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Effect of vacuum annealing on evaporated pentacene thin films for memory device applications

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ABSTRACT

Thin films of pentacene were deposited thermally onto glass substrates and annealed at 323 K, 373 K, 423 K, 473 K and 523 K in high vacuum. Effect of annealing on the morphological and structural properties of these films was studied. X-ray diffraction patterns confirmed the crystalline nature of the films. Electrical studies for the use as write once read many (WORM) memory devices were done for the vacuum deposited pentacene thin films on indium tin oxide coated glass. Due to annealing, a sharp increase in the ON/OFF ratio of current and a decrease in threshold voltage were observed at around 373 K. This device showed a stable switching with an ON/OFF current ratio as high as 10^9 and a switching threshold voltage of 1.35 V. The performance of the device degraded above 423 K due to the changes in the crystallinity of the film.

1. Introduction

Recent progress in the application of organic materials in electronics has attracted a great deal of attention due to its low cost in fabrication, flexibility, biodegradability and light weight. Among the currently used organic materials, pentacene ($C_{22}H_{14}$) is proved to be a promising candidate for solar cells [1–5], thin film transistors [6–8], photo detectors [9] and memory devices [10–12] due to its polycrystalline morphology, large carrier mobility, small optical band gap, long exciton diffusion length and strong absorption in the visible region of solar spectrum. Pentacene is an organic semiconductor consisting of five π-conjugated aromatic benzene rings as shown in Fig. 1. The triclinic structure of pentacene thin films was first reported in 1961 [13]. Four different crystalline phases were identified and reported for pentacene thin films [14]. In all of these phases, pentacene molecule was expected to adopt a herring-bone-type arrangement in the resulting two dimensional layers. Different d-spacing perpendicular to the thin film surface with values of 14.1 Å, 14.5 Å, 15 Å, 15.4 Å were observed. The relative concentration of these phases seems to be strongly dependent upon deposition conditions. When pentacene is deposited on an insulator surface, XRD shows a diffraction at d (001) = 15.4 Å for the metastable or α phase. By heat treatment or by immersing in organic solvents, this phase can be converted into another stable phase with d (001) = 14.4 Å. The first one is metastable or thin film phase or α phase and second one is stable or bulk crystalline phase or β phase.

High density non-volatile memory devices have attracted a lot of attention for the storage of multimedia. Yang et al. [15] reviewed the developments in organic non-volatile memory devices. Organic electrical bistable devices and its applications were also reported in this review. Ma et al. [16] reported an approach to achieve the non-volatile memory effect by controlling the Cu+ ion concentration within the organic layer interposed between two metal electrodes. They demonstrated an organic non-volatile memory device by controlling the Cu+ ion concentration within the active organic layer. Pentacene based bistable memory device using Fe as the top electrode was also reported earlier [11]. They compared the device with Al electrode and suggested that Fe has the advantage over Al as it lowers the switching threshold voltage. Organic electrical memory devices with a simple structure based on a single layer pentacene film embedded between Al and ITO electrodes for different deposition rates of pentacene were studied and the performance of this reliable device with a high ON/OFF current ratio was reported [12]. There are many organic materials that are being used as memory device elements that provide fast, non-volatile memory device with high density data storage, high writing/reading stability and long retention time [17–22]. Several conduction mechanisms were also reported to explain the conductance switching mechanism in these devices.

Several factors influence the performance of organic memory devices like substrate surface treatment, substrate temperature,

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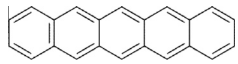

Fig. 1. Chemical structure of pentacene.

level of impurities, depositing conditions, film morphology, molecular packing in ordered regions and carrier mobility of the active layer. Thermal annealing is found to improve the solar cell efficiency of pentacene-based solar cells due to increase in crystallinity and reduction of defects [23]. In order to understand the effect of thermal annealing on the electrical bistability of pentacene devices, we fabricated a WORM memory device with vacuum evaporated pentacene on ITO coated glass substrate with Al as the top electrode and compared the device properties for different annealing temperatures.

2. Experimental section

Thin films of pentacene (99.999% source powder purchased from Aldrich) were thermally deposited onto chemically cleaned glass substrates in a vacuum of around 2×10^{-6} Torr using a Hind hivac coating unit (Model No. 12A4D). For the devices, films were coated on pre-cleaned ITO coated glass substrates kept at room temperature. The distance between the evaporation source and the substrate holder was about 13 cm. Source material was evaporated from a molybdenum boat at a deposition rate of 10 Å/s to get a thickness of around 90 nm. Thermal annealing of this pentacene layer was done in a vacuum of around 10^{-6} Torr at different temperatures like 323 K, 373 K, 423 K, 473 K and 523 K for 10 min and slow vacuum cooled to maintain the crystallinity. Finally, Al pads were deposited thermally at a deposition rate of 20 Å/s from a tungsten basket to complete the device with a structure shown in Fig. 2. Deposition rates and thicknesses of the thin films were controlled by a digital quartz crystal thickness monitor. Structure of the fabricated device was glass/ITO/pentacene (10 Å/s, 90 nm)/Al (150 nm). Overlap of the electrodes defined the dimensions of the memory cell as 9 mm^2. Electrical measurements of the fabricated device were measured using a Keithley 2400 source meter and an Agilent B1500A semiconductor device analyzer. Structural studies were done using a Rigaku X-ray diffractometer. All the electrical tests were conducted at ambient conditions, without any device encapsulation and the measurements were done with a probe diameter of around 14 μm.

