparation of precursors

Before the deposition technique, mass of zinc of Determined: using the formula,

$$m = \frac{M\ of\ (MnCl2.4H2O)\times Mol.of\ (MnCl2.4H2O)\times V\ of\ water}{1000} \quad (1)$$

Where m is the mass of manganese, M is the molar mass of $MnCl_2.4H_2O$, Mol. is the molarity of $MnCl_2.4H_2O$ and V is the volume of water.

Molar mass of ($MnCl_2.4H_2O$) = 197.91 g/mol, Molarity of ($MnCl_2.4H_2O$) = 0.4M and volume of water is 100ml. From calculation using the above figures, the mass of manganese w as found to be 7.92g. 0.2M of aqueous ammonia (NH_4OH) at 2ml solution, were prepared.

Aqueous ammonia was gently added to form a white precipitate of manganese (II) hydroxide [$Mn(OH)_2$] precursor solution. The aqueous ammonia were used as a complexing agent in some undoped films, doped films were non complexed while the remaining film were

undoped and non complexed. All these samples were deposited for 48 and 72 hours intervals respectively.

Iron (Fe) doped manganese solution, have formula as

$$m = \frac{\%\ dopant\times M\times Mol\times V\ of\ water}{1000} \quad (2)$$

The percentages of dopant used were 1% and 2% respectively.

Deposition of manganese oxide (MnO)

Pure and Iron (Fe) doped manganese oxide (MnO) thin films were grown on glass substrates. The deposition solutions were formed by first dissolving weighed amounts of manganese (II) chloride tetra-hydrate ($MnCl_2.4H_2O$) in water to the volume of 100ml with molar concentration of 0.4M.

The growth of MnO thin films, 48 and 72 hourly deposition times were carried out in complexed films, non complexed films and non complexed doped films respectively.

For the Fe doped MnO thin films, a measured amount of Iron (II) tetraoxo sulphate (VI) heptahydrate ($FeSO_4.7H_2O$) was added to the initial solution. MnO thin films were complexed 0.2M NH_4OH, non-complexed, and non-complexed doped at 1% and 2% at 48 and 72 hours respectively

Reaction equations:

Equations (3) - (7) illustrate the chemical reaction related to both undoped complexed and non-complexed doped process:

Undoped complexed process:

$$Mn^{2+}_{(aq)} + 2NH_{3(aq)} + 2H_2O \leftrightarrow Mn(OH)_{2(s)} + 2NH_4^+{}_{(aq)} \quad (3)$$

$$Mn(OH)_2 + 4NH_4(OH)_2 = Mn^{2+} + 2OH^- + 4H_2O \quad (4)$$

During the reaction process, complex Mn^{2+} decomposes with the final formation of $Mn(OH)_2$ precipitation, yielding

$$Mn^{2+} + 4H_2O = Mn(OH)_2 \downarrow + 4NH_4 + 2OH \quad (5)$$

Reaction process, $Mn(OH)_2$ produced in equation (5) will transformed into manganese (II) oxide as shown in (6):

$$Mn(OH)_2 = MnO + H_2O \quad (6)$$

For the Non-complexed doped process, When the Mn^{2+}, is doped with iron (II) tetraoxosulphate (VI) heptahydrate, $FeSO_4.7H_2O$, a configuration of manganese (II), iron (II) ion, $[MnFe]^{2+}$ is formed as shown in equation (7):

$$Mn^{2+} + FeSO_4.7H_2O = [MnFe]^{2+} + 6H_2O + H_2SO_4 + 1/2O_2 \quad (7)$$

Characterization Techniques

The crystal framework plus orientation of the MnO films were studied via X-ray difraction (XRD) method using an X-ray diffratometer with radiation (Ni filtered CuKα) of wavelength λ = 1.5418 Å.

3. RESULTS AND DISCUSSION

The nature of the pure and Fe-doped MnO were propertied by XRD as shown in figure.1. This indicates that the XRD patterns for samples A (Complexed 0.2M NH_3 for 48hrs), B (Complexed 0.2M NH_3 for 72hrs), C (Doped for 72hrs), D (Doped for 48hrs), E (Non complexed for 48hrs) and F (Non complexed for 72hrs) with peaks located at 2θ = 20º,25º,45º,50º,55º,57º,70º,75º,90º,97º and 98º matched well plus the main nature of α-MnO (JCPDS 44-0141). The structural characterization by X-ray diffraction (XRD) showed that manganese oxide (MnO) films showed prominent diffraction peaks at 2θ = 20º,25º,45º,50º,55º,57º,70º,75º,90º,97º and 98º that was similar to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystal plains respectively except the sample C (Doped for 72hrs) which showed only (111) lattice plane at 2θ = 25º thereby lacking other prominent peaks. This indicates that the films have well-crystallized face centered cubic (FCC) MnO crystal structure. The deposited MnO thin films were found to have a strong prefered framework along the (111) plane. It is also observed that prominent peaks were possible in sample D (Doped for 48hrs) because of lesser time of doping the films. This means that more peaks would be generated when the films are deposited purely (undoped) at 48hrs as seen in fig. 1 (e). However, it is noticed in sample F , fig.1 (f)), at 72hrs, the peaks almost were not prominent (showing only two peaks). This implies that the best and suitable time of this deposition lies around 48hrs except when the film is complexed as seen in fig. 1(b). Therefore, the lesser the time of deposition of films, the more prominent peaks are produced (except the case of complexed films).

