MANA

International Center for Materials Nanoarchitectonics

FEATURE:

Next Generation *Innovative* Organic Electronics

Yutaka Wakayama

RESEARCH HIGHLIGHTS:

- EVIDENCE OF A NEW TYPE OF QUANTUM EFFECT
- FLEXIBLE ORGANIC ELECTRONIC DEVICES FOR THREE-VALUED LOGIC CIRCUITRY
- NEW APPROACH FOR THE SYNTHESIS OF CARBON NANOSHEETS

e-Bulletin Vol. 04
September 2018

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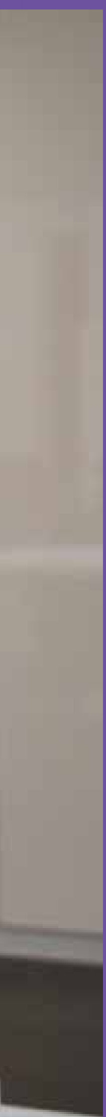

MANA researchers are integrating flexible organic devices for functional logic circuits to process data.

Research in organic electronics has a long history with major breakthroughs including the serendipitous discovery of conducting polymers in the mid-1970s, the implications of which were recognized with the Noble Prize in Chemistry to Heeger, MacDiarmid and Shirakawa in 2000. This and related research on organic materials for applications in electronic devices led to the birth and proliferation of touch screens of smart phones, organic photovoltaic devices, and the dawn of flexible organic electronic devices that can be worn, like a suit and tie.

“The potential of flexible organic materials for fabricating sensors, displays and sources of tunable light, for example, is the driving force pushing research in this area of materials science,” says Yutaka Wakayama, an expert in organic electronics and Deputy Director, MANA. “The challenge facing the organic electronics community is to integrate flexible devices to enable functional, and useful data processing for practical applications such as logic operations and switching. Solving these issues has been the driving force for my research over the last decade or so.”

Highlights of research being undertaken by Yutaka Wakayama and colleagues

Optically controllable organic field-effect transistors

Wakayama is collaborating with experts in chemistry, optics, and organic materials on the development of organic field-effect transistors using photochromic molecules that exhibit reversible changes in conformation, polarity, π-conjugation, and energy levels on irradiation with ultra-violet (UV) or visible light irradiation. Examples of photochromic materials include spiropyran, azobenezene, and diarylethene (DAE).

“Our approach has been based on the direct use of photochromic materials, using vacuum evaporation through shadow masks, in contrast to self-assembly and other chemical methods,” explains Wakayama. “We think that our method is much more practical for real life device fabrication and applications.”

In 2014 Wakayama and his team reported on light induced semiconductor-insulator phase transition in field effect transistor structures with DAE channels [1]. Visible light induced insulating properties and UV changed to a conducting channel. The light-induced electrical current modulation was more than 100. The figures of merit of the devices were significantly improved by using a PMMA (polymethyl methacrylate) interface layer to decrease the off-current and α-6T (α-sexithiophene) interface layer to increase the on-current that led to ON/OFF ratio of 1000 [2].

Laser patterning of electronic circuits is an important application of the ability to switch transistors on and off using light. In 2016 Wakayama and his team reported on the laser pattering of semiconducting and insulating DAE channels using 325 and 633 nm laser light, respectively. Further experiments showed the ability to fabricate “optical valves”, that is, regions on the channels of circuits that can be switched on or off by irradiation with the

Publications

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[2] Ryoma Hayakawa et al., “Interface Engineering for Improving Optical Switching in a Diarylethene-Channel Transistor.” *Organic Electronics*. 21, 149-154 (2015).

[3] Tohru Tsuruoka et al., “Laser patterning of optically reconfigurable transistor channels in a photochromic diarylethene layer.” *Nano Letters*. 16, 7474-7480 (2016).

[4] Kazuyoshi Kobashi et al., “Negative differential resistance transistor with organic p-n heterojunction.” *Advanced Electronic Materials*. 3, 1700106-1-6 (2017).

[5] Kazuyoshi Kobashi et al., “Device Geometry Engineering for Controlling Organic Antiambipolar Transistor Properties.” *J. Phys. Chem. C*. 122, 6943–6946 (2018).

[6] Kazuyoshi Kobashi et al., “Multi-valued logic circuits based on organic anti-ambipolar transistors.” *Nano Letters*. 18, 4355–4359 (2018).

[7] Ryoma Hayakawa et al., “Single-electron tunneling through molecular quantum dots in a metal-insulator-semiconductor structure.” *Advanced Functional Materials*. 21, 2933-2937 (2011).

