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Electrical bistability studies on vacuum evaporated copper phthalocyanine (CuPc)/fullerene (C_{60}) bilayers

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ABSTRACT

In this paper, electrical bistability of ITO/copper phthalocyanine (CuPc)/fullerene (C_{60})/Al structure for organic memory applications was studied. X-ray diffraction studies on the deposited film showed crystallinity with a major peak (100) for CuPc. It was seen that the stored conductivity state was rather stable in ITO/CuPc/C_{60}/Al for use in organic memory cells. ON/OFF resistance ratio of around 10^5 was obtained for the CuPc/C_{60} device. Electrical bistability of this CuPc/C_{60} bilayer device was explained on the basis of filling of the traps and double injection.

1. Introduction

Due to the excellent electrical properties exhibited by metal phthalocyanines [1], the use of phthalocyanine thin films has been increasingly interested for organic electronics such as organic light emitting diodes (OLEDs) [2], organic solar cells [3] and organic field-effect transistors and sensors [4,5]. Most frequently used metal phthalocyanine for organic electronics devices is copper phthalocyanine (CuPc) as it is a stable compound. Main uses of CuPc films have been as a hole injection layer in OLEDs [6], a light absorption and hole transport layer in organic solar cells [7] and a p-type active layer in OFETs [8]. CuPc has been used as a p-type organic semiconductor or hole transport material, even though polycrystalline CuPc films have been known to show similar values for hole and electron mobilities of the order of 10^{-4} cm^2/V for both carrier types [9]. CuPc exhibits low conductivity ranging from 10^{-10} to 10^{-11} S/cm under nitrogen or hydrogen ambient. On the other hand, as absorbed oxygen acts as an acceptor, conductivity of the CuPc films increases and it has been confirmed that polycrystalline CuPc films behave as a p-type semiconductor with negligible conduction by electrons [10]. Phthalocyanines (Pcs) are small organic molecules characterized by their high symmetry, planarity and electron delocalization. Besides, Pcs can be easily sublimed in high vacuum systems resulting in high-purity thin films with excellent growth properties and chemical stability, taking into account that the use of the sublimation technique allows the deposition of thin films with controlled thickness and structural properties. Due to their thermal stability, chemical inertness, high molecular symmetry and favorable optical properties, MPcs (metal phthalocyanines) are of great scientific and industrial interests [11].

A device exhibiting two states of different conductivities, at the same applied voltage can be referred to as electrical bistability. A memory device is composed of organic materials sandwiched between two electrodes possessing at least two stable resistance states which are controlled by an external electrical stimulus. With the advent of thin-film technologies, electronic functionality can be anticipated at very low cost and in very large quantity on substrates such as plastic and paper. Device resistance states can be read without causing any damage to the device and electrical power is not required for the maintenance of the states, which signifies it to be a nonvolatile memory [12–14]. Moreover, the fundamental requirements for a high performance memory, such as a high ON/OFF

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ratio, long endurance and retention characteristics and a fast switching speed have been experimentally confirmed [15,16]. Even though it is complicated to identify the device operating mechanisms, in detail studies of charge conduction mechanisms have contributed to the device physics that brings about the switching phenomena. To improve the device performance, structural and electrical optimizations [17,18] have also been applied successfully. Organic materials have attracted considerable attention in many areas such as organic thin-film transistors (OTFTs) due to their potential application in low-cost, flexible, large area and lightweight organic electronics [19–26], organic light emitting diodes [27–29] and organic photovoltaic cells [30–32] with a remarkable advancement during the last few years. Organic nonvolatile memory has experienced a rapid development recently as a key component for organic integrated circuits. These types of polymer memories are expected to meet the demand for data storage in memory for use as smart label or RFID tags. Two-terminal memory devices have the advantage of a simple process and high-density storage. Most of the reported organic memory devices adopted a two-terminal structure with the active medium (triple layer or single layer) sandwiched between two electrodes. To obtain high-density storage, two-terminal memory devices are mostly fabricated with a cross-point array structure. However, the cross-talk phenomenon appears simultaneously. Investigation of the organic memory integrated circuit has provided a solution for this. Electrical bistable characteristics by CuPc device have been demonstrated by Onlaor et al. [33]. for devices with an active layer deposited at different deposition rates and the study suggested that the stored conductivity state was stable. Organic nonvolatile memories find applications in the next-generation portable devices with a reproducible performance despite of cyclic bending. Organic memories may also provide an alternate technology to the conventional memory technologies and hence investigations in this direction are growing rapidly. Bozano et al. [34] in their study of non-volatile solid state memory cells based on composites of metal nanoparticles and polymers suggested that the organic semiconducting material CuPc when used as a host produced switching devices. A detailed review of the different types of organic memory nanoparticle devices and admixture structures was reported [35]. C_{60} was found as a suitable combinational layer with several polymer composites like polyvinylphenol (PVP), poly vinyl alcohol (PVA) and polymethyl methacrylate (PMMA) due its large electron affinity [36]. Besides, CuPc is the most popular and standard phthalocyanine used due to its low cost and remarkable chemical and thermal stability. With a planar molecular structure, CuPc exhibits electron delocalization and a high symmetry [37]. Although copper phthalocyanine (CuPc) is one of the most studied p-type organic semiconductors, few studies have addressed its electrical bistability. In this paper, we report some preliminary bistability studies on a CuPc-C_{60} interface layer for use as a memory cell.

