Fabrication and photoelectrochemical studies of Bi$_2$Ti$_2$O$_7$ pyrochlore thin films by aerosol assisted chemical vapour deposition

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Phase pure thin film Bi$_2$Ti$_2$O$_7$ photoelectrodes were produced by aerosol assisted chemical vapour deposition at 600 °C for the first time. X-ray diffraction analysis showed that the as-deposited Bi$_2$Ti$_2$O$_7$ film was amorphous in nature; however, post-deposition annealing at 600 °C for 12 h significantly increased the crystallinity to give phase pure Bi$_2$Ti$_2$O$_7$. Scanning electron microscopy revealed that the as-deposited film had a cauliflower-like structure with features ranging from 0.5 to 1.0 μm in size. It was found that the post-annealing step sintered the features together reducing the pores in the structure and giving rise to larger features of 1.0–2.0 μm in size. Optical studies showed that the Bi$_2$Ti$_2$O$_7$ film had a direct band gap of 2.74 eV. The photoelectrochemical properties of Bi$_2$Ti$_2$O$_7$ were tested and it was found that the electrodes exhibited a photocurrent density of 1.8 μA cm$^{-2}$ at 0.23 V vs. Ag/AgCl. Results showed that Bi$_2$Ti$_2$O$_7$ is an attractive material for photoelectrochemical water splitting.

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1. Introduction

Pyrochlores are a class of material with the general structure A$_2$B$_2$O$_7$, which consists of an interpenetrating cuprite-type A$_2$O tetrahedral framework with a corner sharing BO$_6$ octahedron [1]. Bismuth based pyrochlores, in general, have been attracting interest for many diverse applications such as ceramic capacitors, piezoelectric transducers, sensors and dynamic random access memories, due to their high dielectric constants and ferroelectric properties [2]. The photocatalytic properties of Bi$_2$Ti$_2$O$_7$ in particular have been attractive due to the fact that it has a narrower band gap (~2.8 eV) than that of widely studied TiO$_2$ [3,4] whilst maintaining suitable band energetics (i.e. for water splitting reactions). The relatively narrow band gap is achieved by the upward shift in the valence band energy from the Bi 6s orbital [5]. It has also been demonstrated that Bi$_2$Ti$_2$O$_7$ has excellent photo and chemical stability and electron–hole pairs generated under illumination have long life-times [6,7] which should partly resolve the problems associated with electron–hole recombination, especially as it has been shown that p-block elements, such as Bi, show high electron mobility compared to TiO$_2$ [8]. Two recent reports have shown that incorporation of Mn and Fe into the structure can result in further narrowing of the band gap to as small as 2.1 eV [3,4]. Whilst there have been a number of reports on the photocatalytic activity of Bi$_2$Ti$_2$O$_7$; to the best of our knowledge, there is only one previous report for use in water splitting cells using thin film electrodes, which was published during the review process of the present paper [9].

There are a number of reported synthesis methods for Bi$_2$Ti$_2$O$_7$ in the literature, such as co-precipitation [10], metal-organic deposition [11], and sol–gel [2]. However the majority of methods reported in the literature are aimed at preparing the material in the form of a powder (at micro- and nano-scale) rather than thin films. A common problem associated with the existing methods for thin film fabrication is achieving a pure phase, as, for example, impurity phases such as Bi$_4$Ti$_3$O$_12$ have been often observed in the powder synthesis [12]. Aerosol assisted chemical vapour deposition (AACVD) is a relatively simple and highly versatile method for the fabrication of highly nanostructured thin films [13–15]. The method allows deposition of multicomponent films from a single precursor solution and the nanostructure can easily be controlled by carefully selecting the solvent and tuning the concentration, temperature and the deposition flow rates.

In this study, we have prepared phase pure Bi$_2$Ti$_2$O$_7$ thin films by the method of AACVD and characterised them by XRD, SEM and diffuse absorbance spectroscopy. We also report the photoelectrochemical properties of Bi$_2$Ti$_2$O$_7$ thin films.

2. Experimental

AACVD was used to fabricate thin films of Bi$_2$Ti$_2$O$_7$; a detailed description of the experimental setup and theory is given elsewhere.