[8] Ryoma Hayakawa et al., “Vertical resonant tunneling transistors with molecular quantum dots for large-scale integration.” *Nanoscale*. 9, 11297-11302 (2017).

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Yutaka Wakayama
MANA Deputy Director

appropriate wavelength of light [3]. To demonstrate the potential of these results, Wakayama used optical valves to produce rewritable ADDER logic gates.

Organic anti-ambipolar field-effect transistor for flexible logic circuits

Anti-ambipolar transistors were fabricated using pn-heterointerface consisting of α-6T (p-type) and PTCDI-C8 (n-type) [4]. The devices exhibit negative differential resistance with an ON/OFF 1000% at room temperature. These devices have overcome the limitations of conventional negative differential resistance devices that have low on/off ratios of around 30, and only function at cryogenic temperatures. The mechanisms underlying the carrier transport across the hetero-interfaces [5] and examples of multi-level logic circuits have been reported by Wakayama and his group [6].

Single-electron tunneling transistor with molecular quantum dots

Wakayama has also studied multi-level switching using fullerene-based single-electron tunneling transistors, where fullerene —sandwiched between a silicon substrate and metal electrode— forms double tunneling junction. "The fullerenes in these configurations are molecular quantum dots," says Wakayama. "They are excellent for producing tunneling devices."

The devices were produced by vacuum evaporation, where organic molecules and metals were deposited from K-cells in one chamber, and atomic layer deposition used to produce the insulating layer in an adjacent chamber.

This procedure yielded 10^{13} cm^{-2} quantum dots, which is two orders of magnitude larger than silicon quantum dots. The current-voltage characteristics clearly showed Coulomb blockade staircases due to tunneling [7].

"These structures could be stacked for vertical tunnel transistors with side gates," says Wakayama. "The tunneling is controlled by gate bias voltage. Our research underscores the possibility of integrating molecular devices in silicon technology. Organic electronics has wide-ranging potential. There is still a lot of research to do." ■

RESEARCH HIGHLIGHTS

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01 Evidence of a new type of quantum effect

The quantum Hall effect (QHE) is a phenomenon that can occur in a two-dimensional electron gas — a system in which electrons can move in a plane but not perpendicularly to it. Such a system is typically realized in a heterostructure of thinly stacked layers of different semiconductors. The QHE is usually observed at low temperatures and high magnetic fields; it manifests itself through the quantization of values of the electronic conductance (the inverse of resistance) — the values are integer or particular fractional multiples of a fundamental conductance quantum.

Recently, variants of the QHE have been discovered, such as the quantum spin Hall and the anomalous quantum Hall effect. Now, Satoshi Moriyama at WPI-MANA, NIMS, Tsukuba, Japan, and colleagues have observed yet another relative of the QHE: the quantum valley Hall effect.

The notion of 'valleys' refers to electronic states having the same energy but a different crystal momentum; the states are said to lie in different valleys. A new type of electronics called 'valleytronics', based on the valley degree of freedom, is being researched since some years.

Moriyama and colleagues demonstrated the quantum valley Hall effect in a special heterostructure capable of hosting a two-dimensional electron gas: a sheet of graphene sandwiched between hexagonal boron nitride (h-BN) layers. Graphene is a one-atom thin layer of carbon atoms forming a honeycomb pattern. h-BN is similar; it is also a monolayer with a honeycomb structure, but it has a slightly different lattice parameter. Due to the mismatch in lattice size, the periodicity of the combined system is much larger — overlaying the two lattices results in a moiré pattern.

