



# Chemical Vapour Deposition Formation of Porous Films of Photoelectrochemically Active Nano- Hematite Fe<sub>2</sub>O<sub>3</sub>

**Ms. Bhawna Dagar**

Research Scholar  
OPJS University  
Rajasthan.

**Dr. Satish Kumar**

Research Supervisor  
OPJS University  
Rajasthan.

## Abstract

In this study hematite films are formed in a chemical vapour deposition (CVD) growth process from a ferrocene precursor. Films are formed in variable thickness on FTO (fluorine-doped tin oxide) and ITO (tin-doped indium oxide) substrates. Photo-electrochemical experiments are conducted and the effect of thickness and illumination direction discussed in the context of a water splitting process in a mesoporous Fe<sub>2</sub>O<sub>3</sub> film. In contrast to the thin mesoporous films here thicker and denser films are studied. The photo-catalytic efficiency is improved by a factor of 4 due to higher density and potential gradient effects.

## Introduction

The photoelectrochemical conversion of photon energy into chemical fuels such as hydrogen is a promising approach to store solar energy for the increasing demand of energy in future. The key component of a photoelectrochemical cell (PEC) is the photoanode, typically consisting of an n-type metal oxide such as TiO<sub>2</sub>, ZnO, WO<sub>3</sub> or Fe<sub>2</sub>O<sub>3</sub> promoting the oxygen evolution reaction (OER) at the photoanode/electrolyte. In general, a PEC cell involves absorption of sunlight in a semiconductor electrode to generate electron-hole pairs, for oxidation and reduction of water followed by generation of oxygen and hydrogen molecules. The light absorption capability of the semiconductor electrode is of great importance to determine the potential of energy conversion efficiency of the PEC cells. Extensive researches have been carried out to identify suitable semiconductor materials for efficient water oxidation in PEC devices

There are many ways of preparing photo-active films of iron oxide and in particular Chemical Vapour Deposition (CVD) methods have attracted attention as cheap and reliable techniques <sup>(1)</sup>. Iron oxide thin films have been prepared, for example, by using the Metal-Organic Chemical Vapour Deposition (MOCVD) method at temperature of typically ca. 400-600 °C and with the precursor iron acetylacetonate Fe(acac)<sub>3</sub> <sup>(2)</sup>. Nitrogen gas has been used as the carrier gas while oxygen has been introduced as an oxidant for oxide formation and redox state adjustment. At 400 °C β-Fe<sub>2</sub>O<sub>3</sub> was deposited even without flowing O<sub>2</sub>. Whereas at 500 and 600 °C spinel-type Fe<sub>3</sub>O<sub>4+x</sub> was formed as a single phase for a low rate of O<sub>2</sub> flowing. By increasing the O<sub>2</sub> flow rate a mixture of β-Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4+x</sub> were formed, and finally with further increasing the O<sub>2</sub> flow rate β-Fe<sub>2</sub>O<sub>3</sub> was formed as a single phase. In this way compositional control could be achieved by varying the reagents. Other parameters for the compositional control are temperature and substrate material or morphology.

In a similar study, the gas phase decomposition of the iron complex  $[\text{Fe}(\text{O}^i\text{Bu})_3]_2$  was used to prepare  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  (3). Films were formed homogeneously and with a nanometer thickness range. The iron oxide phase and its morphology were controlled by varying the temperature of the substrate. The influence of microstructure and phase on the optical properties has been studied for both  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ . Mathur et al. (3) found that the substrate affects the crystallisation process. For example,  $\text{Fe}_3\text{O}_4$  was obtained at 450 °C on a copper substrate while it needed a higher temperature of 600 °C on quartz. In contrast, the pure hematite phase was found to deposit on quartz in a temperature range of 450-475 °C. At 500 °C a mix of hematite (needle shaped) and magnetite (faceted grains) were found on the quartz substrate. Therefore substrate effects can be essential in controlling the type and crystallinity of the growing oxide phase.

