Electrical Bistable Devices Using Organic Materials

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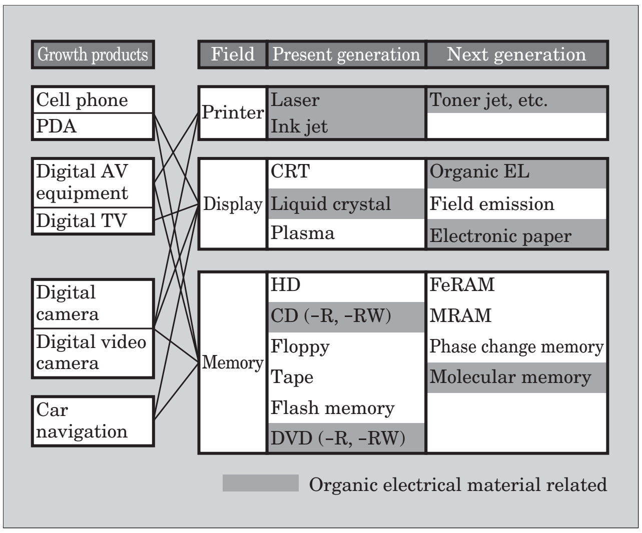
1. Introduction

In development of new products in the field of electronics technology, new materials with high performance are strongly required. Although organic electrical materials have not yet reached the basic performance level of silicon, they are promising to various applications because of their advantages such as good light interaction, low cost processing, suitability for large area devices, and the like. Figure 1 lists product groups in the burgeoning field of information devices together with new device technologies for which application is expected. Organic electrical materials account for a large percentage of these new technologies.

Fuji Electric holds a large share of the global market for organic photoconductors and is presently developing organic light emitting diodes (OLEDs) as next generation products. Organic electrical material forms the basis for these business areas, and advancement of its development is important.

This paper describes the present status and future trends of bistable devices, which are being developed as next generation devices that utilize organic electrical materials.

Fig.1 Technical trends of information device and new technology



2. Features of Organic Electrical Materials

Table 1 compares the charge mobilities of typical organic electrical materials to that of silicon. The highest mobility value is for pentacene single crystal which has a hole mobility of approximately 3.2 cm²/V·s. Electron mobility is even lower. For this reason, devices that use these organic electrical materials generally have a limited response performance. Moreover, some materials may become unstable when exposed to the atmosphere and must be encapsulated or stabilized in some other way. Organic electrical materials, however, have the following features that are not exhibited in conventional electrical materials and device development is being promoted to leverage these features.

(1) Materials can be designed so as to control the energy gap and the interaction with light is easily customizable.
(2) Large area devices are easy to manufacture.
(3) Low cost (spin/dip coating, etc.) processes may be utilized.
(4) New devices can be realized using the particular physical properties of organic molecules (molecular alignment, dipole moment, phase transition, etc.).

For example, the switching speed of organic bistable material described in this paper is said to be approximately 10 ns and would be sufficient for many applications.

Table 1 Charge mobility of representative organic electrical materials

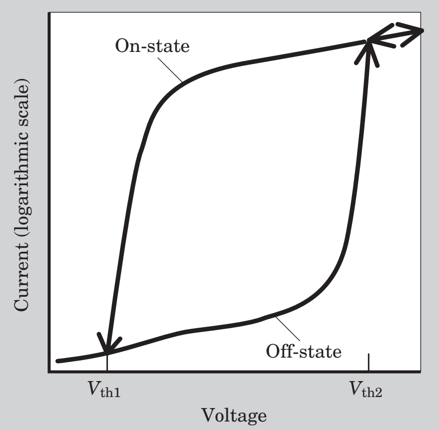
Item	Silicon	Pentacene single crystal	Thiophene aligned film	Conjugated conductive polymer	Liquid crystal	Conjugated small molecule
Hole mobility ($cm^2/V\cdot s$)	450	3.2	0.1	0.1	1×10^{-3}	1×10^{-5}
Electron mobility ($cm^2/V\cdot s$)	1,500	0.5	0.02	–	1×10^{-3}	1×10^{-6}

3. Organic Bistable Materials and Development Trends

In organic electrical materials having certain chemical structure, bistability is observed in which two stable resistance values exist for a single applied voltage value. Figure 2 shows an example of those characteristics. For example, when increasing the voltage gradually from 0 V, there is almost no current flow in the low voltage region and the material remains in a high-resistance state (off-state), however, at a certain threshold voltage (V_{th2}), there is a sudden increase in current by several orders. This low-resistance state (on-state) continues even when the voltage drops below V_{th2}, but when the voltage becomes lower than another threshold voltage (V_{th1}), the material returns to the off-state.