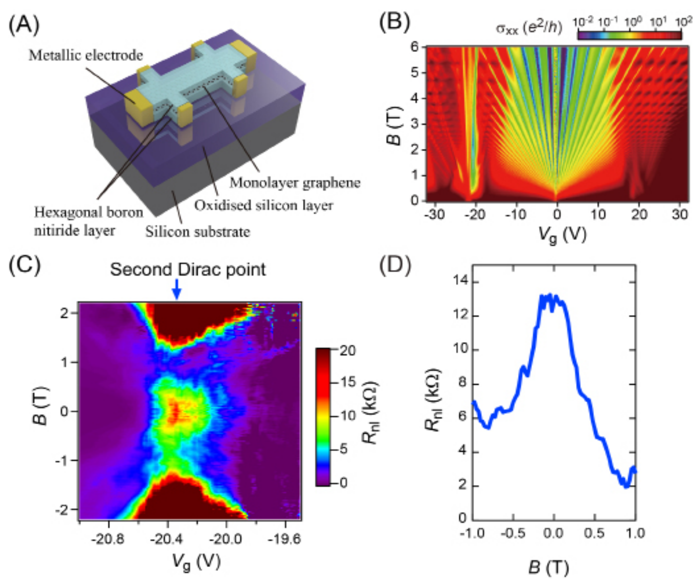

FIGURE: (A) DEVICE STRUCTURE. (B) HOFSTADTER'S BUTTERFLY, A QUANTUM HALL EFFECT IN GRAPHENE/H-BN SUPERLATTICE HETEROSTRUCTURE. (C) AND (D) SIGNATURE OF THE QUANTUM VALLEY HALL EFFECT IN A GRAPHENE/H-BN SUPERLATTICE.

Importantly, the investigated electronic regime in the superlattice was ballistic: the electrons' mean free path (the mean distance travelled between scattering events) was estimated to be 1 to 2 micrometer, which was comparable to the size of the sample.

The researchers varied the magnetic field while measuring resistances, and at a small interval centered around zero field they observed a non-vanishing resistance — a signature of the quantum valley Hall state.

An important fundamental finding on its own, Moriyama and colleagues note that it also may lead to potential applications: "[such] unconventional magnetism should have the potential for engineering the energy-band structure [of devices] even with a weak magnetic field as well as for spintronics applications." ■

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K. KOMATSU ET AL., "OBSERVATION OF THE QUANTUM VALLEY HALL STATE IN BALLISTIC GRAPHENE SUPERLATTICES", SCI. ADV. 4:EAAQ0194 (2018).

02 Flexible organic electronic devices for three-valued logic circuitry

Wearable and flexible integrated-circuit technology is on the rise, especially in the context of the 'internet of things (IoT)' — devices sharing information through the internet. So-called organic field-effect transistors (OFETs), built from organic molecules, are mechanically flexible, and therefore suitable for IoT electronics. OFETs are difficult to downsize, however, making their high-density integration onto flexible chips is problematic. Yutaka Wakayama at WPI-MANA, NIMS, Tsukuba, Japan, and colleagues have now presented an alternative approach. Rather than considering OFETs offering conventional two-valued logic — with zeroes and ones — they developed a circuit element, built from organic materials, capable of handling three logical values.

Multi-valued logic circuits can process more data with a lower integration density than binary circuits. This notion inspired Wakayama and colleagues to build a ternary inverter from organic materials. (In three-valued logic, where an input signal can assume the values 0, 1/2 or 1, a ternary inverter converts these into 1, 1/2 and 0 output values, respectively — similar to the NOT gate in binary logic.)

The scientists' inverter consists of two parts: an OFET and an element called an anti-ambipolar transistor. Although the transfer characteristics for their device did indeed correspond to three-valued logic functionality, its intrinsic operating voltage of 60 V is unrealistic for actual applications. By including a 30-nm thick aluminium oxide (a material with a high dielectric constant) layer in the device substrate, the researchers could bring the voltage down to 10 V.

The anti-ambipolar transistor has the advantage that, by varying the channel length, the in- and output voltage ranges corresponding to 0, 1/2 and 1 signals can be tuned. Lower signal voltages are important as they imply reduced power consumption.

The researchers carried out their measurements at ambient conditions, at room temperature, and demonstrated stability and reproducibility of the operation of the device. Wakayama and colleagues conclude that their "organic ternary inverter has great potential as a key element of future flexible IoT devices". ■

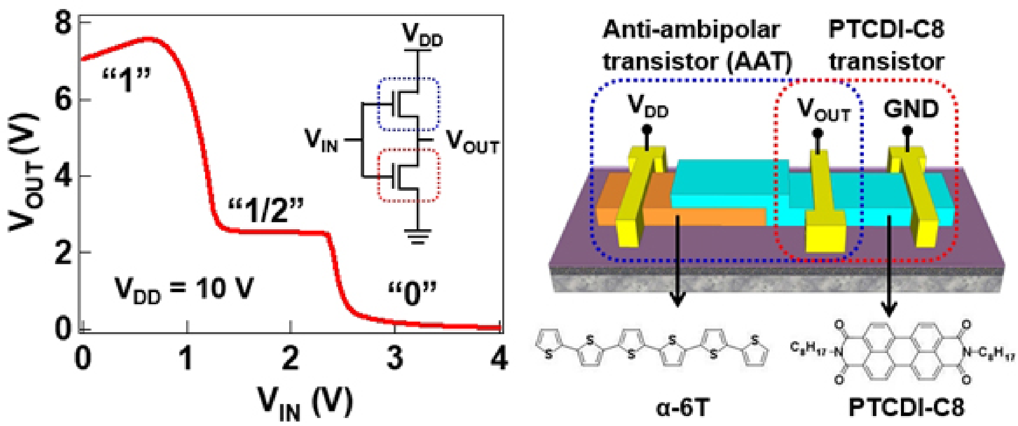

FIGURE: A TERNARY INVERTER BASED ON ORGANIC ELECTRONIC MATERIALS.

