Use of Organic Materials for the Fabrication of Flexible Memory Devices

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Flexible electronics have experienced rapid growth and development in the past decade. Devices such as flexible phones and TVs have already begun to enter the market, and this trend will likely extend to towards non-display technology. Such devices are already under research and development, such as thin film transistors (TFTs) and RFID sensors. As flexible technology progresses, it will naturally become necessary to develop flexible memory devices. This can be done is a myriad of ways, the most exciting of which is through the use of organic materials.

Fabrication methods for flexible electronics can vary widely. In standard electronics, the solid-phase nature of metals often requires a certain amount of rigidity, limiting bending ability. This problem can be somewhat circumvented by designing extremely thin electronics, but this in turn lowers mechanical strength and increases fragility. In contrast, organic materials can often be applied in liquid phase, which opens many possibilities for creative fabrication methodologies. Standard wafer processing techniques can still be used, but in many instances, there are more time and cost-effective ways to achieve the same result.

Inkjet printing is a popular method for quickly creating macro-scale electrode circuits. Using conductive inks, often laced with silver nanoparticles, standard nozzle deposition techniques can be used to print out digitized patterns and arrangements similar to normal ink printers. Precision can be adjusted with different nozzle types and mechanisms, such as piezo-actuated or differential pressure mechanized.

Laserjet printing is a similar method, analogous to actual ink and laserjet printers. Instead of melting plastic polymer inks, high powered lasers can be used to sinter metal nanoparticles to create thin circuits with stronger substrate adhesion. There are two main types of deposition. First, a suspension of nanoparticles may be used to coat the entire surface, then specific patterns may be sintered, washing off any extra ink with solvent. Second, the nanoparticles may be deposited and sintered along the same path, allowing for less material waste at the cost of less uniform electrodes.

Roll-to-Roll manufacturing is a process designed for high throughput applications. Utilizing multiple rollers, thin layers of liquids may be applied to sheet materials successively to the entire surface or just specific patterns. This method is widely used in the textile and marketing industry for posters and newspapers, but it is suitable for the fabrication of flexible electronics, which can often be several organic materials layered on top of one another. With the addition of several precision safeguards to prevent contamination, Roll-to-Roll offers the greatest potential for mass production of flexible memory.

Flexible memory can often be fabricated in the same structures as standard silicon memory. The only difference is that organic non-rigid materials are used in place of metal semiconductors to form transistors. However, the mechanisms involved can be widely varied due to the chemical diversity of different organic materials. Following are examples from three separate families of flexible memory operation.

Researchers from the University of Strasbourg were able to utilize photopolymers to their advantage to create a highly nonvolatile flexible memory device (Leydecker et al. 2016). After mixing the

Photos and data from: T. Leydecker (Reference 1)

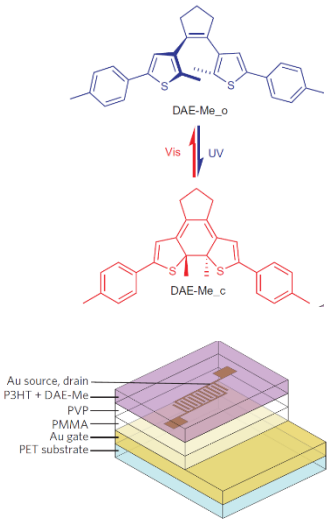

Figure 1: Open and closed states of DAE, along with device structure

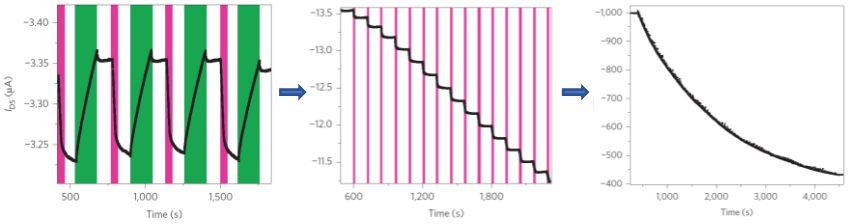

Figure 2: Optical modulation of semiconductor conductivity with laser pulses

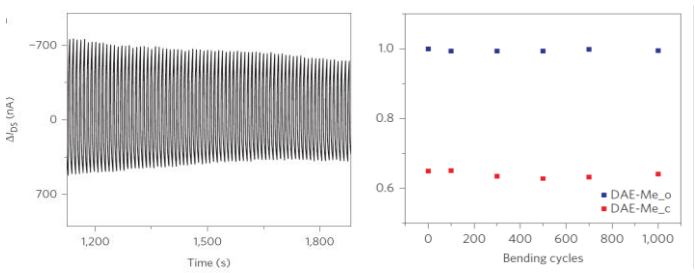

Figure 2: (left) write-erase cycle characterization (right) bending cycle characterization

