Effects of The Acceptor Conjugation Length and Composition on the Electrical Memory Characteristics of Random Copolyimides

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Introduction

For resistive type memory materials, electron donor-acceptor (D-A) polyers were thought to be useful because of the conductivity change comes from charge-transfer (CT) phenomenon between donor and acceptor moieties[1]. Amoung all, functional D-A polyimides (PIs) were thought to be the most suitable candidates due to their good electrical properties, excellent thermal stability, mechanical strength durability, and structural design flexibility[2]. Despite the memory properties of PIs are extensively reported, establishing a clear design concept to modulate volatility properties of memoy behavior were still limited. By introducing a material with long conjugation and high electron affinity (Perylenebisimide, **PBI** for example) to a D-A PI complex, memory properties shifted from original volatile dynamic random access memory (DRAM) to a nonvolatile write once read many (WORM) characteristic in our previous report[3]. In this study, smaller conjugated moieties (naphthalene and pyromellitic diimides) were selected for further investigation.

Results and Discussion

Resistive-switching memories based on copolyimides (coPIs), **PI-NTCDIX** and **PI-BTCDIX**, with different compositions of 4,4'-diamino-4''-methyltriphenylamine (**AMTPA**), 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (**6FDA**), and *N*,*N*'-bis-(4-aminophenyl)-1,8:4,5-naphthalenetetracarboxydiimide (**NTCDI**) or *N*,*N*'-bis-(4-aminophenyl)-1,2:4,5-benzenetetracarboxydiimide (**BTCDI**) have been developed (**Scheme 1**). By varying the feed ratio of monomers, **PI-NTCDIX** and **PI-BTCDIX** showed tunable optical and electronic properties through the charge transfer (CT) between **AMTPA** and **NTCDI** or **BTCDI**. Memory devices were fabricated on glass substrates with the configuration of Al/polymer/Al (cross-point, **Figure 1**). The memory devices based on **PI-NTCDIX** exhibited tunable electrical bistability from volatile dynamic random access memory (DRAM, **Figure 2**) to nonvolatile write once read many (WORM, **Figure 3**) memory characteristics as the **NTCDI** composition increased. The electrical switching transition was mainly attributed to the CT mechanism analyzed by Gaussian 03 calculation with density functional theory (DFT). Also, the volatility of the memory device depended on the stability of CT complex. The long conjugation and high electron affinity of the **NTCDI** moiety stabilized the radical anion generated in the CT complex and prevented the recombination of segregated radical species even through applying the high positive or negative voltage. On the other hand, the memory devices based on **PI-BTCDIX** showed a rather unique behavior compared to those based on **PI-NTCDIX**. At the low **BTCDI** composition, the device exhibited volatile memory property. However, no switching behavior was observed at the high **BTCDI** composition due to the low laying HOMO level of **BTCDI** **(Figure 4)**. Combining these results and our previous study on perylenebisimide (**PBI**), we concluded that memory characteristics could be tailored by changing the conjugation length (**PBI** > **NTCDI** > **BTCDI**) and the acceptor composition in random copolyimides .

Conclusions

We have successfully designed and synthesized random coPIs, **PI-NTCDIX**, **PI-BTCDIX**. The resulting memory properties of the coPIs varied with the loading ratio of **NTCDI** or **BTCDI**. For the case of **PI-NTCDIX**, the memory characteristics transited from volatile DRAM (**PI-NTCDI1**) to nonvolatile WORM (**PI-NTCDI5** and **PI-NTCDI10**), where **PI-NTCDI2.5** showed a transition between DRAM and WORM type memory properties. Meanwhile, **PI-BTCDIX** based memory device exhibited the volatile memory characteristic at a low **BTCDI** composition (**PI-BTCDI1** and **PI-BTCDI2.5**) and no switching behavior was observed at a high **BTCDI** composition (**PI-BTCDI5** and **PI-BTCDI10**). By combining the results of our previous report, the effects of the conjugation length of the acceptor moiety (**PBI** > **NTCDI** > **BTCDI**) to the resulted memory characteristics were fully studied. The stable CT complex was obtained through stabilization of the radical anion by means of long conjugation and high electron affinity of the **NTCDI** and **PBI** moieties, leading to nonvolatile WORM memory characteristics. On the other hand, due to the low HOMO energy level of the **BTCDI** unit, a large energy barrier which prevents the hole injection from the Al electrode to the polymer was generated, resulting in no switching behavior at a high **BTCDI** composition. The study revealed the composition of the acceptor moiety with different conjugation length significantly affected on the memory characteristics of donor-acceptor coPIs.