The effect of the precursor material on iron oxide formation has been investigated. A comparison of nanostructured  $\alpha\text{-Fe}_2\text{O}_3$  produced from iron pentacarbonyl and from ferrocene as vapour precursors has been reported based on Atmospheric Pressure Chemical Vapour Deposition (APCVD) (4). Ferrocene was found to be a much better precursor for the preparation of  $\alpha\text{-Fe}_2\text{O}_3$  with products showing improved optical absorption and two orders of magnitude higher photocurrent densities ( $0.54 \text{ mA cm}^{-2}$  at  $1.23 \text{ V}_{\text{RHE}}$ ). Further benefits of ferrocene are lower costs, less toxicity, and safer handling.

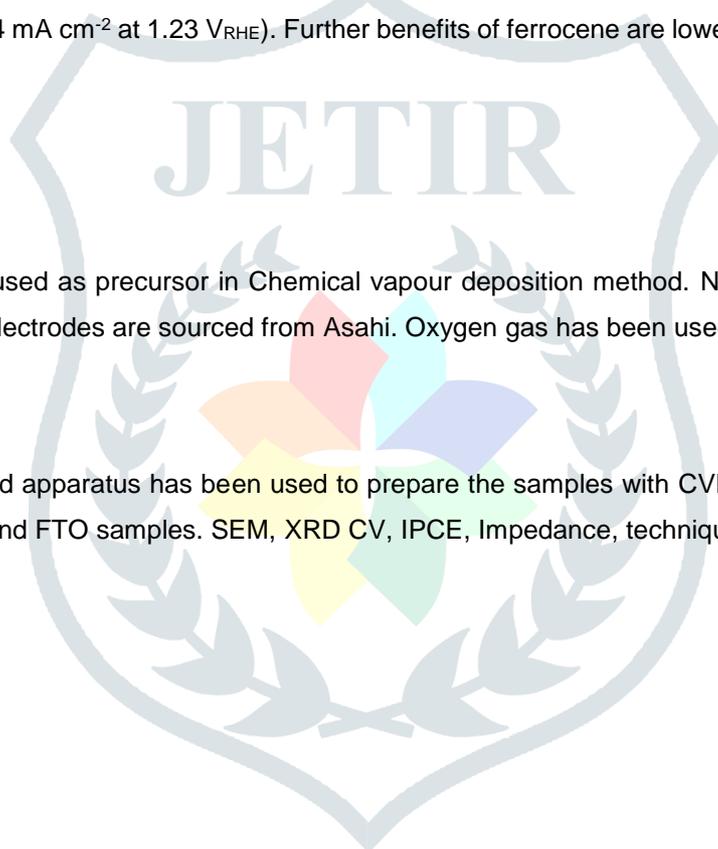
### *Experimental*

#### Chemical Reagents

Ferrocene  $\text{Fe}(\text{C}_5\text{H}_5)_2$  was used as precursor in Chemical vapour deposition method. Nitrogen gas has been used as carrier gas. FTO and ITO electrodes are sourced from Asahi. Oxygen gas has been used as an oxidised gas.

#### Instrumentation

An Electro Gas Systems Ltd apparatus has been used to prepare the samples with CVD method. Sonicator has been used for cleaning the ITO and FTO samples. SEM, XRD CV, IPCE, Impedance, techniques are applied here.



## Chemical Vapor Deposition Experimental Procedure

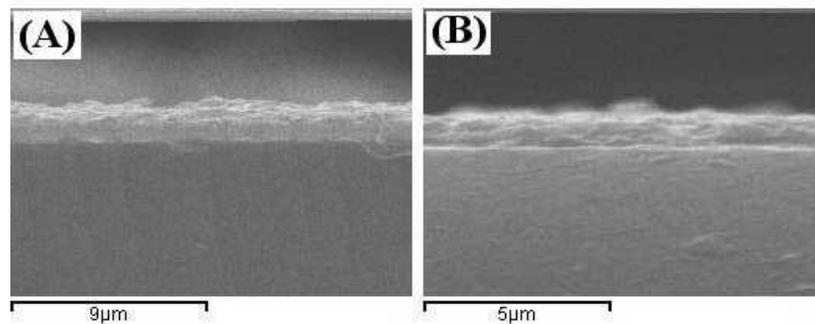
Chemical vapour deposition runs were carried out using an Electro Gas Systems Ltd apparatus in reduced pressure thermal chemical vapour deposition configuration. The precursor was volatilised in a heated precursor tube at 120 °C and delivered to the quartz reactor chamber in a stream of N<sub>2</sub> carrier gas (at a rate of 100 ml/min) through heated stainless steel tubing maintained at 120 °C. The substrate was supported on a graphite wedge heated to 450 °C through the reactor chamber wall by an external halogen lamp. The precursor stream (100 ml/min) was mixed with the O<sub>2</sub> oxidant stream (100 ml/min) at the entrance to the reactor chamber. The precursor and oxidant were transported to the heated substrate and the volatile decomposition products removed from the chamber at a rate of 500 ml/min by means of the main N<sub>2</sub> carrier gas stream. The apparatus was maintained at a pressure of 150 Torr by an Edwards XDS5 dry vacuum pump for the duration of the deposition run.

