Photoelectrochemical properties of morphology controlled manganese, iron, nickel and copper oxides nanoball thin films deposited by electric field directed aerosol assisted chemical vapour deposition

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An efficient deposition method of the morphologically controlled oxides of manganese (Mn$_2$O$_3$), iron (Fe$_2$O$_3$), nickel (NiO) and copper (CuO) spherical shaped nanoball thin films was developed by an in-house built electric field directed aerosol assisted chemical vapour deposition (EFDAACVD) technique. The Mn$_2$O$_3$, Fe$_2$O$_3$, NiO and CuO thin films were grown by using a single source precursor, metal acetate, under the application of an electric field that induces the formation of nanoballs of metal oxide thin films with controlled morphologies. The EFDAACVD-produced metal oxide thin films were characterized by using various suitable analytical characterization techniques. The photoelectrochemical properties of the EFDAACVD-produced Mn$_2$O$_3$, Fe$_2$O$_3$, NiO and CuO thin films were investigated in the presence of 0.1 M Na$_2$SO$_4$ under illumination of simulated solar irradiation of AM 1.5 G (100 mW/cm$^2$). The charge transfer dynamics of the thin films were also explored using electrochemical impedance spectroscopic (EIS) technique.

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1. Introduction

Transition metal semiconductor oxide thin films have found a wide range of applications as functional materials in gas sensors [1], electrochemical sensors [2], biomaterials, photoelectrochemical hydrogen generation [3,4], in electrochromic and photochromic coatings [5] and solid oxide fuel cells [6,7]. Nanostructured metal oxide based semiconductors have recently attracted much attention due to their interesting optical and electrical properties and their potential applications [8]. Metal oxide thin films have been formed to display appealing morphology by different fabrication techniques. Chemical vapour deposition (CVD) techniques have been developed as one of the major methods to fabricate well-designed films, coatings, powders, composites and nanotubes, to mention a few, for multi-functional applications [9,10]. Several methods such as reactive sputtering [11], electrodeposition [12], chemical bath deposition [13], spin coating [14], electrochemical [15] and spray pyrolysis [16] were used to fabricate the metal oxide thin films. However, a well-controlled nanostructured film morphology can be produced by using the above mentioned methods, but each deposition method has its own limitations, such as complicated growth conditions, monotonous processing and expensive equipment. The multiple steps that are used in the process of fabricating thin films are often high-cost and time consuming thus hindering the commercialization of these metal oxide thin films for various domestic applications. Therefore, to fabricate a low-cost and high performance thin film, a single step process is desirable. Aerosol assisted chemical vapor deposition (AACVD) offers a solution to overcome all these problems for the deposition of thin films with reproducible and precise composition of the deposited layer provided a single source precursor is available. Furthermore, AACVD can produce better adhesion thin films since the size of the aerosol droplets can be controlled by varying the deposition parameters such as solvent and frequency of the ultrasonic modulator. The only requirement for the deposition of thin films by AACVD is that the precursor should be soluble in a suitable solvent [17]. Thus, the AACVD method offers a successful route for the deposition of metal oxide thin films using a single step process. Recently, nanostructured columnar NiO and Fe$_2$O$_3$ thin films were prepared by using a single step gas phase process [18,10]. It has also been reported that...
thin films of CuO and Cu metal can be deposited from the same precursor simply by controlling the deposition temperature, stressing upon its importance in CVD process [19].

In the past, considerable attention has been paid for the discovery of suitable low-cost methods for the fabrication of shape and size controlled high surface area and pore volume nanomaterials for various optical and optoelectronic applications [20,21]. While trying to follow the WO3 film growth from AACVD by using impedance measurements, it was observed that the bias of the measuring circuit led to a change in the film microstructure [10]. The effect of an electric field in aerosol assisted chemical vapour deposition reactions of any kind is largely unknown [22–24]. The application of an electric field during AACVD reaction seems to be a way in which the microstructure of a material may be significantly altered [25–29]. Therefore, we were motivated to study the effect of an electric field on the morphology of some metal oxides such as Mn2O3, α-Fe2O3, NiO and CuO thin films fabricated from an electric field directed aerosol assisted chemical vapour deposition (EFDAACVD) method. We believe that the EFDAACVD thin film fabrication strategy adopted in this work will open up new directions to control the texture and morphology of nanomaterials fabricated using similar techniques such as AACVD, spray pyrolysis, aerosol synthesis, combustion synthesis and flame deposition. In this paper we report the morphology controlled deposition method for the fabrication of Mn2O3, α-Fe2O3, NiO and CuO nano ball thin films from readily available single source precursor using a new EFDAACVD technique.