Reference

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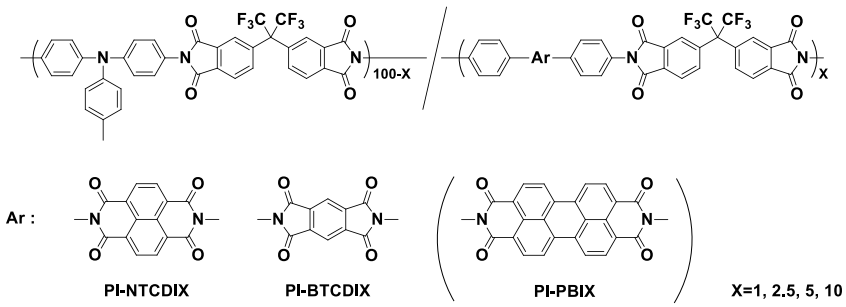
3. Kurosawa, T.; Lai, Y. C.; Higashihara, T.; Ueda, M.; Liu, C. L.; Chen, W. C. *Macromolecules* **45**, 4556(2012).



Scheme 1. Structures of **PI-NTCDIX** and **PI-BTCDIX**

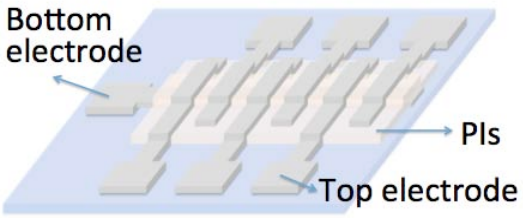
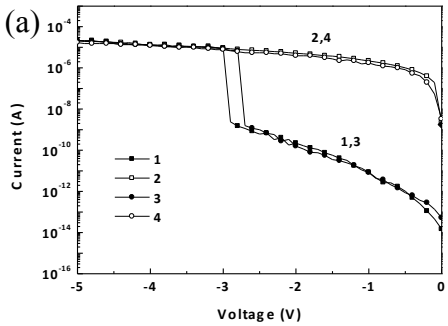


Figure 1. Schematic memory device architecture.



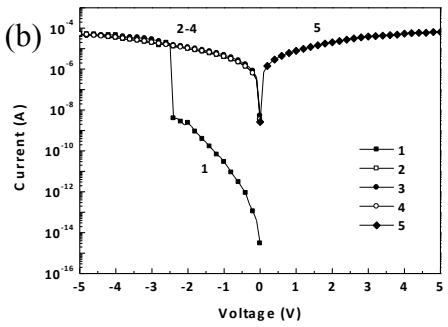
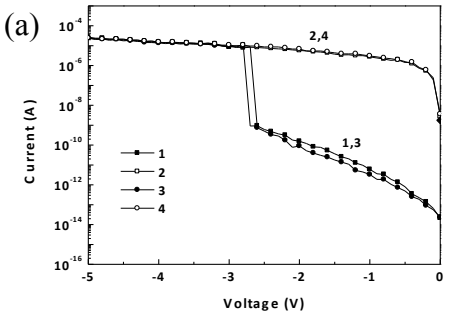


Figure 2. Current-voltage (I-V) characteristics of the (a) Al/**PI-NTCDI1**/Al device and (b) Al/**PI-NTCDI5**/Al device.



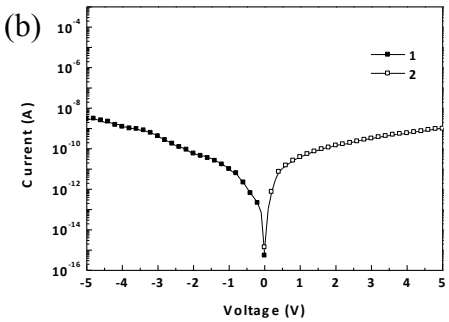


Figure 3. Current-voltage (I-V) characteristics of the (a) Al/**PI-BTCDI1**/Al device and (b) Al/**PI-BTCDI5**/Al device.

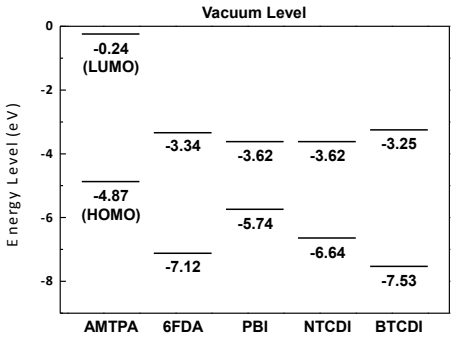


Figure 4. Estimated HOMO and LUMO energy levels of the donor and acceptor moieties.