photopolymer diarylethene (DAE) with the organic semiconductor poly(3-hexylthiopene) (P3HT), the resulting suspension, DAE-me, acted as an optically controlled semiconductor. That is to say the conductivity of the carrier channel could be directly controlled with light. The proposed mechanism was that by modulating the energy of the DAE molecules through green and UV irradiation, DAE-me could be switched gradually between a closed state (DAE-me$_c$) and an open state (DAE-me$_o$) (Figure 1). Doing so shifts the location of high energy electrons from dangling outside to contained inside, altering electron mobility for open and closed states respectively. 3ns Laser pulses were used to finely control this process, achieving up to 1000 distinct energy levels. For the purpose of memory stability, resolution was reduced to 256 distinct levels to enable functional 8bit storage (Figure 2). After depositing the solution onto a flexible substrate to form transistor-based memory cells, various characteristics were testing, including the durability of the device under different flexing conditions. The device displayed a promising long-term stability of 500-day nonvolatility (10^7s) and moderate flex resistance with 1000 bending cycles (5s @ 8mm radius) before significant performance loss. However, the device had a durability problem. It could only complete 70 write-erase cycles before a significant (~15%) reduction in drain current. Other significant disadvantages include a large operation voltage required for biasing the semiconductor (-60V), low switching speeds, and power intensity. Despite these, such a method as photo polymeric semiconductors create exciting opportunities for a wide array of applications.

A slightly more conventional approach was studied by researchers in China, utilizing graphidyne (GD), a 2D carbon allotrope consisting of benzene and triple bonded carbons (Jin et al. 2017). By embedding a bi-layer of GD and aluminum nanoparticles into a polyimide film, researchers were able fabricate a two-stage drop in the film's energy bandgap. Adding electrodes on either side and mounting on a polyethylene-terephthalate (PET) substrate completed the flexible memory cell (Figure 4). As a result, the cell had 3 stages: Pristine OFF, First stage ON, and Final stage ON. Upon applying voltage, carriers would be caught in the sequential electron traps of the GD and Al layers to record information. This type of cell is suitable for write-once-read-many (WORM) memory due to its highly stable,

Photos and data from: Z. Jin (Reference 2)

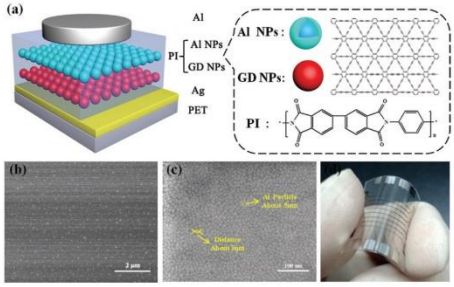

Figure 4: GD-Al np. Memory cell make up and final fabrication

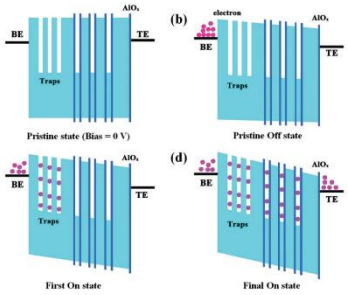

Figure 5: Device states and function

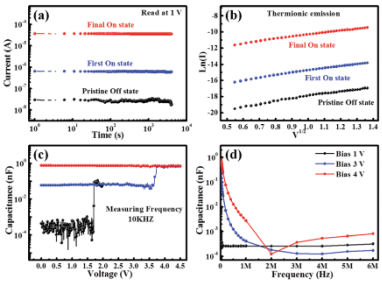

Figure 6: Device characterization

nonreversible energy levels (Figure 5). Further characterization tests of the flexible memory confirmed proper function of the device. Though it has a low switching ratio of 10^2, the device's 3 states are very stable and consistent over multiple tests. Additionally, due to the bilayer chemistry, ordinary operating voltages are needed (1-3V), which is much more practical than the operating voltage of the previous photopolymer example. The First and Final On states have good durability, but the Pristine Off performance begins to degrade at 10^4s, or several hours. Additional capacitance testing indicates good performance up to 1MHz switching frequency, which is fast by current organic memory standards (Figure 6). Despite its lower information density now, the concept is highly scalable. More layers may be added to continuously increase the states count and possibly promise greater stability.

A third mechanism for organic memory was implemented by researchers from Kyungpook National University in the Republic of Korea involving ionic nanoclusters (Lee et al. 2019). PAMPSA (acid) was used to protonate aniline, an organic semiconductor. The resulting molecule, PAMPSA-AN, contains a permanent charge complex of a sulfate group and ammonium group [SO_3^--$^+NH_3$] at the bond juncture (Figure 7). The dipole molecules could then be immobilized by annealing the film at 150°C. After top and bottom electrodes were added, the dipole molecules in the film could be aligned via gate voltage, thus creating a tunable resistance carrier channel (Figure 8). The resulting memory cell had full write-erase capabilities, and further characterization revealed promising properties. When compared to the non-bent state, bending at 30° resulted in little to no change in device characteristics. Only after 1000 bending cycles did it start to performance start to degrade, and without bending performance was still stable for 10^5 WRER cycles when testing concluded. In addition to strong durability, the device was relatively nonvolatile. Under no strain, the device maintained memory for 10^8s and 10^6s when under 8mm bending strain (Figure 9).