2. Experimental methods

2.1. Reagents and chemicals

Anhydrous manganese (II) acetate (Mn(CH3COO)2), and tetrahydrofuran (THF) were purchased from Merck. Copper (II) acetate monohydrate (Cu(CH3COO)2.H2O) was supplied by Fluka, iron(II) acetate (Fe(CH3COO)2) and trifluoroacetic acid (TFAH) were purchased from Aldrich, while nickel(II) acetate (Ni(CH3COO)2) from Friedmann Schmid. Fluorine doped tin oxide (FTO) conducting glass slides with surface resistance of 8 Ω/sq were commercially supplied by Sigma–Aldrich.

2.2. Fabrication of metal oxide thin films by ESASP technique

The deposition of Mn2O3, α-Fe2O3, NiO and CuO thin films on the commercially available fluoride-doped tin oxide (FTO) substrate (1 × 2 cm) were carried out using an in-house built EFDAACVD technique as shown in Fig. 1. Prior to the deposition, the FTO substrates were cleaned ultrasonically by washing with distilled water, acetone and ethyl alcohol. Finally, they were washed with distilled water, stored in ethanol and dried in air before use. In a typical experiment, 200 mg of manganese acetate was added in a 100 mL Schlenk tube containing 15 mL THF. The mixture was stirred for 1 h followed by the addition of 0.2 mL of trifluoroacetic acid to clear the solution and was used for the fabrication of thin films of Mn2O3 nanoballs. The aerosol of the metal precursor was generated by keeping the reaction mixture in a two necked round bottom flask in a water bath above the piezoelectric modulator of an ultrasonic humidifier. The generated aerosol droplets of the precursor were transferred through an injection needle anode that was connected to a power supply. The distance between the edge of the needle (anode) and the substrate was kept at 6 inch and the substrate connected to the cathode was placed on the heater. Argon gas was passed through the aerosol mist at a flow rate of 200 mL/min to carry the aerosol droplets. A potential of 9.5 kV was applied across the terminals while the aerosol was flowing through the needle and the deposition were conducted at 400 °C for 45 min. The power supply and the ultrasonic humidifier were switched off and the aerosol line was closed. The substrate was then cooled down to room temperature before it was removed from the heating plate to obtain thin films of Mn2O3 mesoporous nanoballs. A similar procedure was adopted for the synthesis of α-Fe2O3, NiO and CuO nanoball thin films. The deposited nanoball thin films of Mn2O3, α-Fe2O3, NiO and CuO were greyish black, reddish brown, light grey [30] and black [31], respectively. All the films were uniform and stable under atmospheric conditions and do not adhere strongly on FTO glass substrates.

2.3. Characterization techniques

The surface morphology of metal oxide thin films was studied using a field emission scanning electron microscope (FESEM, FEI Quanta400) coupled with energy dispersive X-ray spectrometer (INCA Energy 200 (Oxford Inst.)), at an accelerating voltage of 2.0 kV, 50,000 and 100,000 magnification and a working distance of 3.5, 3.6 and 3.7 mm. The fabricated thin films were characterized by using X-ray diffraction (XRD) on a D8 Advance X-ray Diffractometer–Bruker AXS using CuKα radiation (λ = 1.540 Å), at a voltage of 40 kV and current of 40 mA at ambient temperature. The FT-IR spectra were recorded on a single reflectance ATR instrument (4000–400 cm−1 with a resolution of 4 cm−1). Raman spectra of the thin films were acquired using a Renishaw inVia Raman microscope with green laser excitation (532 nm). The optical absorption spectra of the thin films deposited at 400 °C using THF solvent were recorded on a Lambda 35 PerkinElmer UV–vis spectrophotometer in the wavelength range of 300–900 nm.

2.4. Photoelectrochemical study

The photoelectrochemical properties of the EFDAACVD produced metal oxide thin films were studied by using Princeton Applied Research (PAR-VersaSTAT-3) electrochemical work station with a conventional three-electrode system. The metal oxide thin films were used as a working electrode, platinum as a counter and Ag/AgCl as a reference electrode. For photocurrent measurement, the metal oxide thin films were dipped into the supporting electrolyte (0.1 M Na2SO4) and irradiated with a 150 W xenon arc lamp (Newport, Model) containing a simulated AM 1.5G filter.