2. Experimental section

A schematic representation of the bistable device Glass/ITO/CuPc/C_{60}/Al layered structure used in this work is shown in Fig. 1.

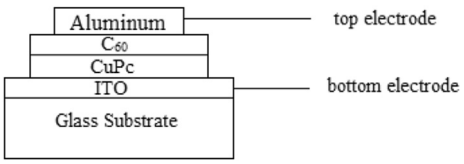

Fig. 1. Device architecture for Glass/ITO/CuPc/C_{60}/Al memory device.

Photo-lithographically patterned indium tin oxide (ITO) coated glass substrates were used for deposition. All the chemicals for ITO etching were imported from AZ (Germany). Prior to loading into the evaporation chamber, substrates were cleaned ultrasonically and then dried. Pure CuPc powder used in this work was purchased from Sigma Aldrich and no further purification was done. Films were prepared by a thermal evaporation technique in a vacuum of 10^{-6} Torr (Hind Hivac model 12 A4). Deposition rates and thicknesses of the films were controlled and measured using a digital quartz crystal thickness monitor. For ITO/CuPc/C_{60}/Al device, a 90 nm CuPc (deposition rate of 2 nm/s) along with a 50 nm C_{60} (deposition rate of 1 nm/s) sandwiched between a 100 nm aluminum top electrodes (pad size 3 mm × 3 mm, device area 9 mm^2) and bottom ITO electrode was used. Active layers were deposited from molybdenum boats and Al was deposited using a tungsten basket. Structure and purity of the CuPc films were verified using X-ray diffraction (XRD) technique and optical band gap of CuPc film was determined by optical transmission. X-ray diffraction studies on the deposited films showed crystallinity and a major peak with preferred orientation for CuPc. In the XRD pattern in Fig. 2 for CuPc thin film, *hkl* value was assigned for the main peak with preferred orientation of 2θ at 7° (100) [38] with interplanar distance d of 1.26 nm. Optical band gap for the CuPc film as calculated from the transmission spectrum was around 2.2 eV. All the electrical measurements were done using an Agilent 4339B high resistance meter, a lab tracer test integration software and a Keithley 2400 source measuring unit in the two probe measurement mode. From the electrical measurements, ON and OFF states of the retention characteristics for the device were also studied.

3. Results and discussion

3.1. Bias switching

Resistance state changes from high resistance to a low resistance by a current voltage measurement in a voltage sweep mode yielding the ON and OFF states of a memory device generally referred to as bias switching. OFF to ON state (forward cycle) is considered as the write cycle and the ON to OFF (reverse cycle) as a read cycle for a digital memory cell. Applying a negative voltage to the device yields an erase cycle equivalent to the erasing process in a digital memory cell or makes the device rewritable. Fig. 3 shows current–voltage (*IV*) characteristics for the CuPc/C_{60} memory

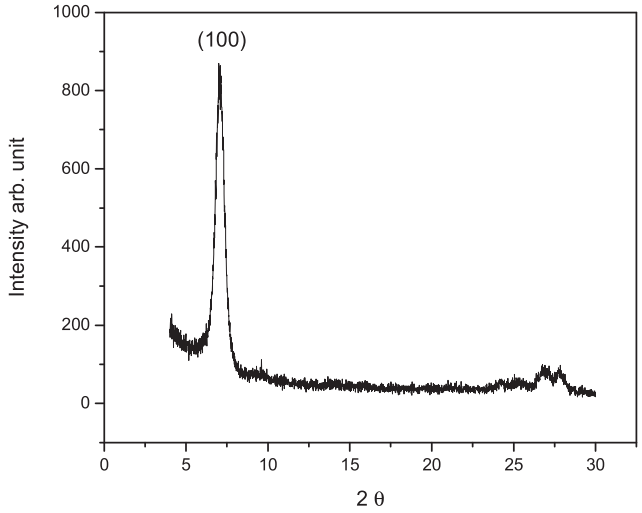

Fig. 2. XRD pattern for CuPc thin film.