## Results and Discussion

Films of iron oxide from CVD deposition from ferrocene precursor appear uniformly brown and dense. A summary of the types of films investigated here (different thicknesses and two different substrates) is given in Table 1. The average thickness of these films is estimated based on cross-sectional SEM images (see Figure 1.) and consistent with a growth of typically 30 nm per minute.

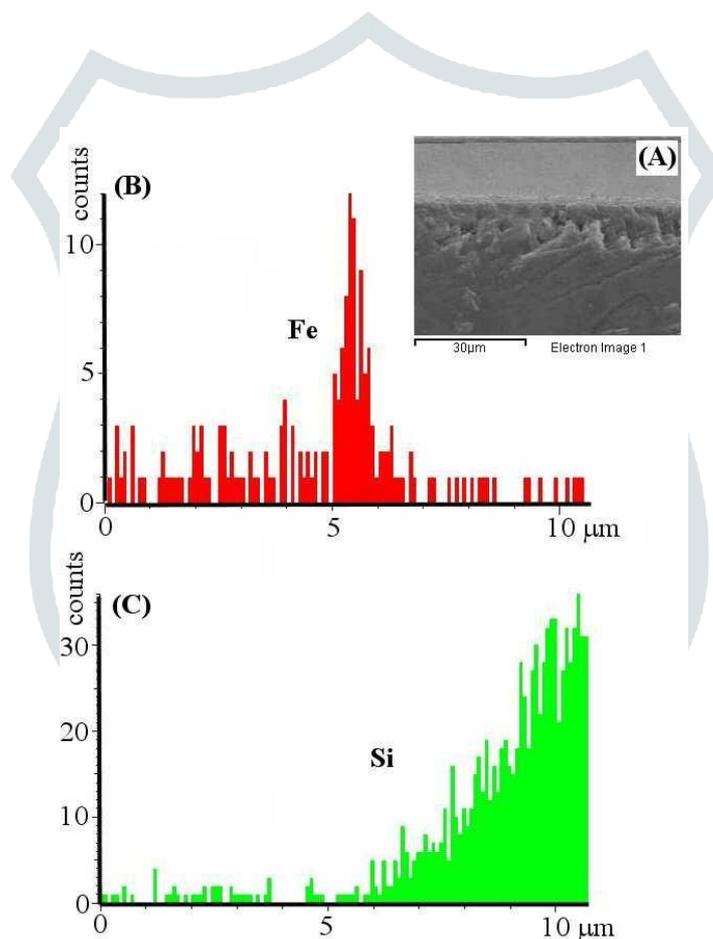
Table 1. Summary of Fe<sub>2</sub>O<sub>3</sub> samples prepared by the CVD method from ferrocene precursors at 450°C and varying the deposition times

Sample number	Substrate type	Deposition time / minutes	Approximate thickness / nm
FTO10	FTO	10	300
FTO15	FTO	15	450
FTO20	FTO	20	600
FTO25	FTO	25	750
FTO30	FTO	30	900
FTO35	FTO	35	1050
ITO10	ITO	10	300
ITO15	ITO	15	450
ITO20	ITO	20	600
ITO25	ITO	25	750
ITO30	ITO	30	900
ITO35	ITO	35	1050



**Figure 1.** Cross-sectional SEM images for (A) sample FTO25 and (B) sample ITO25.

During cross-sectional SEM imaging also an EDX profile for the films was obtained. Figure 2. shows that a film of typically  $1\ \mu\text{m}$  is formed at the glass surface (for sample FTO35) as expected for the estimated film thickness. Cross-sectional EDX data for Fe and Si are consistent with the film structure.