3. Results and discussion

Metal carboxylates with their unique properties of high volatility, suitable decomposition temperature and stability during transport in the gas phase make them versatile CVD precursors for the fabrication of thin layers of metal oxides for various technolog-
ical applications. The different coordination modes (monodentate or terminal, chelating, bridging and bridging chelating) of the carboxylate ligand force the metal into strict molecular regimes that enhance their potential to perform as CVD precursor (Fig. S1). We therefore selected carboxylates of manganese, iron, nickel and copper for deposition of thin films of Mn$_2$O$_3$, α-Fe$_2$O$_3$, NiO and CuO by using a new EFDAACVD technique. The drive to use EFDAACVD was to obtain thin films of high crystallinity, well defined structure with excellent control over homogeneity, stoichiometry and reproducibility in a single step with the concomitant reduction in CVD parameters. The films produced by EFDAACVD were analyzed by FT-IR, Raman scattering, XRD, FESEM and EDX and evaluated for their photoelectrochemical performance.

3.1. FTIR studies of ESASP-produced metal oxide thin films

The FT-IR spectra of Mn$_2$O$_3$, α-Fe$_2$O$_3$, NiO and CuO thin films recorded in the range of 450–4000 cm$^{-1}$ are shown in (Fig. S2). The FT-IR spectrum of Mn$_2$O$_3$ consists of two bands centred at 461 and 604 cm$^{-1}$ respectively [32,33], and this is in good agreement with the Mn$_2$O$_3$ bands reported by Nilsen et al. [34]. The absorptions at 476 and 556 cm$^{-1}$ correspond to the iron–oxygen (Fe–O) vibrational modes that are characteristic of spinel compounds [35]. These two sharp and weak bands of low intensity are attributed to Fe–O vibration and are in good agreement with the literature [36]. For the NiO thin film, the band that appeared below 482 and 606 cm$^{-1}$ corresponds to a stretching vibration of the Ni–O bond [30]. This could be recognized by the obtained FT-IR result as shown in (Fig. S2). The FT-IR spectrum of CuO thin film shows peaks at 804, 621 and 520 cm$^{-1}$ ascribed to the Cu–O stretching mode of vibration [37,38].

3.2. Raman analysis of nanoball thin films

Raman scattering is a sensitive means to reveal the crystallinity and phase purity of a material. The Raman spectra of synthesized nanoballs of Mn$_2$O$_3$, α-Fe$_2$O$_3$, NiO and CuO recorded in the range of 200–1000 cm$^{-1}$ as shown in Fig. 2 are indicated by a strong peak at 620 cm$^{-1}$ with a left shoulder at 580 cm$^{-1}$ which is associated with a symmetric Mn–O stretching vibration as reported earlier [39]. Iron oxide exists in several forms such as magnetite (Fe$_3$O$_4$), hematite (α-Fe$_2$O$_3$), maghemite (γ-Fe$_2$O$_3$) and wustite (FeO). Raman spectroscopy can identify each of these forms better than any other tool. The Raman spectrum of iron oxide Fig. 2 shows the entire three strong bands at 222, 288, 401 cm$^{-1}$ and one peak of medium–strong intensity at 659 cm$^{-1}$ as reported in the literature that are characteristic for α-Fe$_2$O$_3$. However the Raman band for the magnetite (Fe$_3$O$_4$), maghemite (γ-Fe$_2$O$_3$) and wustite (FeO) also fall at 663 cm$^{-1}$ [40]. The possibility of the existence of FeO is excluded because of the absence of its characteristic peak at 655 cm$^{-1}$ while the existence of maghemite is eliminated because its phase is formed only at temperatures above 400 °C. It can therefore be safely concluded that the thin film consists of mainly hematite (α-Fe$_2$O$_3$) with a minor impurity of magnetite.

The Raman spectrum of NiO, Fig. 2, shows a characteristic strong peak at 505 cm$^{-1}$ with a shoulder at 407 cm$^{-1}$ and a weak signal at 706 cm$^{-1}$ [41]. It is reported in the literature that the Raman spectrum, Fig. 2, of CuO has three Raman active modes at 297, 337 and 558 cm$^{-1}$ [42]. All these modes of vibration have been identified in the spectrum and assigned to CuO with no extra peak due to Cu$_2$O found. Therefore, it can be inferred that CuO nanoball thin film is free from Cu$_2$O impurity.