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K. KOBASHI ET AL., "MULTI-VALUED LOGIC CIRCUITS BASED ON ORGANIC ANTI-AMBIPOLAR TRANSISTORS", NANO LETT. 18, 4355-4359 (2018).

03 NEW APPROACH FOR THE SYNTHESIS OF CARBON NANOSHEETS

Carbon nanosheets — thin materials consisting of only carbon — have many useful properties, including energy-storage and catalytic functionality. The large-scale production of carbon nanosheets, however, has been challenging.

Now, Taizo Mori and Katsuhiko Ariga at WPI-MANA, NIMS, Tsukuba, Japan, and colleagues have discovered a relatively simple method for the fabrication of large carbon nanosheets.

The researchers started from a solution of specially designed organic molecules, CPPhen (cyclopenta phenanthrene) provided by Kenichiro Itami at the Nagoya University, in chloroform. CPPhen molecules have an ellipsoidal shape and consist of several hexagonal benzene rings — typical precursors for graphitic (i.e., layered carbon) networks. The solution was put dropwise onto an air–water interface undergoing vortex flow (the type of motion observed when stirring a liquid in a glass). The centrifugal rotation helped to spread the CPPhen molecules uniformly on the air–water interface. After stopping stirring, the chloroform was left to evaporate, and the resulting self-assembled thin film was put on a substrate. The final step was to 'carbonize' the on-substrate film by heating and exposure to nitrogen gas flow.

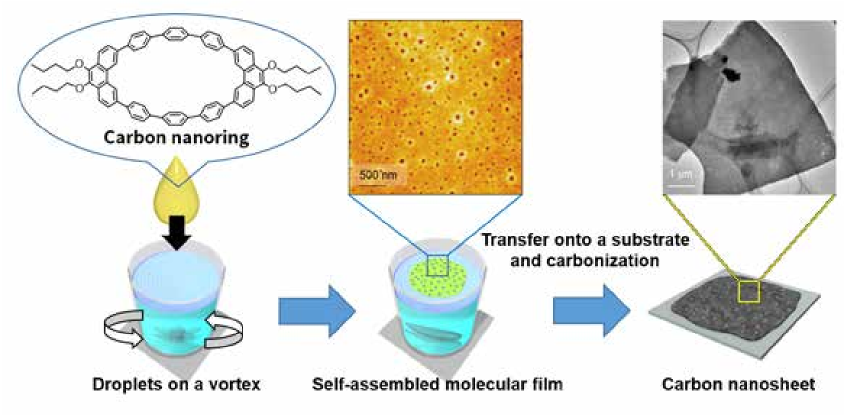

FIGURE: SYNTHESIS OF CARBON NANOSHEETS FROM CPPHEN MOLECULES.

Importantly, the produced film, having a thickness of about 10 nanometer, indeed showed uniform two-dimensional morphology. Mori and colleagues also noted that the sheets were highly porous — pore sizes were about 20 to 30 nanometer.

The researchers attribute the success of their approach to the role of the intermolecular interactions between the CPPhen molecules; applying the same procedure to molecules containing elements of the CPPhen structure did not lead to the formation of planar carbon sheets.

The scientists also explored the synthesis of nitrogen-doped carbon sheets with their carbonization method. Mixing CPPhen with pyridine, a nitrogen-containing compound, before dripping it onto the vortex air–water interface, resulted in sheets with high nitrogen content — Mori and colleagues assume the pyridine molecules were trapped within the CPPhen molecules or between them during carbonization. The electrical conductivity of the nitrogen-doped carbon sheets was significantly higher than that of the undoped ones, which is promising for applications. Indeed, the scientists conclude that this "would allow the utilization of nitrogen-doped carbon nanosheets as highly efficient catalysts for oxygen-reduction reactions for high-performance fuel cells." ■

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T. MORI ET AL., "CARBON NANOSHEETS BY MORPHOLOGY-RETAINED CARBONIZATION OF TWO-DIMENSIONAL ASSEMBLED ANISOTROPIC CARBON NANORING", ANGEW. CHEM. INT. ED. 57, 9679-9683 (2018).