The world's first sterilizable flexible organic transistor

March 7 2012, By Karen McNulty Walsh and Peter Genzer

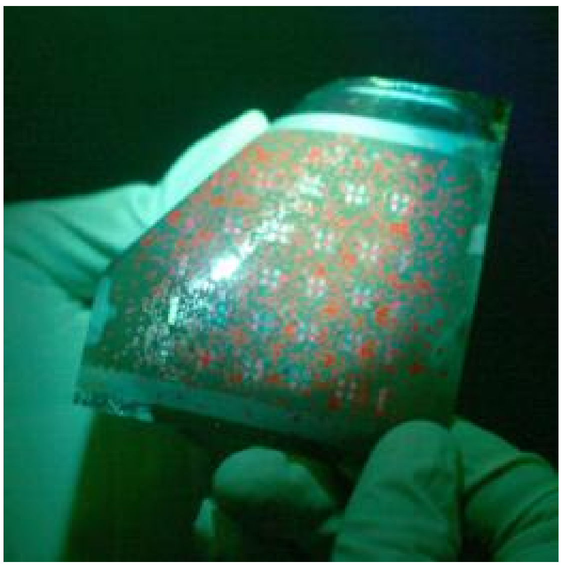

Figure 1: A highly thermostable organic transistor manufactured on a thin plastic film. The team succeeded in building a low drive-voltage and a high thermostable organic circuit on a plastic film by using SAM molecule for the gate insulator, and high heat resistant semiconductors for semiconductor layer.

An international research team has succeeded in manufacturing on a polymeric film the world's first flexible organic transistor that is robust enough under high temperature medical sterilization process. The study is to be published online in *Nature Communications* on March 6, 2012.

In a serious aging society with a declining birthrate, electronics are increasing their importance in the health and medical area as more IT devices are being introduced. Upon this background, an expectation is getting higher on an organic transistor, which is a soft electronic switch. A flexible organic transistor can easily be manufactured on a biocompatible polymeric film, and this is the reason why it is expected to adopt it to a wearable health monitor without a stress, and/or implantable devices such as a soft pace maker. For practical implementation, it is crucial (1) to make the best use of its softness and biocompatibility, simultaneously (2) to decrease driving voltage down to a few V, and (3) to decrease the risk of infections by sterilization, for a security reason. Up until now, however, the existing organic transistors had huge obstacles towards the practical usage in the health and medical field. For example, typical driving voltage for displays is high (i.e. 20 to 80 V) and/or and it is not durable under high temperature sterilization.

The team has succeeded in manufacturing on a polymeric film an organic transistor that has high thermal stability and driving voltage of 2V at the same time. The new type organic transistor can be sterilized in a standard sterilization process (150 °C heat treatment) without being deteriorated in its electrical performances. The key to realize heat resistant organic transistor is in the forming technique of an ultrathin insulator film: The team develops a technique to form extraordinarily densely packed self-assembled monolayer (SAM) films, whose thickness is as small as 2 nanometers, on a polymeric film. This allows them to elevate substrate temperature up to 150 °C without creating pinholes through SAM films during the high temperature treatment. It is believed that ultrathin monolayer film like SAM degrades easily by thermal processes; however, it is unexpectedly demonstrated that densely packed SAM is stable at 150 °C or higher. This result is also proved by systematic characterization of crystallographic structures of SAM using a synchrotron radiation beam. Furthermore, by adopting a novel encapsulation layer comprising organic/metal composite materials and extremely thermally stable and high mobility organic semiconductors, the thermal stability of organic transistors is now improved up to 150 °C.

It should be benefited more from applying this heat-resistant organic transistor to long term implantable devices, or to some medical devices such as a smart catheter. With these applications, it is expected to broaden the usage of the transistor to medical apparatus such as thin film sensor that will detect tumors, inflammations, and or cancers.

The international team is led by Dr. Takao Someya, who is a professor of the University of Tokyo (President: Jyunichi Hamada, Ph.D.), a research director of ERATO (Exploratory Research for Advanced Technology) “Someya Bio-Harmonized Electronics Project” of Japan Science and Technology Agency (JST, President: Michiharu Nnakamura, D.Sc.), and a global scholar of Princeton University (President: Shirley M. Tilghman, Ph.D.), in collaborations with Associate Professor Tsuyoshi Sekitani of the University of Tokyo and Professor Yueh-Lin (Lynn) Loo of Princeton University. This joint research project was also carried out with the following institutions: Max Planck Institute for Solid State Research, Germany, National Institute of Standards and Technology, NIST, U.S., Hiroshima University, and Nippon Kayaku Co., Japan.