Organic materials called "charge transfer complexes" are known as organic bistable materials that exhibit these types of characteristics. These charge transfer complexes are molecular compounds formed from the two molecules of an electron donor molecule and an electron acceptor molecule, and precise control of the composition ratio of these molecules is necessary. On the other hand, a group at the University of California has recently succeeded in achieving bistable performance, similar to that of the abovementioned charge transfer complex, with a single-component organic bistable material formed by providing an extremely thin metallic middle layer within a thin film layer of organic bistable material. With this structure, controllability of the composition is better than with the conventional two-component material of a charge transfer complex, however, the addition of the new process of fabricating a metallic middle layer adds difficulty.

Fig.2 Electrical characteristics of bistable devices



Through its development of proprietary organic bistable materials and processes, Fuji Electric has succeeded in achieving bistable performance, similar to that of the abovementioned charge transfer complex, in a single-component organic material without the provision of the abovementioned thin metal middle layer within the organic layer. This has enabled bistable devices to be made with a simple structure in which a single organic layer is sandwiched between metal electrodes.

The detailed mechanism of the bistable phenomenon in these materials is not yet well understood. In particular, there are many unknowns concerning the relatively recently developed materials that exhibit bistability in a single molecule. In the bistable devices developed by Fuji Electric, mechanisms are presumed to function such that (1) current flow is restricted by means of a charge injection barrier existing at the interface between the organic bistable material layer and the metal electrode (off-state), (2) charge accumulates at the charge injection barrier and causes the electric field to increase locally, and (3) the rise in electric field causes the charge injection barrier to

Table 2 Representative bistable devices

Organization	Material	Summary	Current density (mA/cm^2)	Switching voltage (V)	On/off ratio	Reference
Indian A.C.S	Rose, Bengal, etc./dye	Electrostatic self-assembled film, spin coated film	0.3	4.5	10^5	(6)
Univ. of Wales	Thiophene polymer	ITO/electrochemical deposition/Al	0.004	5.0	10	(7)
Kyushu Univ.	Melamine cyanurate	Evaporated film	16.0	12.0	10	(8)
Chitose Institute of Science	Cu–TCNQ	Evaporated film	8.0	10.0	10^2	(9)
Univ. of California	AIDCN	Evaporated film	100.0	3.0	10^6	(4)
Yale Univ., Rice Univ.	Nitro-amino molecule	Self-assembled monolayer	–	5.0	–	(12)
Hewlett Packard	rotaxanes	Self-assembled monolayer	–	1.5	10^3	(13)
Fuji Electric	DODMT	Evaporated film	2.0	20.0	10^3	(6)
Philips	ZnCdS	Sputtered film	80.0	0.5	10^6	(10)
Tokyo Univ. of Agriculture and Technology	porous Si	–	1.0	17.0	10^5	(11)

collapse and charge to flow toward the organic bistable material film (transition from off-state to on-state). However, there are many remaining issues to be investigated concerning details of the characteristics and their relation to the physical properties of the organic materials.

This bistability is suitable for application to high density recording media and switching devices and, in recent years, there has been an increase in the number of organizations pursuing development of this technology. In addition to organic materials, inorganic materials should also be developed and materials development is ongoing. Major developments of bistable devices are listed in Table 2.

4. Development and Results at Fuji Electric

Fuji Electric is promoting the development of devices that utilize this bistability. Since these device use organic material as a raw material, the manufacture of large area devices at low-temperature processes is possible. Moreover, since theses devices may also be used with a plastic substrate, they are believed to be particularly well suited for application to the driving devices for organic EL or other types of display panels.

At present, display panel driving methods are classified as either a passive matrix method that causes each pixel to emit light in a time-sequential manner or an active matrix method in which a control circuit is provided at each pixel to continuously emit light. In the passive matrix method, since pixels in the panel are illuminated sequentially in rows, the duration of light emission is limited for the light-emitting element of each pixel and it is necessary to instantaneously emit a bright light for the duration of the light emission. Accordingly, lower cost is possible, but there are problems involving power consumption and lifespan. On the other hand, in the active matrix method, each pixel is provided with a control circuit formed from a thin film transistor or the like, and since the light emitting state can be maintained continuously, it is acceptable for the light-emitting element of each pixel to have a low average brightness when lighted. In general, as the brightness level of organic EL material decreases, both the emitting efficiency and the light emission lifespan increase and although this is advantageous in terms of power consumption and lifespan, the high cost is a disadvantage.

