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Memory and ferroelectric photovoltaic effects arising from quasi-reversible oxidation and reduction in porphyrin entrapped aminopropyl-silicate films

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ABSTRACT

We report non-zero-crossing bipolar current–voltage characteristics, and ferroelectric photovoltaic-like effects in flexible organosilicate polymer films. These film are composed of 5,10,15,20-terakis(4-hydroxyphenyl)-21H,23H-porphine and 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine embedded in (3-aminopropyl)trimethoxysilane network. The films were prepared on gold coated bi-axially oriented polyethylene terephthalate (BoPET) substrate by sol–gel method. For electrical characterizations, gold (40 nm) was deposited on the film for using as top contact. The current–voltage characteristics of devices, BoPET/gold/film/gold, have shown hysteresis with two current peaks in opposite direction. The open circuit voltage (~±0.8 V) and short circuit current (~±6 μA) that arise from non zero-crossing current–voltage characteristics have been utilized to read the ON and OFF states for non-volatile memory application of the devices. Furthermore, the studies on redox induced polarization in the polymer matrix by charge–voltage, capacitance–voltage, and positive-up and negative-down measurements reveal the characteristics of ferroelectric materials. The photovoltaic behaviors such as short circuit photocurrent were studied under blue LED source after polarizing BoPET/gold/polymer film/gold device by electric field as done for classical ferroelectric materials. The observed memory, ferroelectric-like and photovoltaic effects of organosilicate film were explained from quasi-reversible oxidation and reduction of moisture that diffuse into the film and dissociate to ions under applied electric field. These findings are important for designing new solution processible polymer materials which could find applications in flexible memory, ferroelectric based memory and switchable photovoltaic effects.

1. Introduction

The recent studies on electronic devices reveal that electrochemical oxidation and reduction of solid state devices can induce novel electronic properties which otherwise are beyond imagination [1–11]. The examples include memory and ferroelectric-like effects in redox switching devices which are composed of neither magnetic nor ferroelectric materials [1–11]. The redox switching memory devices have metal–insulator–metal (M–I–M) structures with I being metal oxides such as TiO_2, SiO_2, etc. [3–5]. These memory devices work on the principle of the changes in resistance under applied electric field. The most accepted mechanism is based on the resistance changes because of the dissolution of metal ions due to the oxidation of electrochemically active metal electrode such as Cu and Ag. These metal ions on positive bias form filamentary current leading to the lowering of resistance i.e. ON state. The reduction of metal ions annihilates the metal-like filament resulting in an increase of resistance i.e. OFF state [6,7]. In $Ag/SiO_2/Pt$ devices, Valov et al. have demonstrated bipolar switching characteristics which they attributed to Ag^+ ions and OH^- ions, within the SiO_2 film [3]. These ions are generated within the SiO_2 films owing to the dissociation of absorbed moisture in the film and the electrochemical oxidation of Ag during switching cycles [3]. As a result, these devices exhibit an open circuit voltage (OCV) in hundreds of mV and a short circuit current (Jsc) in hundreds of pA [3]. It has been suggested that OCV could be useful to read ON/OFF states of a devices as ON states are set by one polarity voltage and OFF states are reset by reversed polarity voltage [3]. Redox induced other phenomena, such as memcapacitive, memresistive and meminductive effects, have also been reported in a single

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redox switching Pt/TiO_2/Pt device [10]. These three memory components that exist in a single device could find applications in cellular neural networks and neuromorphic implementations [10]. Moreover, redox based switching devices are emerging as a strong contender for next generation memory applications due to their capability to meet the present major challenges of memory technology including scalability, high operational speed and low operational voltage as discussed in International Technology Roadmap of Semiconductor (ITRS) report-2013 [2].

Another intriguing effect generated by the redox phenomenon is the appearance of ferroelectric-like properties in non-ferroelectric materials [11]. For example, TiO_2 (a non-ferroelectric material) exhibited electromechanical activity, remanent polarization and hysteresis loops during scanning probe microscopy studies due to electrochemical phenomenon [11]. These results add new dimension to the redox switching devices. If redox induced ferroelectric-like properties could be found in non-ferroelectric materials, these would have immense potentials to be used in futuristic low-powered memory applications [12,13]. However, these materials should have easy processibility and flexibility because the existing ferroelectric materials are not environmental friendly and have limited processibility and flexibility making these materials unsuitable for next generation low powered portable, flexible devices [12]. To meet these requirements for next generation ferroelectric-like materials, the use of polymer materials is one of the suitable options because the polymers have easy processibility and flexibility [12,14]. However, organic ferroelectric materials are not abundant, and therefore demand the new concepts and design for synthesis of new polymer materials exhibiting ferroelectric-like characteristics [12]. Thus this work deals with redox switching based ferroelectric-like properties in polymer by mimicking the redox switching nature of inorganic materials. In this case, replicating SiO_2 is a viable option as this could be achieved from organosilicate polymers having —O—Si—O— network. Such polymers are good conductors of protons (H^+ and OH^-) that could be generated by dissociation of water in the film [15,16]. These protons could be explored for resistive switching analogous to SiO_2-based ReRAMs, where OH^- ions are involved in redox process [7,9].

