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Improvement in the structural, optical, electronic and photoelectrochemical properties of hydrogen treated bismuth vanadate thin films

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ABSTRACT

In the present study structural, optical and electronic properties of bismuth vanadate ($BiVO_4$) thin films prepared by rf-sputtering technique were modified by post-hydrogen treatment to improve the photoelectrochemical (PEC) performance for water oxidation. X-ray diffraction and Raman analysis do not reveal any major structural changes but show increase in crystallite size and creation of defect states, however, optical absorption studies shows changes in band gap energy values due to the creation of inter-band states on hydrogen treatment. X-ray photoelectron spectroscopy studies show that the hydrogen treatment reduces surface Bi^{4+} considerably and increases the density of hydroxyl groups on the $BiVO_4$ surface. The combined effect of these changes manifests in terms of enhanced photocurrent density of 3.31 mA/cm^2 (at applied potential 1.0 V versus Ag/AgCl), which is about nine time higher than the pristine $BiVO_4$ and reduced photocurrent onset potential.

Introduction

The technological vision of solar energy conversion to generate hydrogen was conceptualized on the basis of the initial studies on TiO_2 in 1972 by Fujishima and Honda [1]. Subsequently, various transition metal oxide semiconductors, such as, WO_3, SnO_2, ZnO, Fe_2O_3, Cu_2O etc have been intensively studied as they are abundantly available, low cost, exhibit high photostability and sufficient mobility of charge carriers [2–4]. Each of these binary metal oxides has its own merit and demerit as either they have intrinsic limitation on visible light absorption due to high bandgap energy or possess poor semiconductor characteristics [5–9].

In recent years, studies on ternary metal oxide semiconductor, such as, bismuth vanadate ($BiVO_4$) have demonstrated new opportunities for developing efficient photoanode material, as modulation of the stoichiometric ratio can tune the electronic bands and bandgap energy. The narrower bandgap monoclinic structure of $BiVO_4$ (E_g = 2.4 eV) exhibits higher photocatalytic activity and has a favourable

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conduction band (CB) edge position very near to the thermodynamic H_2 evolution potential (at pH 7) [10–12]. However, excessive electron–hole recombination, poor charge transport properties, and inefficient water oxidation kinetics have proven to be the key limiting factors. To overcome these limitations, various material modification techniques, such as, doping, morphology control, formation of composite structures, and coupling of $BiVO_4$ with oxygen evolution catalysts have been developed [13–17].

In recent years, hydrogen induced modification in metal oxide semiconductors has been of substantial interest to alter the optical band gap and electronic properties. Chen et al. have reported that titanium dioxide nanocrystals treated in hydrogen atmosphere under 20 bar H_2 atmosphere for 5 days show a colour change to black with a reduction in bandgap energy upto ~1.54 eV [18]. These nanocatalysts also exhibit enhanced photocatalytic activity. Subsequent to these reports, hydrogen treatment has been used in other metal oxide thin films like TiO_2, ZnO, Fe_2O_3, $BiVO_4$, etc [19–22]. Various hydrogen treatment process such as high pressure hydrogen annealing [18], electrochemical hydrogenation [23] and hydrogen plasma [21,24] have been used for making the disordered metal oxide nanoparticles and thin film material. Wang et al. [22] reported that the hydrogen treatment in $BiVO_4$ under 1 bar pressure with 50 sccm H_2 flow in a tube furnace exhibits an improvement in photocurrent density due to the formation of oxygen vacancies which act as shallow donors according to the DFT calculations [25].

In the light of the above background, $BiVO_4$ thin films have been grown in a controlled manner by rf sputtering technique followed by vacuum hydrogen treatment (at a base pressure of 2.5×10^{-5} Torr) under mild hydrogen (5% H_2 in Ar, 20 sccm) condition at different temperature. The effect of hydrogen treatment on the structural, electrical, optical and junction characteristics has been studied in detail and the changes is these properties have been correlated with the improvement in photoelectrochemical characteristics.