In consequence of a serious declining birthrate and a growing proportion of elderly, information technology (IT) devices are rapidly introduced in the health and medical area. One of the good examples is the internet connection of a healthcare device between a patient’s home and a hospital. The internet allowed a doctor to monitor patience’s heart rates and weights away from his/her home. The miniaturization of medical apparatuses such as endoscopes succeeded in minimizing patients’ burdens and/or invasiveness. In this way, in the medical and the healthcare field, electronics are increasing their importance. Indeed, in the health and medical market, electronics are expected to grow 120% every year successively until 2015.

In this background, an organic transistor, which is a flexible electronic switch, attracts much attention because it is easily manufactured on a biocompatible polymeric film. A biocompatible organic transistor would be suitable for applications to a stress free wearable health monitoring system and implantable devices such as a soft pacemaker. For practical implementation, it is crucial (1) to make the best use of its softness and biocompatibility, simultaneously (2) to decrease driving voltage down to a few V, and (3) to decrease the risk of infections by sterilization, for a security reason. Up until now, however, the existing organic transistors had huge obstacles towards the practical usage in the health and medical field. For example, typical driving voltage for displays is high (i.e. 20 to 80 V) and/or and it is not durable under high temperature sterilization.

The team has succeeded in manufacturing on a polymeric film an organic transistor that has world's first 150 °C thermostability and simultaneously its driving voltage of 2V. The keys to realize the heat resistant organic transistor are (1) self-assembled monolayer (SAM) and (2) a sealing film, which are to be discussed later. The highly thermal stability that we had realized exploded the typical theory that an ultrathin monolayer film of nanometers in size was easily affected by heat. This result was also proved by the systematic analysis of precise crystallographic characterizations using a synchrotron radiation beam, which will be described in (3) in detail. Furthermore, the organic transistor has successfully been sterilized under a standard sterilization process (150 °C heat treatment) without being electrically deteriorated. This will be discussed in (4).

(1) Highly thermostable self-assembled monolayer (SAM) gate insulator

A key technology towards the development of sterilizable organic transistor is the 2-nm-thick ultrathin self-assembled monolayer (SAM) film. To reduce a thickness of a gate insulator film is known as the effective way to reduce the driving voltage of an organic transistor. From the security reasons, it is necessary to thin down a gate insulator film to a few nanometers thickness in order to reduce the driving voltage down to 2V. The team employed SAM film for a gate insulator in the past. They attempted to optimize manufacturing process of SAM from heat resistance point of view. As a result, by substantially improving crystalline ordering of densely packed SAM films on a polymeric film, they succeed in forming an insulator film that does not create pinholes, the cause of a leakage current, even under a high heat treatment. This becomes possible by optimizing plasma condition during the shaping process of aluminum-oxide thin films on top of the polymeric film, resulting in a way to avoid the film from being damaged during a plasma process.

(2) An encapsulation layer comprising organic and metal composite films

An improvement of thermal stability of a SAM gate insulator is not enough to accomplish the high thermal stability of an organic transistor. Normally, organic semiconductors that compose the channel layer in organic transistor are known to be easily degraded by heat. Thereby, an organic semiconductor, which is carefully chosen among heat resistant materials, is dinaphtho-thieno-thiophene (DNTT) in the experiment. Furthermore, after manufacturing an organic transistor, the transistor is completely covered by a flexible, heat-resistant encapsulation layer comprising organic and metal composite films (Figure 2). The encapsulation layer restrains DNTT from subliming with heat, and it prevents elements from substantial deterioration. Moreover, it is demonstrated that electronic characteristic of organic transistor remains practically unchanged even after dipped in the boiling water.

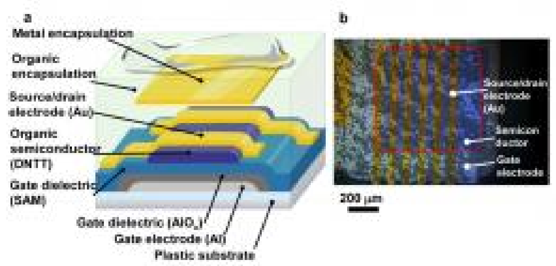

Figure 2: A schematic device structure (a) and a picture (b) of a thermally stable organic transistor. An organic transistor is covered with a flexible encapsulation layer that has both sealing characteristic as well as thermal stability.

(3) Structural characterization of nanometer-thick films by synchrotron radiation beams

The crystallographic structures of SAM films are examined. To be accurate, the gate insulator film used in the experiment consists of two layers, namely, 4-nm-thick aluminum-oxide and 2-nm-thick self-assembled monolayer. The thermal resistance of aluminum-oxide has been long known; however, there has been no report published on a structural analysis on SAM film, nor a report to prove structural stability of SAM film embedded in the devices at high temperature. This is because of the difficulty in analyzing the structure of such a thin SAM film with single molecular layer thickness using x-ray analysis.