However, by connecting an organic EL device in series with a bistable device as shown in Fig. 3 for example, and applying a bias voltage at both ends to maintain the on/off-state of the bistable device, light emission can be made continuous even with a structure similar to that of the passive matrix method. The on/off-state is switched by applying control pulse voltages that correspond to each switching voltage. As a result, the power consumption and lifespan of the display can be improved without the use of an expensive control circuit.

Fig.3 Configuration in which a bistable device is connected in series to an organic light emitting diode

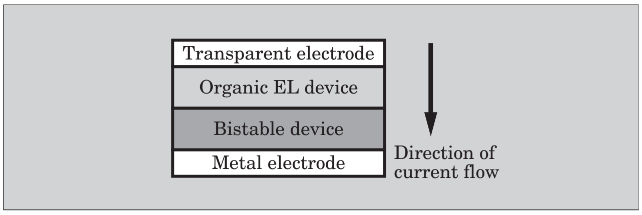


Fig.4 Operating condition of the bistable device and organic light emitting diode

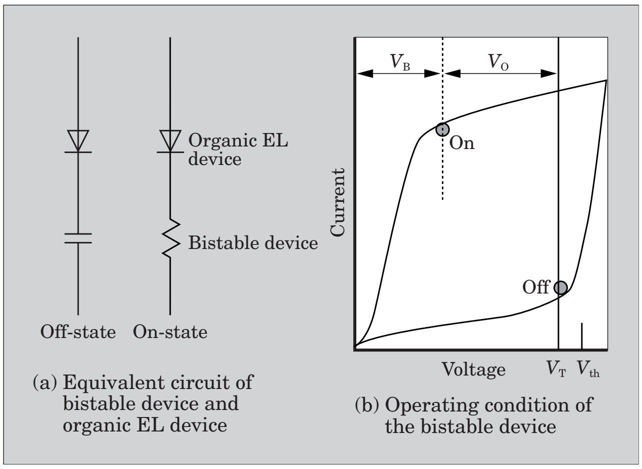


Figure 4 shows details of the operation of a pixel in which the abovementioned organic EL device is connected in series with a bistable device. When the bistable device is in the on-state, the voltage V_T applied to both devices is divided according to the resistive values of the bistable device and organic EL device. If the respective voltage values at this time are V_B and V_O, then V_O becomes the operating voltage of the organic EL device and generally requires a voltage of approximately 10 V (max.). In the off-state, the bistable device is equivalent to a capacitor and the entire V_T across both devices is applied to the bistable device. For the bistable device to be in a stable state, the voltages V_B (on-state) and V_T (off-state) applied to both states must be within the range of the abovementioned V_{th1} and V_{th2}. In other words, in order to support the driving voltage and current of the organic EL device in this application, the switching voltage V_{th2} from the off-state to the on-state must be greater than V_T (typically 15 V or higher) and the on-state must have a high current density. Using originally developed organic bistable materials, Fuji Electric has realized bistability with a single-component, single-layer structure and with this type of device, has achieved the world's highest switching voltage V_{th2} of 20 V.

Figures 5 and 6 show example characteristics of these bistable devices. Figure 5 shows characteristics

Fig.5 Electrical characteristics of bistable devices (single-layer structure)