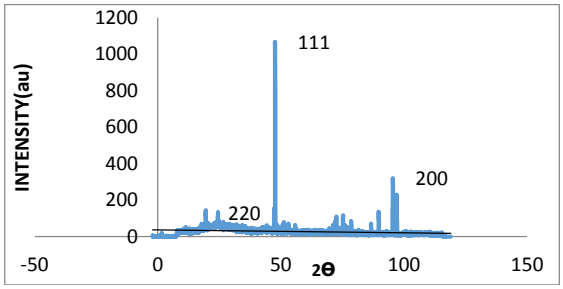

Fig. 1(A), Showing XRD diffraction for Complexed (undoped) 0.2M NH_3 for 48hrs

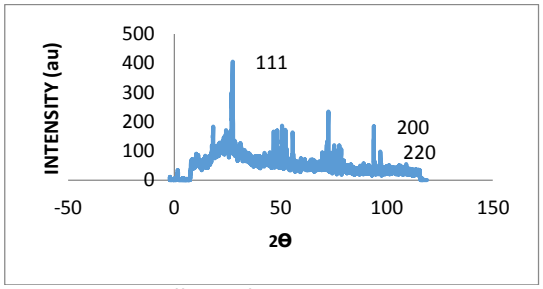

Fig. 1(B), Showing XRD diffraction for Complexed (undoped) 0.2M NH_3 for 72hrs

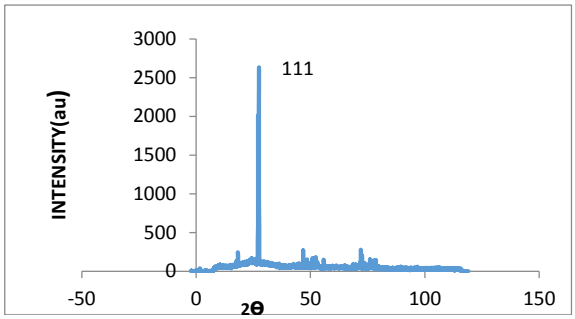

Fig. 1(C), Showing XRD diffraction for Doped for 72hrs

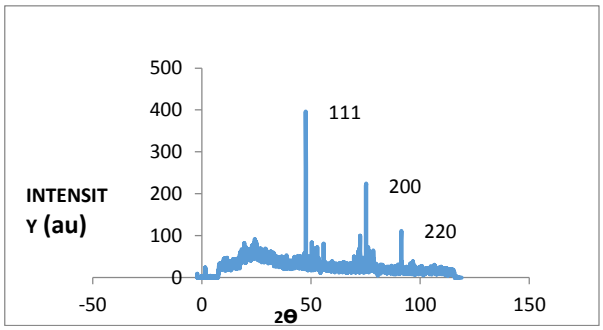

Fig. 1(D), Showing XRD diffraction for Doped for 48hrs

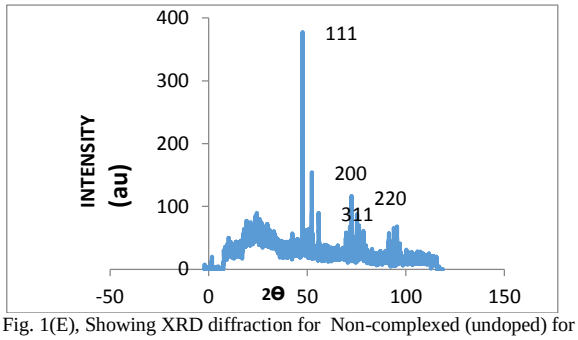

Fig. 1(E), Showing XRD diffraction for Non-complexed (undoped) for 48hrs

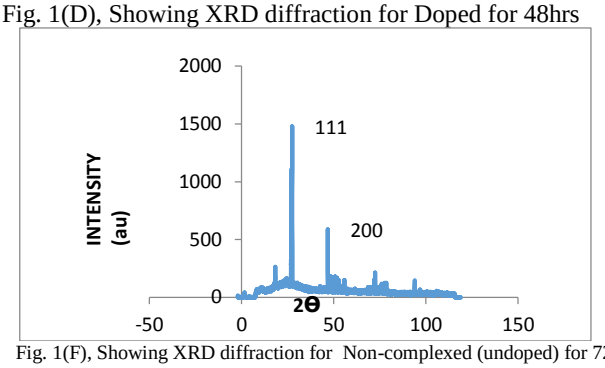

Fig. 1(F), Showing XRD diffraction for Non-complexed (undoped) for 72hrs

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CONCLUSION

Undoped and Iron (II) doped MnO thin films with different samples A, B, C, D, and E have been successfully synthesized by CBD technique on glass substrates. The XRD analysis showed that deposited MnO thin films were found to have a strong preferred orientation along the (111) plane. From the XRD analysis, It was observed that prominent peaks were possible in sample D (Doped for 48hrs) because of lesser time of doping the films. This means that more peaks would be generated when the films are deposited purely (undoped) at 48hrs.

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