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Modified structural, morphological and photoelectrochemical properties of 120 MeV Ag^{9+} ion irradiated $BaTiO_3$ thin films

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ABSTRACT

The effects of high electronic energy deposition on the structure, surface topography, optical property and photoelectrochemical behavior of barium titanate thin ($BaTiO_3$) films have been investigated by irradiating films with 120 MeV Ag^{9+} ions at different ion fluences in the range of 1×10^{11}–3×10^{12} ions cm^{-2}. Barium titanate thin films were deposited on indium tin oxide-coated glass substrate by sol–gel spin coating method. The structure of the film was crystalline with tetragonal phase. Surface topography was studied by atomic force microscopy detailing the values of roughness of the films. Maximum photocurrent density of 1.78 mA cm^{-2} at 0.4 V/SCE and applied bias photon-to-current efficiency (ABPE) of 0.91% was observed for $BaTiO_3$ film irradiated at 1×10^{11} ions cm^{-2}.

1. Introduction

Irradiation of materials with energetic ions leads to the creation of a wide variety of defect states in the material system, which changes the physical and chemical properties such as structure, optical and electrical transport properties of the material. The changes are strongly dependent on the mass of the incident ion, the irradiation energy and fluence. During irradiation, swift heavy ions (SHIs) traverse in solids with a velocity comparable to the Bohr velocity ($\sim 2.8 \times 10^8$ m/s) of electrons and lose energy primarily to the target electrons. When this energy loss, known as the electronic energy loss (S_e) exceeds a certain material dependent threshold value (S_{eth}), SHIs induce amorphized latent tracks along their path in a crystalline matrix. The rapid energy transfer during the electronic excitation can result in a variety of effects in materials including defect creation, defect annealing, crystallization, amorphization, crystalline-to-crystalline phase transition etc. within a narrow cylindrical region along the path of the heavy ion beam [1,2]. Several models such as thermal spike and Coulomb explosion have been proposed to explain the transfer of the electronic energy to the lattice during beam irradiation. According to the thermal spike model, the energy transfer from the heavy ion to the lattice takes place by electron–phonon coupling resulting in a transient temperature spike in the medium that leads to melting of the material along the ion trajectory up to depths for which the electronic energy loss exceeds a certain critical value. This melt phase is followed by fast cooling and re-solidification so that an amorphous track is formed within a crystalline matrix [2,3]. According to the Coulomb explosion model [4], a highly positive charged zone of target material produced around the ion path by electronic excitation on a time scale of 10^{-15}–10^{-14} s explodes due to Coulomb repulsion before electrical neutrality is restored. The information about these energy relaxation processes can be explored from the resulting physical changes produced, as the changes occurring in the medium are not directly observable, during or immediately after their occurrence. Hence, the irradiation may cause ionization or excitation and possibly displacement of atoms from their sites in the lattice of the materials [5].

Oxide semiconductors are eminently attractive candidates for solar water photoelectrolysis and photocatalytic environmental remediation applications [6,7]. Several semiconductors such as TiO_2 [8,9], $SrTiO_3$ [10], Fe_2O_3 [11,12], ZnO [13,14] and $BaTiO_3$ [15,16]

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have been investigated as photoanodes in photoelectrochemical cell systems for hydrogen production. Among these, $BaTiO_3$ exhibits mixed ionic–covalent chemical bonding with the Ba–O bonds being almost entirely ionic. The Ti–O substructure, on the other hand has a substantial covalent contribution leading to a unique structure, which makes it a fascinating material substantiating its usefulness in a wide range of high technology applications.

Despite its large band gap ($E_g = 3.2$ eV), $BaTiO_3$ is a preferred material due to its extraordinary stability in aqueous environments. Its conduction and valence band edges straddle H_2O/H_2 and OH/O_2 redox levels, a mandatory requirement for spontaneous photo-splitting of water. Advantages of $BaTiO_3$ for the photoelectrode in hydrogen production by photoelectrochemical water splitting include its: i) high resistance to corrosion and photocorrosion in aqueous media, ii) easy availability at low cost, iii) environmental friendliness, iv) well-matched energy band edges with the redox level of water, and v) electronic properties that can be varied by changing the lattice defect chemistry or the oxygen stoichiometry. Nanostructured semiconductors compared to bulk counterparts show significant alteration in band gap, porosity and surface area; which are crucial for PEC (photoelectrochemical) applications [17–19]. Irradiation of semiconductors by a swift heavy ion (SHI) beam is also known to modify the material properties and it can be used to obtain materials with better PEC response [9–13,20,21].

In this work, $BaTiO_3$ thin films were synthesized by sol–gel spin coating technique. The chemical route involving sol–gel spin coating process is an industrially promising technique for the preparation of thin films as it offers many advantages in terms of low energy cost, low material consumption rate, simplicity and speedy deposition on substrates with good homogeneity. Films prepared through chemical routes are mostly amorphous. Annealing at high temperatures leads to the development of crystalline phase. In the present study, modifications of properties of $BaTiO_3$ thin films are attempted by irradiating films with 120 MeV Ag^{9+} irradiation at four different fluences of 1×10^{11}, 2×10^{11}, 5×10^{11} and 3×10^{12} ions cm^{-2}. To our knowledge, use of SHI irradiation in modification of properties of $BaTiO_3$ films for PEC application has been undertaken for the first time in the present study.

