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Electrical bistable properties of copper phthalocyanine at different deposition rates

K. Onlaor *, B. Tunhoo, P. Keeratithiwakorn, T. Thiwawong, J. Nukeaw

Electronics and Control System for Nanodevice Research Laboratory, College of Nanotechnology, King Mongkut's Institute of Technology Ladkrabang, Chalongkrung Road, Bangkok 10520, Thailand
Thailand Center of Excellence in Physics, Commission on Higher Education, Ministry of Education, 328 Si Ayutthaya Road, Bangkok 10400, Thailand

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ABSTRACT

Organic bistable memory device is a next-generation of the electrical memory unit. In this paper, we report about the influence of structural properties on electrical bistable behavior of copper phthalocyanine organic memory device. Copper phthalocyanine (CuPc) layer was prepared by thermal evaporation technique at different deposition rates. When the deposition rate is increased, the film crystalline decreases and the surface morphology gradually changes from large flat grain to fine grain structure. Structural parameters such as the crystalline size of CuPc films and dislocation density can be calculated from XRD spectra. Moreover, the effect of deposition rate of CuPC layer on the bistable properties can be performed by current–voltage characteristics, retention measurement, impedance spectroscopy and temperature dependence measurement. The conduction mechanism in both ON and OFF states of the bistable device was analyzed by theoretical model, which can be proposed as a possible trap center of the carrier trapping and de-trapping process by structural defects in CuPc layer. Furthermore, the reliability issue such as cycling endurance and data retention is presented.

1. Introduction

Recently, several works have been done in the field of organic semiconductor electronic devices such as light-emitting diodes, field-effect transistors and solar cells [1–3], etc. There have shown great potential towards future technologies. One of the promising organic devices is the organic memory device. The electrical bistable phenomenon of the metal–insulator–metal (MIM) diodes with organic material as the insulator layer has been first reported by Gregor in 1968 [4]. Interest in the organic bistable device (OBD) has rapidly increased due to promise of a next-generation memory device. The major advantage of OBD has been studied intensively because of their merits of simple device structure, simple fabrication process, low power and low cost. The basic feature of an OBD is to exhibit bistable behavior having two different conduction states at the same applied voltage. During the device operation, when applied voltage exceeds a certain value. The device suddenly switched from a low conductivity state to a high conductivity state, with a conductivity difference of several orders of magnitude. Since then similar phenomena have been observed in a variety of organic materials and device structures [5–7], including both polymer and small-molecule MIM devices [8,9], donor–acceptor complex devices [10] and nanoparticle blend device [11]. In addition, several mechanisms have been proposed to explain the conductance switching such as formation of conducting filaments [8,12], formation of charge transfer complexes [13] charge-trapping-defect states inside the band gap [14] and change of molecular orientation [15]. However, the switching mechanism is still a matter of debate.

Phthalocyanine (Pc) is a class of organic semiconductor with alternate single–double bond structure. Metallophthalocyanines (MPcs) are planar phthalocyanine organic molecules associated with one metal atom in the molecule's center, and typically, the central atom is one in the first row of transition metals such as copper, cobalt and iron. The core structure of the MPc macrocycle was formed by four isoindole units, which endows the molecule with a two-dimensional conjugated π electron system [16]. The MPcs are found to exhibit conductive properties. Therefore, an attempt has been made to use the MPcs in electronic devices such as organic-light emitting diodes (OLED) [17] and organic solar cells [18]. CuPc is a member of MPcs family with the central atom as Cu^{2+}. CuPc is a dark-blue material. The CuPc has been interested for its gas sensing property [19] and the schottky diode solar cells [3]. Many of these applications are based on the electrical properties and detailed understanding of the some requires an accurate knowledge of molecular as well as crystal structures. Dependence of crystal structure becomes more significant if the compound exists in more than one crystalline modification. Depending on the preparation parameters, the phthalocyanine films have been reported being composed of many different polymorphs [20,21].

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* Corresponding author at: College of Nanotechnology, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand.
E-mail address: korakot.onlaor@gmail.com (K. Onlaor).