	Advantages	Disadvantages
Photopolymers	High storage density, flex resistant, non-volatile, simple structure	Power intensive, high voltage operation, slow switching speed
Graphidyne	Easily scalable and altered, fast switching speed, simple structure	Low voltage operation, low switch ratio, relatively volatile
Ionic Nanoclusters	Extremely durable, flex resistant, non-volatile, high hysteresis, simple structure	Low voltage operation, low switch ratio, slow switching speed

Table 1: Comparison of 3 different mechanisms

Photos and data from: C. Lee (Reference 3)

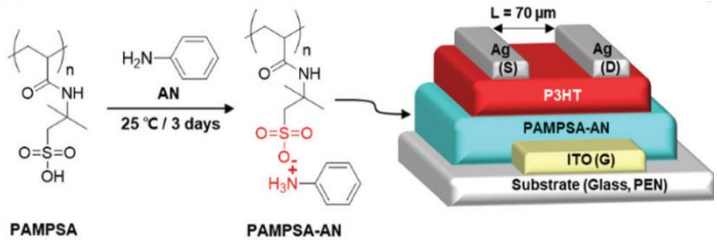

Figure 7: (left) protonation of Aniline with PAMPSA (right) final device structure

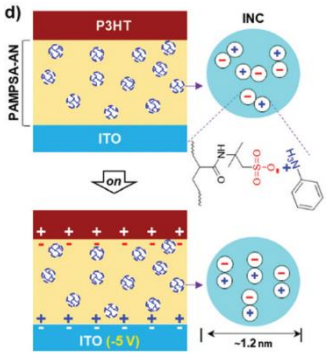

Figure 8: Working principle of ionic nanoclusters

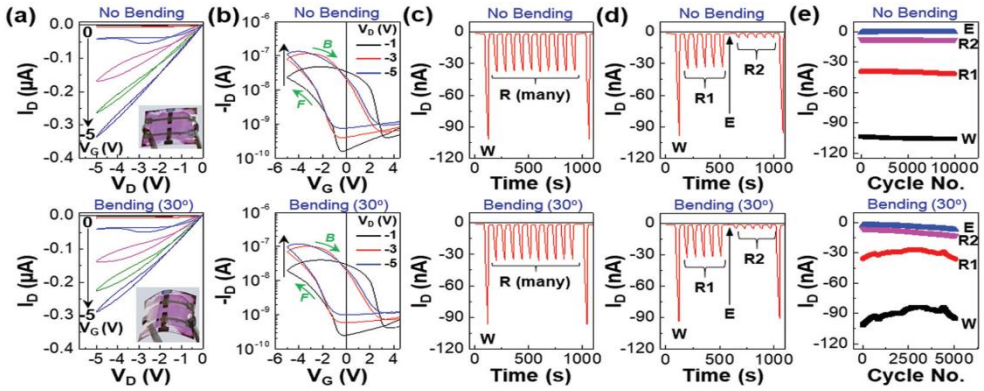

Figure 9: No bending vs. bending tests (a) IV characteristics (b) Symmetry and hysteresis examination (c) WORM test (d) WRER tests (e) WRER cycle vs bending cycles comparison

Table 1 briefly outlines the advantages and disadvantages of the three organic semiconducting materials specific mechanisms discussed. Though they each have their advantages, significant advances need to be made before any practical memory system can be made. One of the most significant flaws is currently switching speed, which is on the 10^0s regime. Such speeds are due heavily to the slow relaxation times necessary for proper hysteresis. Significant increases in switching speed would require high power or different methodologies altogether. Another major concern for organic semiconducting materials is that they are much more prone to degradation via thermal effects, humidity, pressure, oxidation, or even due to over flexing by consumers. Special efforts must be made to ensure the preservation of materials especially during function, which delays when the devices will reach full maturity. Despite these issues, organic memory devices still show a lot of promise. Particularly, they can be incredibly information dense, another major advantage of analog devices, and are verified to be functional under flex.

Quite possibly, all development efforts will be worth the effort. The above three mechanisms were specific to the organic semiconductor used, and there are as many mechanisms as there are organic semiconductors. The drives to advance chemistry and material science with undoubtedly have positive peripheral effects, and eventually viable solutions will be found. Flexible memory represents a significant milestone in the integration of technology into everyday society.

References:

1. Leydecker, T., Herder, M., Pavlica, E., et al., 2016. Nature: Nanotechnology. 11. 769-777.
2. Jin, Z., Chen, Y., Zhou, Q., et al., 2017. Materials: Chemistry. 1. 1338-1341
3. Lee, C., Jeong, J., Kim, H., et al., 2019. Materials: Horizons. 6. 1899-1905