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Briefly, a flask containing the AACVD precursor (40 cm³) solution was placed above a piezoelectric transducer to generate an aerosol. Air (109 cm³ min⁻¹) was used as the carrier gas to transfer the aerosol to a second flask where the larger droplets fall out of the stream. A secondary flow of air (2340 cm³ min⁻¹) was used to transfer the finer aerosol droplets onto an FTO substrate (TEC 8 Pilkington, 8 Ω/sq), which was heated by a hotplate to 600 °C. The aerosol decomposed on the hotplate to give the desired thin film. The AACVD precursor solution was prepared by dissolving bismuth nitrate pentahydrate (0.02 mol) in acetylacetone (7.0 cm³), after which it was diluted by the addition of methanol (50 cm³), then titanium isopropoxide (6.75 × 10⁻³ mol) was added and the solution was then made up to 100 cm³ by addition of methanol. The FTO coated glass was cut (1 cm²) and ultrasonically cleaned with doubly distilled water, acetone, propan-2-ol and ethanol prior to use. All chemicals were purchased from Sigma Aldrich and were of 99% purity or higher. The deposition process was carried out for 1 h to obtain a film with an appropriate thickness (approx. 1 µm). A post-deposition annealing step, typically 12 h at 600 °C, was used to improve the crystallinity of Bi₂Ti₂O₇ thin films.

The phase and crystallinity of the films were characterised using a Bruker AXS Advance X-ray diffractometer with primary monochromatic high intensity Cu Kα radiation (1.541 Å) radiation. The current–voltage (J–V) characteristics of the Bi₂Ti₂O₇ thin films were tested using Galvanostat/Potentiostat (Eco Chemie micro-Autolab type III), under illumination by an AM 1.5 Class A solar simulator (Solar Light 165 – 300 solar simulator), at 100 mW cm⁻² light intensity, calibrated by a silicon pyranometer (Solar Light Co., PMA2144 Class II). The films were measured in a standard, three-electrode configuration in a quartz cell using a platinum wire counter-electrode and a Ag/AgCl/KCl reference electrode. The electrolyte was 1 M sodium hydroxide and the scan rate was maintained at 10 mV s⁻¹. Diffuse absorbance measurements were carried out on a Lambda 35 Perkin-Elmer UV/Vis Spectrometer. The surface morphology was studied using a Leo 1530 VP emission gun scanning electron microscope (FEG-SEM) at an accelerating voltage of 5 kV and a working distance of 5 mm.

3. Results and discussion

Bi₂Ti₂O₇ thin films were produced by AACVD at 600 °C on FTO glass substrates. Fig. 1 shows the X-ray diffraction (XRD) patterns of an as-deposited thin film and a film after 12 h of post-deposition annealing at 600 °C. The XRD pattern for the as-deposited films show peaks only from the F:SnO₂ layer from the substrate. The peaks at 26.8°, 34.0°, 38.0°, 51.7°, 54.7°, 61.7° and 65.7° correspond to the (110), (101), (111), (211), (220), (310) and (301) reflections of SnO₂, respectively (ICDD 00-041-1445). This showed that the as-deposited film had an amorphous nature. To increase the crystallinity of the thin film, it was subjected to post-deposition annealing for 12 h at 600 °C. The XRD pattern for the post-annealed film presents the presence of a cubic Bi₂Ti₂O₇ phase, with peaks at 15.0°, 27.3°, 28.8°, 30.1°, 34.8°, 38.0°, 46.0°, 49.9°, 51.9°, 59.4° and 62.4° corresponding to the (222), (602), (622), (444), (800), (622), (1022), (880), (1062), (1244) and (888) reflections of Bi₂Ti₂O₇, respectively (ICDD 00-032-0118). The XRD pattern shows no other reflections for impurities such as TiO₂, Bi₂O₃ or Bi₄Ti₃O₁₂.

The surface morphology of the thin films before and after the post-deposition annealing step was studied by FEG-SEM and are shown in Fig. 2a and b, respectively. It can be seen that the Bi₂Ti₂O₇ film consists of cauliflower shaped structures ranging in size from 0.5 to 1 µm.