Experimental

In the present work, thin films of $BiVO_4$ were deposited onto single-crystal Si wafer (100) and indium-doped tin oxide (SnO_2:In, ITO) substrate by reactive rf magnetron sputtering of bismuth vanadate target (99.99% purity). The sputtering chamber was initially pumped down to approximately 2×10^{-6} Torr. The sputtering was carried out at optimized rf-power of 80 W at room temperature. To deposit the $BiVO_4$ thin films, 20 sccm argon was used while maintaining the deposition pressure of 2.5×10^{-2} Torr. After the thin film deposition, the as-deposited $BiVO_4$ samples were annealed at 400 °C in air for 4 h. For hydrogen treatment, the air annealed $BiVO_4$ samples were further annealed in 5% H_2 balanced Ar atmosphere at temperatures ranging from 200 to 500 °C for 10 h. In this study structural, optical and electronic properties of $BiVO_4$ and H:$BiVO_4$, (400 °C) was investigated in detail. The photoelectrochemical performance was investigated as a function of hydrogen annealing temperature ranging from 200 to 500 °C.

The glancing angle X-ray diffraction pattern were recorded by using Philip's X'Pert PRO-PW vertical system operating in reflection mode using Cu Kα (λ = 0.15406 nm) radiation and Raman analysis were carried out on a Invia Raman microscope under excitation by 514 nm Argon ion laser pulse, to determine the structural behaviour of $BiVO_4$ before and after hydrogen treatment. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a load-locked Kratos XSAM 800 apparatus equipped with a dual anode X-ray source using an Mg Kα (1253.6 eV) excitation source. The high magnification analyser mode was chosen to collect electrons from the smallest possible area on the specimen (~4.0 mm^2). All spectra were calibrated using the C1s photoelectron component peak of amorphous carbon (284.8 eV) present in the sample and data analysis was performed with Casa XPS software using a Shirley background subtraction. The surface morphology/roughness was examined using scanning electron microscope (SEM) and atomic force microscopy (AFM) by using field-emission SEM (Quanta™ 3D FEG) and Digital Instruments (Nanoscope IIIA) equipped with SCM-PIT cantilever under non-contact, respectively. To understand the optical behaviour, the optical measurements were carried out using the UV–visible spectrophotometer (Perkin–Elmer Lambda 35) in the wavelength range 400–800 nm and the optical absorption coefficient (α) was estimated by assuming, $\alpha = A/d$, where d is the overall film thickness (determined by cross-sectional FE-SEM) and A is the measured absorbance. The electrochemical measurements were carried-out using a three-electrode photoelectrochemical cell. The working electrodes were pristine and H:$BiVO_4$ films with an approximate illumination area of 0.45 cm^2, the counter electrode was a platinum mesh and Ag/AgCl was used as reference electrode. For all electrochemical measurement, 0.5 M Na_2SO_4 was used as electrolyte. The photoelectrochemical cell was controlled using CIMPS-2 (Controlled Intensity Modulated Photospectroscopy) system consisting of Zennium Electrochemical Workstation (X-Pot Potentiostat). Linear sweep voltammetry scans under dark and illumination and Mott–Schottky measurement in dark condition were carried out in the potential range −1.0 to +1.0 V versus Ag/AgCl with a scan rate of 20 mV/s. The light source used in the present study was a white light having output illumination intensity of 100 mW/cm^2 equipped with a filter to remove light of wavelength below 350 nm. The electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range from 100 kHz to 0.01 Hz with AC signal amplitude of 10 mV under open bias condition (i.e. 0.0 V versus Ag/AgCl reference electrode).

Results and discussion

Fig. 1 shows the XRD spectra of pristine and H:$BiVO_4$ samples deposited on Si(100) substrates. All the peaks in pristine and H:$BiVO_4$ samples are assigned to monoclinic phase of bismuth vanadate. The relative intensity of diffraction peaks and improvement in orientation corresponding to (112), (020) and (114) planes increases notably indicating an increase in crystallinity of these planes with hydrogen treatment (Fig. 1a). The particle sizes for pristine and H:$BiVO_4$ samples were calculated using Debye–Scherrer equation. From particle size data