Organic Electronics 14 (2013) 2896–2901

Contents lists available at ScienceDirect

Organic Electronics

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

Incorporation of non-conjugated polymer chain in conjugated polymer matrix: A new single step strategy for free standing non-volatile polymer memory

Purushottam Jha, Shankar P. Koiry *, Vibha Saxena, Putta Veerender, Abhay Gusain, Anil K. Chauhan, Dinesh K. Aswal *, Shiv K. Gupta

Technical Physics Division, Bhabha Atomic Research Center, Mumbai 400085, India

ARTICLE INFO

Article history:
Received 25 March 2013
Received in revised form 19 July 2013
Accepted 10 August 2013
Available online 2 September 2013

Keywords:
Non-volatile memory
Interfacial polymerization
Polypyrrole
Free-standing film
RRAM

ABSTRACT

A new single step strategy for polymer memory materials has been explored using free-standing polypyrrole (PPy) film in which non-conjugated polymer chains are incorporated as trap states during synthesis. The PPy film was synthesized by the acidic oxidation of 2,2′:5′,2″-terpyrrole at the air/water interface. The free-standing PPy films show large hysteresis along with current peaks in opposite directions during current voltage (*I–V*) characteristics. Hysteric behavior has been utilized to show rewritable memory effect. Furthermore, once electrical state (high or low conduction state) is set, the state is stable for months in ambient condition unless the state is reset by applying a voltage of opposite polarity. Thus the PPy film can be used as read once memory. The memory effect of the film is due to the conformational changes of non-conjugated polymer chains in the PPy matrix. The changes in conformation were confirmed from UV–Vis and FTIR spectra. This new strategy leads free-standing film based all organic polymer memory devices at ultra low cost.

1. Introduction

The immense interest in the research of polymer memory materials is due to the possibility of realizing flexible memories, even printed electronics on flexible substrate like paper and polyethylene terephthalate (PET) for next generation low cost flexible and portable devices [1–3]. Generally, polymer memory devices consist of polymer layers sandwiched between two metal electrodes showing at least two conduction states under external electric field (resistive random memory, RAM) [1]. In practice, polymer layers of different structures are used such as composite of inorganic nanoparticles and polymer layers, bilayer of two different polymers or tri-layers stack where nanoparticle are embedded between two polymer layers [4]. Among other structures, the composite of nanoparticles and polymer have been received the considerable attention because such hybrid polymer layers show non-volatile memory effects and nanosecond writing time [1,2]. For example, such behaviors are shown in Cu/poly(3-hexylthiophene)/Al, Al/polystyrene (PS) + Au NPs/Al device, tri-layers stack of organic/nanoparticles/organic single polymer layer (Al/AlDCN/Ag), the composite of CdSe/ZnS nanoparticles embedded conducting poly(N-vinylcarbazole) polymer layer on flexible polyvinylidene difluoride and polyethylene terephthalate substrates [1,2,5,6]. The memory effects in such polymer devices arise from changes in conductivities (two conduction states) under electric field (RAM) due to the presence of nanoparticle in polymer matrix [1,6]. Thus composition and distribution of nanoparticles in such systems need to be properly controlled during fabrication. Moreover, the fabrication of

* Corresponding authors. Tel.: +91 25593911.
E-mail addresses: shankarkoiry@gmail.com (S.P. Koiry), dkaswal@barc.gov.in (D.K. Aswal).

1566-1199/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.orgel.2013.08.009

such devices involves more than single step such as layer by layer deposition, incorporation of nanoparticles in polymer matrix. Therefore, the most preferred device structure is the single-layer-polymer based RAM which has been shown using single layer of polyfluorene derivatives in metal organic semiconductor structure [1,7]. Polyfluorene derivative has been synthesized by a palladium-catalyzed Suzuki coupling, thereafter, the polymer has been deposited on Si by spin coating for device fabrication [7]. However, if the layer were a free standing polymer film, it would have further reduced fabrication steps. In addition, if the free-standing films are synthesized economical way involving minimum steps and chemicals, the cost of the devices would be drastically reduced too. Till date, design and synthesis of such free standing films are not reported, even though, the driving force in the research of polymer memory is low cost and ease of fabrication [2].

