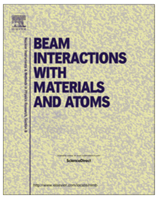
Nuclear Instruments and Methods in Physics Research B 323 (2014) 7–13

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb



Swift heavy ions induced surface modifications in Ag-polypyrrole composite films synthesized by an electrochemical route

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ARTICLE INFO

Article history:
Received 5 August 2013
Received in revised form 15 December 2013
Available online 3 February 2014

Keywords:
Polypyrrole composite
Silver nano particles
Electrochemical synthesis
Ion irradiation

ABSTRACT

The general aim of this work was to study the effects of swift heavy ions on the properties of electrochemically synthesized Ag-polypyrrole composite thin films. Initially, polypyrrole (PPy) films were electrochemically synthesized on indium tin oxide coated glass surfaces using a chronopotentiometery technique, at optimized process conditions. The prepared PPy films have functioned as working electrodes for the decoration of submicron Ag particles on the surface of the PPy films through a cyclicvoltammetry technique. Towards probing the effect of swift heavy ion irradiation on the structural and morphological properties, the composite films were subjected to a 40 MeV Li^{3+} ion beam irradiation for various fluences (1×10^{11}, 1×10^{12} and 1×10^{13} ions/cm^2). Comparative microstructural investigations were carried out after the different ion fluences using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy and micro-Raman spectroscopy techniques. Raman and SEM studies revealed that the structure of the films became disordered after irradiation. The SEM studies of irradiated composite films show significant changes in their surface morphologies. The surface was smoother at lower fluence but craters were observed at higher fluence.

1. Introduction

Metal and conducting polymer composites have the potential to combine two frontier technologies to yield materials with improved properties. The conducting polymers (CPs) have inherent property to combine with different materials due to their redox behaviour. CPs have the potential because of their good conductivity [1] and wide range of applications in sensors [2–4], EMI shielding [5], light-emitting diode [6], optoelectronics and energy storage devices [7]. Currently, there has been a considerable interest in the use of CPs, particularly polypyrrole in the forms of thin films or blends with metal particles. Ag-polypyrrole (Ag-PPy) composites attracted a lot of attention due to their environmental stability, electrical conductivity and excellent redox process [8–10]. Various authors have been reported synthesis and characterization of metal conducting polymer composites via different synthetic routes [11–17].

The swift heavy ion (SHI) irradiation technique is used as a unique tool to modify the material properties in a controlled manner. SHI crosses through material and loses its energy mainly via two independent processes: (a) elastic collisions with the nuclei of the target atoms, and (b) in exciting or ionizing the atoms by an inelastic collision. Both the processes occur simultaneously and their contribution to the total energy losses of the traverses ion is given by stopping power i.e., $\left(-\frac{dE}{dx}\right)_e$, which is a function of energy, linear energy transfer, ion fluence, mass, charge and the nature of the target material [18]. The Coulomb-explosion model [19] and Thermal-spike model [20,21] are generally used to understand the mechanisms of the material modifications induced by heavy ions interaction with the target material. The energy loss by impinging particles is centred inside the track and is accompanied by radical formation, formation of multiple bonds, loss of volatile molecules, main chain scission and intermolecular crosslinking [22–26].

Hussain et al. [27] conducted the irradiation of PPy using 160 MeV Ni^{+2} ions and a sharp increase in the degree of crystallinity of the polymer was obtained. Furthermore the absorbance peak has shifted towards the higher wavelength region. Kaur et al. [28] performed the study to evaluate the effect of 100 MeV SHI's on the morphological and electrical properties of PPy. The surface structure of PPy films became smoother and the conductivity of the irradiated PPy film was doubled. The controlled reduction in size of

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http://dx.doi.org/10.1016/j.nimb.2014.01.009

metal nanoparticles (NPs) embedded in different matrices was carried out various authors under SHI irradiation [29–32].

In our previous work, we reported electrochemical synthesis of metal conducting polymers composites and analysis of its electrodeposition mechanism [33,34]. The effects of irradiation on the properties of metal conducting polymer composite films were studied [35,36]. Studies were also conducted to investigated the effect of irradiation on the properties of different non-conducting polymers, including polyallyl diglycol, polyethylene terephthalate, PM-355 films, etc. [37–39]. However, no investigation has been performed on the SHI irradiation induced modifications in Ag-PPy composites, according to the authors' knowledge. Taking account of the above the aim of this study was to study the effects of SHI irradiation on the structural and morphological properties of the Ag-PPy composite films.

In this work, we report an electrochemical synthesis of Ag-PPy composite films and the evaluation of the structural and morphological changes in the composites caused by the heavy ion irradiation. The scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy and Raman spectroscopic studies of the films were carried out before and after irradiation after various ion fluences. The study of heavy ion induced modifications of Ag-PPy films is significant due to their applications in various fields such as gas sensing and radiation zones in space or close to reactors.

2. Experimental details

All the reagents and solvents used for the syntheses were procured from Merck and used without further purification. For all purposes double distilled water was used.