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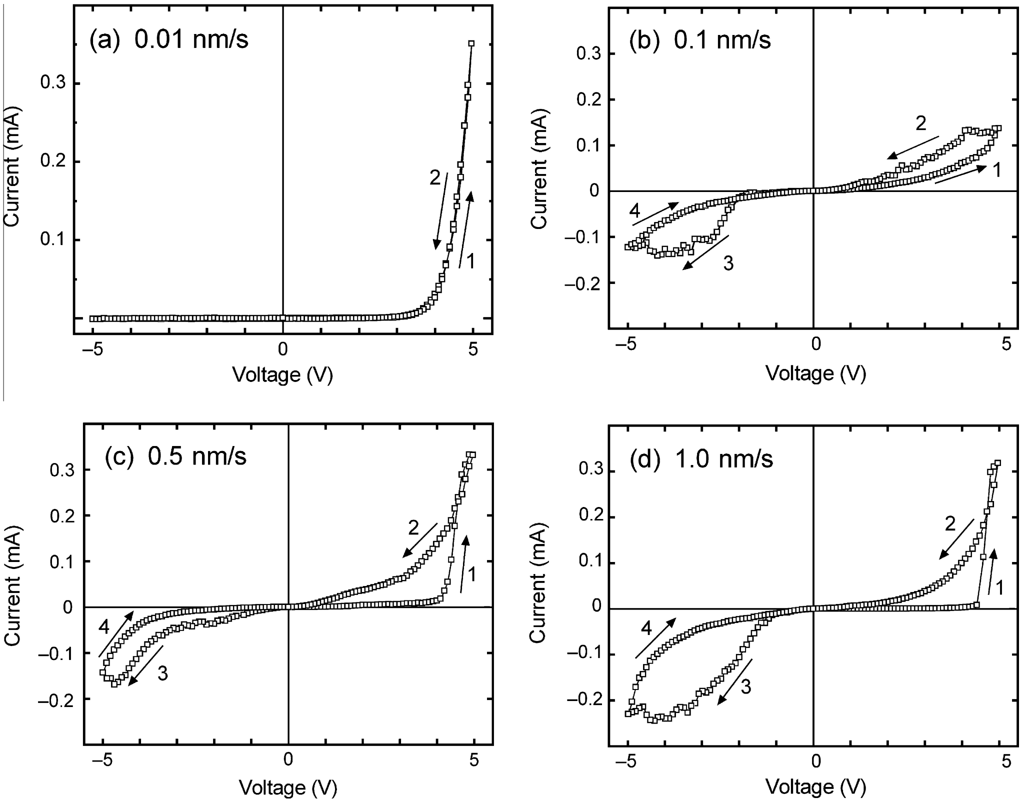

Fig. 1. *I–V* characteristics of CuPc bistable device with different deposition rate of CuPc layer at (a) 0.01 nm/s, (b) 0.1 nm/s, (c) 0.5 nm/s and (d) 1.0 nm/s.

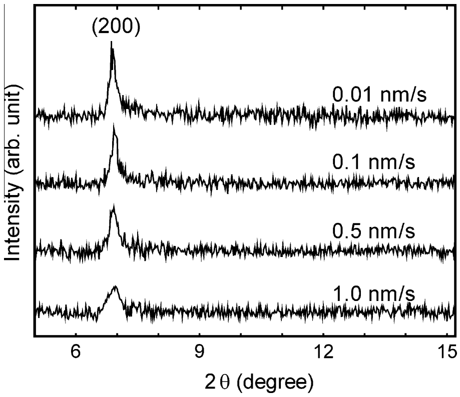

Fig. 2. XRD patterns of CuPc films deposited on glass substrate at fixed film thickness of 100 nm for deposition rate of 0.01 nm/s, 0.1 nm/s, 0.5 nm/s and 1.0 nm/s.

Table 1
Structural parameters (crystalline size, dislocation density and lattice microstrain) of the CuPc films deposited at different deposition rates with fixed film thickness of 100 nm.

Deposition rate (nm/s)	*D* (nm)	*d* (10^{14} lin m^{-2})	*e* (10^{-3} lin^{-2} m^{-2})
0.01	67.70	2.18	2.28
0.1	59.22	2.85	2.61
0.5	39.22	6.50	3.94
1.0	26.41	14.34	5.86

Here, we report on the fabrication of the CuPc bistable device with MIM structure at different deposition rate of CuPc layer. The electrical characteristics of the CuPc bistable devices were investigated by current–voltage measurement. The influence of deposition rate on the structural properties of the CuPc films can be observed with X-ray diffraction pattern and surface morphology measurement.

2. Experimental

The CuPc bistable device was glass/ITO/CuPc/aluminum (Al) structure. Indium tin oxide (ITO) conducting glass with sheet resistance of 10 Ω/□ is used as a substrate. Prior to loading into evaporation chamber, substrates were cleaned using ultrasonic bath of deionize water, acetone, methanol, isopropanol for 15 min and dried with nitrogen gas, respectively. The CuPc powder used in this work was purchased from Aldrich Chem. Co. (purity >97%) and used without films adopted in this study are prepared by thermal evaporation technique with a base pressure of 2×10^{-6} mbar for both substrates. The deposition rates and thickness of CuPc films were controlled and measured by a thickness controller (Inficon, XTC2). The deposition rate was varied with 0.01 nm/s, 0.1 nm/s, 0.5 nm/s and 1.0 nm/s, respectively, while the thickness of CuPc films was fixed at 100 nm. For ITO/CuPc/Al devices structure, a 100 nm aluminum top electrode with 2 mm × 2 mm was prepared on CuPc layer by thermal evaporation. Therefore, the device had an area of 4 mm^2. The device fabrication has been done in a 10 *k*-class clean room. The crystalline structure of CuPc films was studied using X-ray diffraction (XRD) technique (Bruker, D8 Explorer) with Cu Kα radiation source ($\lambda = 0.1542$ nm). Surface morphology of CuPc films was investigated using an atomic force microscope (AFM), (SEIKO, SPA400), in non-contact mode. A precision LCR meter (Agilent, E4980A) was used to measure the current–voltage characteristics, impedance characteristics and to monitor the current during the temperature-dependent measurement under a dark condition. For the retention abilities and read/write cycles