2. Experimental

2.1. Sample preparation and SHI irradiation

$BaTiO_3$ (BT) thin films were grown on indium-doped tin oxide (SnO_2:In) conducting glass substrates using sol–gel spin coating technique. The precursor solution containing barium acetate [$Ba(CH_3COO)_2$, Aldrich 99%] and titanium isopropoxide [$Ti(OC_2H_4CH_3)_4$, Aldrich 97%] dissolved in glacial acetic acid (CH_3COOH, Qualigens 99.5%) and 2-methoxyethanol (CH_3OCH_2-CH_2OH, Aldrich 99.3%) was spin coated on substrate at 1500 rpm for 20 s. Multiple layers were achieved by successive deposition of the gel over the previously deposited layer. The number of layers was optimized with respect to the best photocurrent obtained. In this study, three coatings of the gel were deposited resulting into best photocurrent density in case of pristine sample. After each successive layer, the film was allowed to dry for 10 min at 80 °C. Resulting films were sintered at 600 °C for 1 h in air and slowly cooled. The films were then irradiated using the 15 UD Pelletron accelerator at Inter University Accelerator Centre (IUAC), New Delhi with 120 MeV Ag^{9+} at fluence 1×10^{11}, 2×10^{11}, 5×10^{11} and 3×10^{12} cm^{-2}. The beam current was maintained ~1 pnA (particle nanoampere) to avoid heating effects during irradiation. The ion beam incident at an angle of ~90° to the surface, normal to the thin film, was made to scan over an area of 10 mm × 10 mm to achieve dose uniformity across the sample area.

The projected range of 120 MeV ions in the films as calculated using SRIM 2008 code is about 22.87 μm, which is much greater than the thickness of the film (170 nm), indicating that the entire passage of ions is dominated by the electronic energy loss. Thus, the bombarding ions pass through the entire film and come to rest in the substrate beneath the film. For this energy the electronic and nuclear energy losses per ion and unit depth in the BT layer are 8.775×10^2 and 4.007 eV/A°, respectively.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded by glancing angle X-ray diffractometer (Bruker AXS D8 Advance, Germany) and CuK_α ($\lambda = 1.5405$ Å) as the radiation source, with angular accuracy 0.001° and the angular resolution better than 0.01°. Crystallite size was estimated using Scherrer's formula. Surface morphology of films was examined using scanning electron microscopy (Hitachi SU-70) and atomic force microscopy (Digital Nanoscope 3A). Absorption spectra of $BaTiO_3$ films were recorded with respect to the bare substrate by employing double beam UV–vis spectrophotometer (UV-2450, Shimadzu, Japan) to determine the band gap. X-ray photoelectron spectroscopy (XPS) measurements were made on a Kratos Axis-165 operating in hybrid mode using monochromatic Al KR X-ray radiation (1486.6 eV). The XPS spectra were background subtracted using the Shirley method. All spectra were referenced to the C 1s line at 284.8 eV. The intensity ratios were evaluated using sensitivity factors supplied by the instrument manufacturer.

2.3. Preparation of photoelectrodes

To utilize BT thin films as photoelectrodes in a PEC cell, ohmic electrical contacts were obtained using silver paste and copper wire, from the uncoated area of the conducting glass substrate. The area of contact was later covered with non-transparent and non-conducting epoxy-resin (Hysol, Singapore). PEC studies were conducted using three-electrode configuration electrochemical cell. The semiconductor working electrode was used in association with a platinum foil counter electrode (CE) and saturated calomel reference electrode (SCE) in an aqueous solution of NaOH (pH = 13) as electrolyte. Potentiostat (PAR, Model: Versastat II, USA) and 150 W Xenon Arc lamp (Oriel, USA, used as light source) were employed to record current–voltage (I–V) characteristics of the cell, both under darkness and illumination. The photocurrent density was extracted from I–V curves, by taking the difference between the current observed under illumination and under darkness per square centimeter exposed area of the working electrode.

To obtain the Mott–Schottky curves, capacitance (C) at semiconductor/electrolyte junction with AC signal frequency of 1 kHz was measured using LCR (Inductance, Capacitance, Resistance) meter (Agilent Technology, Model: 4263B, Singapore) at varying electrode potentials. These curves were used to calculate the flat-band potential and donor density for all the samples.

3. Results and discussions

3.1. X-ray diffraction

The X-ray diffraction patterns of the pristine and irradiated $BaTiO_3$ thin films with 120 MeV Ag^{9+} ions for the fluence of 1×10^{11}, 2×10^{11}, 5×10^{11} and 3×10^{12} ions cm^{-2} are presented in Fig. 1. The obtained patterns have predominance of sharp, intense peak corresponding to underlayer of SnO_2:In. These peaks have been marked in Fig. 1 by the symbol asterisk. Pristine sample exhibited