One of the reasons for the non-availability of such films is the poor insight of the memory effect in polymer. However, the effect is broadly explained as trapped states inside the polymer matrix control the flow of the charge which results two conduction states (RRAM). For instance, the two conduction states in metallic nanoparticles embedded polymers arise from charge hopping between nanoparticles [8]. In single layer polyfluorene film, the memory effect has been explained from the filling and de-filling of trap states under bias [7]. Thus, to show memory effect, the free-standing polymer should have defect states which can be accessible by external electric field. We anticipated that the one way to introduce such states in conjugate polymers would be the incorporation of non-conjugated chain in the conjugated polymer matrix during synthesis. Our anticipation is based on the reported dynamic (reversible) localization of an injected charge in the polymer due to structural disorder [9]. For example, such dynamic localization of charge has been reported in a single-polymer chain of MEH-PPV and conjugated polymer nanoparticle of poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) [9–11]. The localization of charge in MEH-PPV has been studied by fluorescence quenching in single-molecule fluorescence spectroscopy, and that in F8BT has been investigated by single-molecule spectroelectro-chemistry. The observed hysteresis of fluorescence intensity in MEH-PPV has been explained from the self-trapping of charge (structural distortion). Similarly, after initial charge injection, the dynamic localization of charge arises in F8BT due to its charging and discharging. Moreover, the hysteresis that observed in many organic field effects transistor measurements is related to dynamic localization of charge [9].

Thus, to explore the possibility of memory effect in free-standing film with defects in it, we considered polypyrrole (PPy) as conjugated matrix because free-standing PPy films have good mechanical flexibility, biocompatibility, good environmental stability, relative ease of processing, and easy tunability of electrical properties [12]. Furthermore, the free-standing PPy can be synthesized in one pot and single step by interfacial polymerization either at liquid/liquid or liquid/air interface [13,14]. Our group has reported the different synthesis methods of freestanding PPy at the interface, for example, PPy films having unique morphologies (i.e. dense base and porous top) have been synthesized using interfacial polymerization at aqueous $FeCl_3$/pyrrole interface [14]. Similarly, a new method has been reported for synthesis of dense and mechanically strong freestanding PPy nanosheets at air/liquid interface using J-aggregate of porphyrin derivative as *in situ* template [13].

In this article, we report the synthesis of free-standing PPy film for re-writable and read only memory (ROM). These memory effects are due to the presence of non-conjugated chains in PPy matrix which are incorporated during synthesis of PPy by the acidic oxidation of 2,2′:5′,2″-terpyrrole at the air/water interface.

2. Experimental section

Pyrrole (98%, procured from Aldrich) distilled under reduced pressure prior to use. Dichloromethane (AR grade), hydrochloric acid (AR grade) were purchased from sigma–aldrich and used as received. Millipore water was used for dilution and washing purposes. Twenty milliliter hydrochloric acid (18%) solution was slowly added to the 20 mL of 0.1 M pyrrole solution in dichloromethane (DCM), and the mixture was kept in a 50 mL beaker. In order to investigate the polymerization mechanism, the absorption spectra were recorded for the samples taken from the aqueous phase (using microsyringe) at different periods.

JASCO, V-530 spectrometer was used for UV/Vis spectroscopy. Fourier transform infrared (FTIR) spectra of the PPy films were recorded using Bruker spectrometer (Vertex 80 V) in reflectance mode at 4 cm^{-1} resolution. Raman spectrum was collected using a microscopic confocal Raman spectrometer (HORIBA JobinYvon, Lab RAM HR) employing a 514 nm laser beam and using 100X objective. For morphological characterization, the freestanding films were imaged using scanning electron microscope (SEM, Model: TESCAN, TS5130MM) and AFM (Multiview4000, Nanonics). For studies the redox activity of the film, cyclic voltammetry (CV) measurements were carried out using PPy film on ITO as a working electrode, the platinum (Pt) plate as counter electrode and the Ag/AgCl wire as the reference electrode, respectively. 0.1 M tetrabutylammonium perchlorate (TBAP) in dichloromethane was used as supporting electrolyte. CV scans were recorded by potentiostat/galvanostat system (model: autolab PGSTAT 30). Frequency response analyses (FRA) were carried using signal of 10 mV and frequency in the range from 50 kHz to 1 mHz by FRA module in autolab PGSTAT 30.

3. Results and discussion

The synthesis of the PPy film was carried out by slowly adding 20 mL hydrochloric acid (18%) solution into the 20 ml of 0.1 M pyrrole solution in dichloromethane (DCM), and the mixture was kept in a 50 mL beaker under a stationary state. It was observed that with passage of time, the color of acid phase progressively changed from transparent to yellowish to dark black (Fig. 1a), and after a period of 5 days, freestanding films formed at air-aqueous interface. Fig. 1b illustrates the main steps involved