Electrochemical synthesis was carried out using a CHI 660D electrochemical workstation under computer control. The standard three electrode setup was employed in one a compartment electrochemical cell. A rectangular conducting ITO sheet of size $20 \times 10 \times 0.7\ \mathrm{mm}^3$ was used as a working electrode whereas a platinum sheet of size $20 \times 40 \times 0.25\ \mathrm{mm}^3$ was used as a counter electrode. The reference electrode was an Ag/AgCl electrode. The first step involves the aqueous electro polymerization of pyrrole containing 80 ml aqueous solution onto an ITO substrate using a chronopotentiometery technique. The electrolyte solution was composed of 0.23 M pyrrole monomer and 0.55 M pTS. The surface modification of synthesized PPy film was conducted in an aqueous solution of 80 ml containing 0.001 M $AgNO_3$ and 0.05 M KCl solution using cyclic voltammetery (CV) between potential windows of −0.3 to +0.8 V at a scan rate of 40 mV s^{-1}. The surface of PPy film was uniformly decorated by Ag nanostructures by controlling the scan rate and applied potential during the synthesis process. The thickness of the synthesized composite film was 30 ± 4 μm. The thickness of the composite films was measured by a dial type micrometer gauge.

The samples were exposed to 40 MeV Li^{3+} beam in material science beam line at Inter University Accelerator Centre (IUAC), New Delhi, India under high vacuum ($\sim 5 \times 10^{-6}$ Torr). The fluences were taken varying from 1×10^{11} to 1×10^{13} ions/cm^2. The beam was scanned in the x–y plane to irradiate the whole target sample area. The irradiation time has been calculated by using the formula $t = \phi Aqe/I$ (where ϕ is the fluence, A is area of irradiation and I is the current in particle nano ampere). The fluence ϕ in the present work can be calculated by the formula ϕ = ions s^{-1}/area. Ion fluence calibration was achieved by determining the beam current with a Faraday cup. The uncertainty in the ion fluence measurement can be up to 20%, due to the ambiguity in the ion beam area, fluctuation in the current, integrated charge etc. Irradiations were performed at room temperature with a low ion current of 0.5 pnA to avoid the thermal degradation of the samples.

SEM images and EDX spectra were obtained using a JEOL JSM-6490LV microscope at 25 kV after covered with a thin layer (~10 nm) of sputtered gold. SEM micrographs were taken at different resolution. The micro-RAMAN investigation was carried out using a Renishaw InVia Raman microscope in the range of 200–2000 cm^{-1}. An Ar ion laser excitation of 514.5 nm at a very low power (<1 mW, 20×objective) was used to avoid any heating effects.

3. Results and discussion

3.1. SRIM analysis

In order to get the information about the range (R_p), electronic (S_e) and nuclear (S_n) energy loss in the grafted copolymers, the SRIM (Stopping and Range of Ions in Matter, version 2010) program was used [40]. S_e and S_n values for 40 MeV Li^{3+} ions in Ag/PPy film were 83.05 and 4.87×10^{-2} keV/μm, respectively. SRIM calculations for the 40 MeV Li^{3+} ions in the Ag-PPy composite films showed a maximum range of 287.32 μm, indicating that the entire passage of ions through the film was dominated by electronic energy loss. Fig. 1 shows the electronic energy loss as a function of penetration depth range for lithium ion irradiated Ag-PPy composite film. The SRIM calculation clearly indicates that the electronic energy loss is greater than the nuclear energy loss. Therefore, the electronic energy loss is dominant in the present case and responsible for the materials modifications. Thus, it is expected that such a large electronic excitation may induce breaking of original bonds, creation of excited and ionized species and the formation of free radicals which are responsible for the physio-chemical modifications. The induced modifications in the target materials can be considered mostly to the electronic energy loss, which is dominant mechanism at the high energy.

3.2. Electrochemical study

In the present investigation we have electrochemically synthesized polypyrrole film with optimized process parameters (viz. concentration of monomer and dopant, applied current density, deposition time, etc.) on ITO coated glass substrate. These parameters have a strong influence on the nature of the polymerization process. It is well reported in literature that the concentration of dopants usually determines the morphology, conductivity, rate of

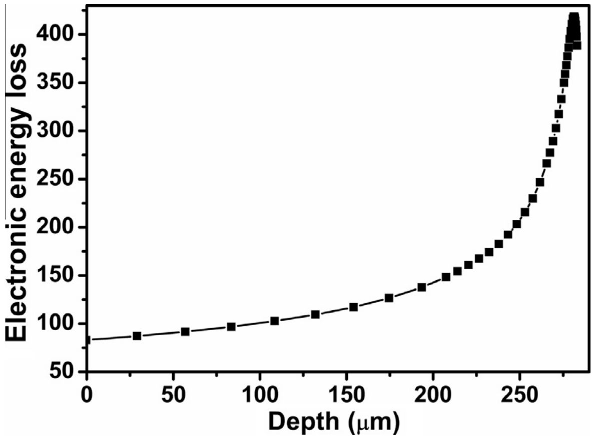

Fig. 1. Plot of the electronic energy loss versus penetration depth of Li^{3+} ions at 40 MeV in a Ag-PPy composite film calculated with SRIM 2008.