**Figure 2.** (A) SEM cross-sectional image for sample FTO35. (B) EDX scan across the sample cross section with Fe counts. (C) EDX scan with Si counts, which contained in the conducting glass

The photo-electrochemical processes observed in this study for the CVD iron oxide films are likely to be best considered intermediate between the two cases of models. Due to the higher density of the CVD hematite the pores provide less space for electrolyte to penetrate to the substrate electrode and therefore potential gradients within the films are likely to contribute to the overall characteristics. Subtle changes in the growth conditions (e.g. ITO versus FTO substrate) can result in significant changes in the grain orientation and porosity of films and this is the reason why significant changes in reactivity are observed.

## Conclusions

It has been shown that high quality CVD hematite films can be grown from ferroceneprecursors onto both ITO and FTO substrates. Both types of films give complex photo-current responses with anodic and cathodic regions. When focusing on the anodic photo-currents associated with oxygen evolution from aqueous electrolyte characteristic effects of thickness and illumination direction were observed. Difference between ITO and FTO substrates were significant in the morphology of films but less dramatic in photo-electrochemical behaviour. Photo-electrochemical transient were discussed in the light of the mesoporous film model and it was concluded that the complex behaviour observed in these films is based on a mixed behaviour with contributions from both semiconductor and mesoporous film models.

## References

- (1) Satsangia, V. R.; Kumaria, S.; Singha, A. P.; Shrivastavb, R.; Dassb, S., *International Journal of Hydrogen Energy*, 2008 , 33, 312-318.
- (2) Ueyama, R.; Kuribayashi, K.; Itoh, N., *Journal of the Ceramic Society of Japan* 1996, 104 (10) 949-952.
- (3) Mathur, S.; Sivakov, V.; Shen, H.; Barth, S.; Cavelius, C; Nilsson A.; Kuhn, P., *Thin Solid Films*, 2006, 502, 88-93
- (4) Saremi-Yarahmadi, S.; Tahir, A. A.; Vaidhyanathan, B.; Wijayantha, K.G.U., *Material Letters*, 2009, 63, 523-526
- (5) Tahir, A. A.; Wijayantha, K.G.U.; Saremi-Yarahmadi, S.; Mazhar M.; McKee, V., *Chem. Mater.* 2009, 21, 3763-3772
- (6) Qiao, Q.; Beck, J.; Lumpkin, R.; Pretko, J.; Mcleskey Jr, J. T., *Solar Energy Materials & Solar Cells*, 2006, 90, 1034-1040.
- (7) Aouaj, M. A.; Diaz, R.; Belayachi, A.; Rueda, F., Abd-Lefdil, M., *Materials Research Bulletin*, 2009, 44, 1458-1461.
- (8) Bitht, H.; Eun, H.-T.; Mehrtens, A.; Aegerter, M. A., *Thin Solid Films*, 1999 351, 109-114
- (9) Shin, H. -S.; Kwon, S. -J., *Yoop Hakoechi (Journal of the Korean Ceramic Society)*, 1993, 30, 499-509.
- (10) Langford, J.I.; Wilson, A.J.C, *J. Appl. Cryst.*, 1978 11, 102-113.
- (11) Krishnan, R. R.; Vinodkumar, R.; Rajan, G.; Gopchandran, K. G.; Pillai, V. P.M., *Materials Science and Engineering b-Advanced Functional Solid-state Materials*, 2010, 174, (1-3), 150-158.
- (12) Beermann, N.; Vayssieres, L.; Lindquist, S.E.; Hagfeldt, A., *J. Electrochem. Soc.*, 2000, 147, 2456
- (13) Peter, L. M., Walker, A. B., Boschloo, G., Hagfeldt, A., *J. Phys. Chem. B*, 2006, 110, (28), 13695.