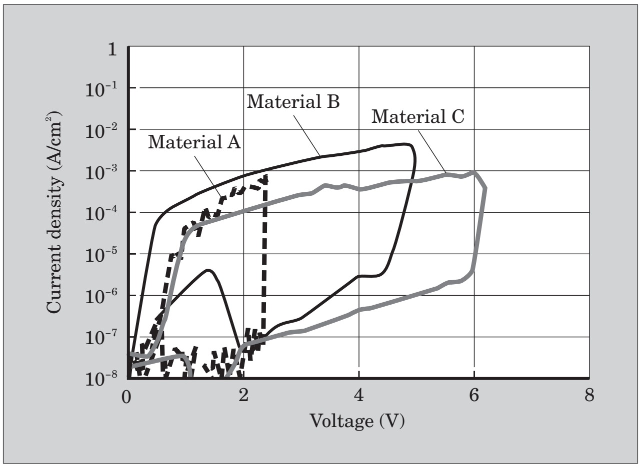
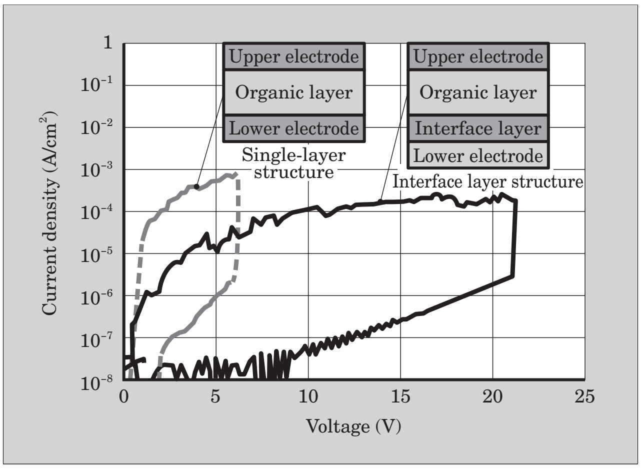


Fig.6 Electrical characteristics of bistable devices (material C)



of various materials in a single-layer structure. Fuji Electric was able to achieve bistability with material A, which had previously achieved bistability only with a middle layer structure, in a simple single-layer structure (in which the organic bistable material layer is sandwiched by metal electrodes). Materials B and C are organic bistable materials that Fuji Electric has developed originally. Material B conducts positive charges (holes) and will provide a higher current than material A. Material C conducts negative charges (electrons). In the case where an organic EL device is to be connected, these materials having different polarities may be selected for use according to the device configuration. Figure 6 shows characteristics of a device that uses material C and is provided with an interface layer between the electrode and the organic bistable material layer. The switching voltage from an off-state to an on-state has been successfully improved to 20 V or higher with this configuration. The interface layer is organic material in which conductive nano-particles have been dispersed and which functions to bear a portion of the voltage applied to the bistable device and also to boost the switching voltage by controlling the injection of charge to the device.

Fig.7 Overview of performance of bistable characteristics

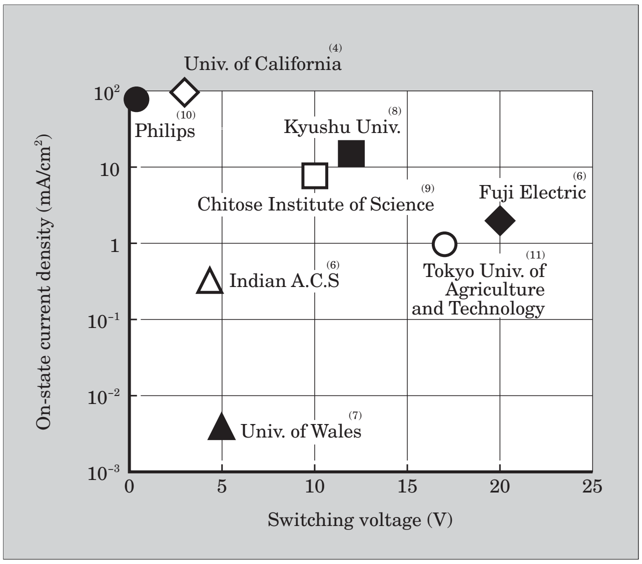


Figure 7 compares the switching voltages and on-state current densities of bistable devices that have been publicly reported by various research organizations. The highest switching voltage was achieved with material C using Fuji Electric's interface structure and the highest on-current density was achieved with material A using the University of California's middle layer structure. Fuji Electric is aiming to improve the characteristics even further and is continuing its efforts to develop new organic materials and to optimize layer configurations.

5. Conclusion

This development work has only just begun and many unresolved issues remain. In particular, during the on-state, in addition to current density, issues relating to reliability and stability, such as repetition durability, environmental dependence and so forth, are expected to be difficult to resolve. Moreover, an understanding of the mechanism behind the phenomenon of bistability is crucial for resolving these technical issues, but as mentioned above, there are many unknowns surrounding this issue at present. In order to resolve these issues, in addition to in-house efforts, broad ranging cooperation with various external organizations will be indispensable. In the future, while seeking this cooperation, we intend to advance development towards the goal of practical applications.

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