In this paper, photoactive organosilicate polymer films were prepared on gold coated bi-axially oriented polyethylene terephthalate (BoPET) substrate by sol–gel method. The polymer film is composed of 5,10,15,20-terakis(4-hydroxyphenyl)-21H,23H-porphine (THPP) and 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine (TPyP) embedded in (3-aminopropyl)trimethoxysilane (APTMS) network. The current–voltage (*I–V*) characteristics of the films sandwiched between gold electrodes show bipolar and non-zero-crossing behaviors due to quasi-reversible oxidation and reduction of moisture in the polymer matrix. We observed the OCV (~±0.8 V) and Jsc (~±6 μA) in such devices which have been utilized to read the ON and OFF states for non volatile memory characterization of the devices. Furthermore, the redox induced polarization in the polymer matrix has been investigated for ferroelectric photovoltaic effects.

2. Experimental

2.1. Synthesis of organosilicate polymer composite

50 μL of 1 mM THPP (Sigma–Aldrich) in methanol, 1 mM of TPyP (Sigma–Aldrich) in chloroform were added to APTMS (Sigma–Aldrich) in 1:1:0.2 ratios (v/v). After the blend was mixed thoroughly, a drop was made on gold coated (50 nm thick) bi-axially oriented poly terephthalate (BoPET) substrate. The drop was allowed to air dry which first formed liquid gel then to solid (<40% relative humidity).

2.2. Characterization techniques

The films were characterized by JASCO, V-530 spectrometer for UV/Visible spectroscopic studies. Fourier transform infrared (FTIR) spectra of the films were recorded using Bruker spectrometer (Vertex 80 V) in reflectance mode at 4 cm^{-1} resolution. For morphological characterization, the films were imaged using scanning electron microscope (SEM, Model: TESCAN, TS5130MM). For studying the redox activity of the film, cyclic voltammetry (CV) measurements were carried out using the film deposited on gold coated BoPET as a working electrode, the platinum (Pt) plate as counter electrode and the Ag/AgCl wire as the reference electrode, respectively and 0.1 M tetrabutylammonium perchlorate (TBAP) in methanol as the supporting electrolyte. The reference electrode was prepared by depositing AgCl on Ag wire from 1 mM HCl at 1 mA for 900 s. CV measurement were also carried out for the solution of THPP and TPyP, where working electrode was bare gold coated BoPET, and rest was same as for the film. The CV scans were recorded by potentiostat/galvanostat system (model: Autolab PGSTAT 30). The thickness of films was measured by Veeco DEKTAK 150 Profilometer.

The polarization characteristics, (polarization vs. voltage) were carried out using a ferroelectric tester (Easy check 300, aixACCT system GmbH, Germany) by administrating triangular signals of amplitude (1–3 V) and frequency from 1 to 100 Hz. The change of capacitance with voltage was measured using signals of 10 mV and frequencies ranging from 50 kHz to 1 mHz by frequency response analyzer (FRA) module on Autolab PGSTAT 30. Current–voltage characteristics (Kiethely electrometer) were measured by cycling the voltage in ambient condition and inside Mbruan make glove box (atmosphere, 1 ppm oxygen and moisture). For electrical characterization in humid atmosphere, a carrier gas (O_2 or N_2) was bubbled through water and was introduced into chamber in which samples were kept. The relative humidity of the chamber was monitored by hygrometer that was installed inside the chamber.

All the measurements were carried out at room temperature unless it is mentioned. Photovoltaic measurements were carried out using Sciencetech SolarSimulator (Model SS-150) under uniform intensity of 100 mW cm^{-2}. The different light sources of 5 mW cm^{-2}, blue, red, amber and green LEDs were Luxeon make.

3. Results and discussion

3.1. Characterization and explanation

To design the experiment, our main aim was to investigate bipolar switching characteristics in the solid state electrochemically active film analogous to SiO_2. Moreover, the preparation of such films should be simple and easy. Therefore, we chose APTMS which polymerize to aminosilicate polymer films in ambient conditions [17]. In general, acid-base is used as catalysis for the polymerization of APTMS [18,19]. In present case, we chose light absorbing and environmentally stable acidic and basic molecules, THPP and TPyP. THPP can donate proton and TPyP accepts proton so that these protons donating/accepting capacity would facilitate the interaction of these molecules with APTMS network in addition to their catalytic behavior [18,19]. The molecular structures of THPP and TPyP are shown in Fig. 1(a).

Briefly, the formation of APTMS film involves following reactions—silanols (Si—OH) are formed by hydrolysis of methoxy group in the presence of atmospheric moisture which then reacts with other such silanols to form Si—O—Si network [20,21]. The amino