3.3. XRD studies

Fig. 3 shows the XRD patterns of Mn$_2$O$_3$, α-Fe$_2$O$_3$, NiO and CuO thin films deposited on the FTO glass substrate by the EFDAACVD technique. The peaks indexed by the symbol (●) correspond to the SnO$_2$ in the FTO substrate [4,42–46]. The XRD pattern of cubic Mn$_2$O$_3$ with (2 1 1), (4 0 0) and (6 2 2) diffraction planes observed at
20 values of 22.5°, 37.8° and 65.6° respectively matched well with the JCPDS card No. 00-002-0896 [32].

Fig. 3 shows three strong peaks, namely, (0 1 2), (1 0 4) and (1 1 0), which are the reflections of α-Fe₂O₃ (hematite) as indicated in JCPDS card No. 86-0550 [4]. The X-ray diffraction data (Table S1) have been recorded for NiO thin films as shown in Fig. 3 displaying distinct peaks at 20 values of 37.1°, 43.1° and 62.6°. These peaks have been assigned to cubic NiO crystallography having various diffracting planes (1 1 1), (2 0 0) and (2 2 0) respectively revealing the formation of the NiO cubic phase (JCPDS card No. 47-1049) [38]. The two broad peaks at 20 values of 35.5° and 38.7° match the reflections from the (1 1 1) and (2 0 0) planes respectively, which is attributed to the structure of cubic CuO (JCPDS card No. 01-085-1326) [37, 47]. (Table S1) summarizes the 20 values and the reflection planes of Mn₂O₃, α-Fe₂O₃, NiO and CuO thin films.

3.4. Surface morphology and elemental analysis of nanoball thin film

The field emission scanning electron micrographs of metal oxide thin films at magnification 100,000 are presented in Fig. 4. The surface morphology of the thin films grown on fluorine doped tin oxide (FTO) substrate by EFDAACVD affects the surface morphology of the films as compared with AACVD [22]. The application of electric field is one of the key process parameters to control the morphology of the deposited film by chemical vapour deposition. The effect of electric field on the morphology of the films was studied by depositing films using air as a carrier gas at 400 °C substrate temperature. In the presence of an electric field, the morphology of the thin films showed particles caked as nanoballs onto the substrate surface. The smooth surface spherical shaped nanoballs of α-Fe₂O₃, NiO and CuO appeared on the FTO surface while the surface morphology of the Mn₂O₃ films turned into independent nanoballs sticking on the rough surface of the bulk. The precursor was assumed to be completely deposited on the substrate in the presence of an electric field of 9.5 kV. The distance of needle from the substrate, deposition time, and strength of the electric field play a key role in the morphology control of the metal oxide thin films. The Mn₂O₃ aggregated rough-surfaced nanoballs and the spherical shaped smooth-surfaced α-Fe₂O₃ nanoball thin films have average sizes ranging from 396 to 898 and 325 to 529 nm, respectively. The NiO films by AACVD adopted a columnar structure with flower-like surface morphology [10], while with EFDAACVD method nanoballs with average sizes of 273–471 nm were formed. The morphology of the thin films of CuO fabricated by simple AACVD gave densely packed globular aggregates [48] with particle sizes of 600–800 nm while the film deposited in the presence of the electric field yielded nanoballs of CuO with sizes ranging from 195 to 401 nm. All these observations indicate that the morphology and size of the thin films can be controlled by the application of an electric field of appropriate strength independent of the nature of the metal precursors.

The EDX spectrum of large areas of nanoball thin films confirms the presence of only Mn, Fe, Ni, Cu and O elements in the respective deposits are shown in Fig. S3. The tin and fluorine signals appear from the FTO substrate. The EDX analysis recorded at randomly different places confirms the uniform distribution of all the components of the metal oxide in the respective thin films.