3. Results and discussion

3.1. Structural and morphological studies of pentacene thin films

XRD patterns of the pentacene thin films obtained at different annealing temperatures are shown in Fig. 3(a) and (b). These

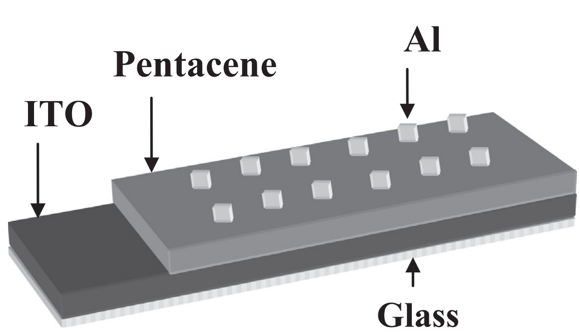

Fig. 2. Schematic view of the fabricated pentacene device.

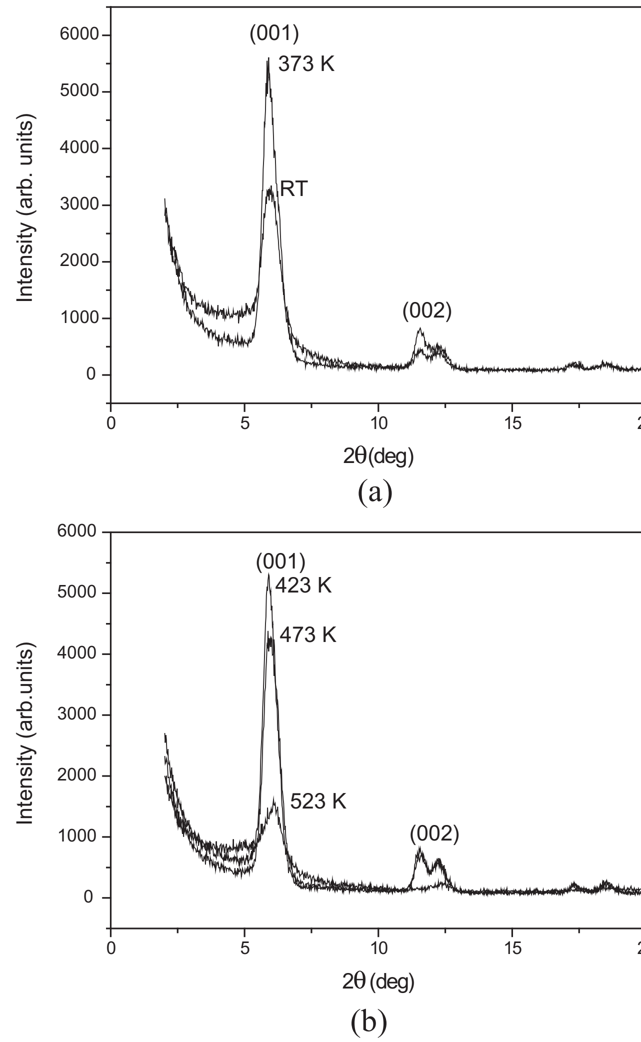

Fig. 3. X-ray diffraction patterns of pentacene thin films (a) deposited at room temperature and annealed at 373 K, (b) annealed at 423 K, 473 K, and 523 K on glass substrates.

XRD patterns exhibit crystalline nature with the major diffraction peaks indexed and matched with the previous results [24,25]. Reported studies of pentacene thin films revealed the existence of two to four polymorphs [24]. One is a thermodynamically stable phase called "bulk phase" and the other one, a metastable phase called "thin film phase" in two polymorph case. But for our samples, such polymorphs were observed with a second diffraction peak (0 0 2) for higher annealing temperatures of 373 K, 423 K and 473 K. Table 1 gives the lattice parameters calculated from the XRD patterns. From the XRD patterns, the first order diffraction peaks are observed at around 2θ = 5.9° corresponding to triclinic

Table 1
Lattice parameters of pentacene thin films vacuum annealed at different temperatures.

Annealing temperature (K)	2θ (deg)*	d_{001} (Å)*	Crystal particle size D (Å)
Pentacene: RT	5.94	14.9	141
373	5.90	15.0	144
423	5.92	14.9	150
473	5.88	15.0	143

* 2θ-values corresponding to the peaks, d_{001} (interplanar distance) was calculated for λ = 1.5406 Å.