A cross-sectional image of a post-annealed film is shown in Fig. 2c, which shows a film thickness of around 1 µm after 60 min of deposition by AACVD. It can be seen that post-deposition annealing for 12 h at 600 °C causes sintering of the nanostructure, resulting in the formation of larger size features in the range of 1–2 µm, compared to the 0.5–1 µm size before annealing. Also, it can be seen that there is a reduction in void space between the individual features after annealing, which may result in lowering the surface area.

Diffuse absorbance measurements were carried out on post-annealed films. Fig. 3 shows the absorbance spectrum for Bi₂Ti₂O₇ and it can be seen that the optical absorption onset occurs at around 430 nm. It has been shown by several previous studies that Bi₂Ti₂O₇ is a direct band gap semiconductor and so a plot of (αhν)² vs. photon energy (Tauc plot) can be used to estimate the band gap of Bi₂Ti₂O₇. In the present work, the band gap was estimated to be 2.74 eV, which also agreed with the recently reported work.

The PEC properties of the Bi₂Ti₂O₇ were investigated in 1 M NaOH aqueous electrolyte under AM 1.5G illumination. The chopped photocurrent–voltage curve is shown in Fig. 4. The photocurrent onset occurs at around 0.38 V vs. Ag/AgCl, and the films showed a photocurrent of 1.8 µA cm⁻² at 0.23 V vs. Ag/AgCl (1.23 V vs. NHE), which increased to around 3 µA cm⁻² up to the dark current onset at 0.7 V vs. Ag/AgCl [18]. The photocurrent corresponds to water oxidation under illumination. Unlike other well studied materials such as TiO₂ [18] there were no signs of recombination in the Bi₂Ti₂O₇ film under the chopped illumination. Usually, in the presence of recombination in an n-type semiconductor, positive spikes in the photocurrent transients are observed under illumination (termed the instantaneous hole current), which decays to a steady state current after recombination with electrons then, when the illumination is interrupted, the hole current ceases immediately and the trapped holes recombine with electrons giving a current spike in the negative direction [19,20]. The absence of these recombination features illustrates that the electron–hole lifetime is indeed longer in Bi₂Ti₂O₇ than in TiO₂ and suggests that the electron mobility may be higher in Bi based pyrochlores compared to TiO₂ as already reported in the literature [6,7].

Also, it is known that direct band gap materials are likely to be more efficient in photocatalytic and PEC applications compared with indirect band gap materials as it minimises recombination due to trapping of excited electrons as they move from the valence band to the conduction band [1]. This makes Bi₂Ti₂O₇ a good material for such applications. The photocurrent onset method can be used to estimate the flatband potential of Bi₂Ti₂O₇, so as can be seen from the inset of Fig. 4, the flatband potential can be
estimated to be $-0.38 \text{ V vs. Ag/AgCl}$. Taking into account the flatband potential and the band gap, the conduction and valence band energies are estimated to be 0.64 V and 3.38 V vs. NHE, respectively. This indicates that the valence band is sufficiently positive to give a large overpotential for water oxidation.

With our findings, we anticipate there to be an increase in interest in these materials, especially as it has been demonstrated recently that the band gap of $\text{Bi}_2\text{Ti}_2\text{O}_7$ can be further reduced by substitution of Fe and Mn into the structure, to as low as 2.2 eV [3,4]. Studies are currently under way to attempt to produce such substituted films by AACVD and investigate their PEC properties.

4. Conclusions

Phase pure $\text{Bi}_2\text{Ti}_2\text{O}_7$ thin films were prepared by AACVD for the first time. A post-deposition annealing step was necessary to improve the crystallinity of highly amorphous as-deposited thin films. The photoelectrochemical properties of $\text{Bi}_2\text{Ti}_2\text{O}_7$ thin films were reported with a photocurrent density of 1.8 $\mu\text{A cm}^{-2}$ at 0.23 V vs. Ag/AgCl. The direct band gap of $\text{Bi}_2\text{Ti}_2\text{O}_7$ was calculated to be 2.74 eV. This shows that $\text{Bi}_2\text{Ti}_2\text{O}_7$ has the potential to be a more useful photoelectrochemical material than TiO$_2$ as it absorbs a greater proportion of the solar spectrum, has a direct band and exhibits less recombination.

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