3.5. Optical characterization of thin films

The optical absorption spectra of EFDAACVD-deposited thin films were recorded in the wavelength range of 300–900 nm using a similar FTO coated glass substrate as a reference to exclude substrate contribution in the spectrum. The UV–visible spectra of the Mn₂O₃, α-Fe₂O₃, NiO and CuO nanoball thin films were used to calculate the band gaps by means of Tauc’s plot of (αhv)² versus energy, Fig. 5, to give the values of 1.2, 2.2, 1.9 and 0.9 eV, respectively, for the direct band gaps. The band gap values for Mn₂O₃ and
α-Fe₂O₃ are in good agreement with the corresponding values of 1.2 and 2.2 eV [4,46], while the band gap values for NiO and CuO films showed lower band gap energies of 1.9 and 0.9 eV respectively as compared to the reported values of 3.2 and 1.7 eV [10,38]. This lower band gap energy may be due to absorption involving defect states.

This scatter in reported values may be attributed to two factors. First, the optical properties depend critically on the physical properties of the films, which are subsequently affected by the deposition and post-deposition conditions. Secondly, different models have been used to extract the optical properties from measured quantities. For example, $\alpha$, $\alpha^2$, $(\alpha E)^2$, $(\alpha E)^{2/3}$, and $(\alpha E)^{1/2}$ were all plotted against the photon energy to determine the band gap. This not only affects the value of the band gap but also affects the interpretation of the nature of the gap i.e. direct or indirect.
3.6. Photoelectrochemical properties of EFDAACVD-produced metal oxide thin films

The photoelectrochemical behavior of the EFDAACVD-produced metal oxide (Mn$_2$O$_3$, α-Fe$_2$O$_3$, NiO and CuO) thin films were investigated for water oxidation using linear sweep voltammetry (LSV) technique under simulated solar AM 1.5G irradiation in the presence of 0.1 M Na$_2$SO$_4$ at a scan rate of 50 mV/s. Under applied bias, the metal oxide thin films undergo photo-induced charge separation thereby promoting the valence band electrons to the conduction band resulting in the formation of holes at the valence band. The holes produced at the valence band can be readily scavenged through water oxidation that produces O$_2$ and H$^+$ ions. The electron present in the conduction band can be collected as a photocurrent generated by this EFDAACVD-produced metal oxide thin films. These overall photo-induced charge separation obtained for the metal oxide thin films in the photoelectrochemical cells are schematically shown in Fig. S4. The photocurrent density-applied voltage responses observed for the various metal oxide thin films indicate that with increasing applied potential, the photocurrent density increases as depicted in Fig. 6.

It can be seen that among the various thin films, the Mn$_2$O$_3$ thin film showed a higher photocurrent density than the α-Fe$_2$O$_3$, NiO and CuO thin films due to its hierarchical and roughened morphology. The lowest photocurrent density was generated by the α-Fe$_2$O$_3$ thin film (120 μA/cm$^2$), whereas, the maximum photocurrent density of 1.132 mA/cm$^2$ at 0.7 V versus Ag/AgCl (~1.23 V versus RHE) was obtained for the Mn$_2$O$_3$ thin film. In the case of CuO and NiO thin films, photocurrent densities of 129 and 226 μA/cm$^2$ respectively, were obtained. The difference in the photocurrent response of EFDAACVD-produced metal oxide thin films is mainly attributed to two important factors i.e. morphology and optical band-gap. These two factors significantly accelerated photocurrent generation in terms of light absorption, charge recombination and charge transport.

The variations in the photocurrent responses of the thin films were further understood by recording the electrochemical impedance spectroscopy (EIS) measurements in the frequency range of 0.01 Hz–10 kHz. The Nyquist plots obtained from the EIS measurements in the presence of 0.1 M Na$_2$SO$_4$ are displayed in Fig. 7. It can be seen that the Mn$_2$O$_3$, NiO and CuO thin films show a well-defined semicircle due to the charge transfer resistance of the thin films, whereas, the α-Fe$_2$O$_3$ thin film exhibits a straight oblique line, which shows better conductivity and an increase in charge carriers due to low interfacial charge transfer resistance. Moreover, the Mn$_2$O$_3$ thin film shows a semicircle with a small diameter, which reveals a lower charge transfer resistance between the electrode and the electrolyte. It is known from the literature [49] that the corresponding value of the intercept on the x-axis at high frequency represents the ohmic resistance of the electrolyte.
The applicability of EFDAACVD-produced metal oxide thin films in the photovoltaic performance of the metal oxide thin films. These text controlled nanostructured thin films of metal oxides fabricated by a single deposition method opened up new possibilities to improve their physical and chemical properties and could be a potential candidate for light energy harvesting assemblies.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mtcomm.2015.06.004

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