The team attempted to precisely characterize crystallographic structures of a SAM film in order to evaluate the heat resistance of an organic transistor. Note that the thickness of a SAM film is as small as 2 nanometers. By using a synchrotron radiation beam, it is proven, for the very first time, to the best of our knowledge, that crystallographic structure of a SAM film exhibits any deterioration in molecular ordering even at 150 °C or higher temperature. This outcome unexpectedly overthrew what it had been believed that an ultrathin monolayer film of a few nanometers thinness must degrade easily by heat.

The analysis was carried out together with Professor Yueh-Lin (Lynn) Loo from Princeton University and a group at NIST, and a synchrotron radiation beam at Brookhaven National Laboratory is used.

(4) The creation of medical flexible electronics

The high thermostable organic transistors are capable of being sterilized without electrically deteriorated. The team evaluated elements' heat resistance for three different standard heating sterilization processes that are widely used to sterilize medical apparatuses: they are (1) a heat treatment at a temperature of 150 °C for 20 seconds at atmospheric pressure, (2) a heat treatment at 2 atmospheric pressures, 121 °C for 20 seconds, and (3) a sterilization by boiling.

First, the thermal stability of the manufactured organic transistor is improved by annealing process at 160 °C, which is slightly high than the typical annealing temperature for sterilization. Second, bacteria are cultured on the above mentioned transistor. Finally, the number of bacteria and the electric characteristics are measured before and after the medical sterilization process. As a result, almost all the bacteria died off after the sterilization; however, electrical characteristics of the transistor are practically unchanged (a negligible level).

Unlike the conventional inorganic materials, organic transistors are capable of making lightweight and mechanically flexible electronic devices, since they can be built on polymeric film by a low temperature processing. Organic transistors can be manufactured through printing process as well: This allowed a drastic cost reduction when making large area transistors, compared with those made with silicon. One of the major driving applications for organic transistors is e-paper. Up until now, Someya and his coworkers have intensively investigated the application of organic transistors to large-area sensors or large-area actuators. The team has shown the feasiblity of implementing organic transistors to large area electronics. A series of their achievements include a robot e-skin (2003), a sheet type scanner (2004), an ultrathin braille sheet display (2005), a wireless power transmission sheet (2006), a communication sheet (2007), an ultrasonic sheet (2008), a flash memory (2009).

Recently, organic transistors are longed to be implemented to medical and healthcare devices because of their biocompatibility. However, it is indispensable that those devices are sterilized. Therefore, it has been required that those organic circuits built on plastic films to be stable through heat treatment, and that they are driven with low voltage.

Someya and his coworkers have succeeded in making an organic transistor which stays undeteriorated after heating up to 150 °C in 2004. Though, a thick organic polymer that was used as an insulator film caused the driving voltage to be very high, and it was the reason why it did not suit for bio/medical usage. The team had attempted to build a few nm organic/inorganic materials on a plastic film using a molecular self-assembly, and they have finally proved the feasibility of heat resistance of SAM film for the first time.

In the last year, they invented a new medical electronics called “an intelligent catheter” using flexible organic transistor technique: the new narrow catheter is covered with a pressure sensor network (published in *Nature Materials*, UK in 2010). It was inevitable to develop a thermostable organic transistor so that the new catheter to be used practically at the hospitals. They finally overcame the barrier.

Organic transistors are mechanically flexible and expectedly biocompatible since they are made of soft organic electronic materials such as organic semiconductors. Attractive applications that are expected to be realized by flexible biocompatible organic transistors include “a wearable electronics” which reads out bio-information from outside of a skin, or “an implantable electronics” that directly extracts bio-information by implanting the electronics in a body. Indeed, Someya and his coworker also came up with applying the ultraflexible organic electronics to cover a narrow catheter. This opens a new path to the development of a thin film sensor that detects tumors, inflammations, early cancers. The invention will surely broaden the usage of the organic transistors as medical devices. Since a flexibility, a large coverage, and an electric stability are indispensable for implementation of these medical devices, the present invention will serve as the core technology when developing the future medical devices.

Up to this point, displays and solar cells have been considered as main driving applications of organic devices. Organic EL displays and organic flexible solar cells are implemented rapidly. However, they are only a glimpse of vast potentials that organic devices possess. Indeed, world’s researchers are competing in developing health and medical applications utilizing softness of organic devices. The team has led the field of flexible devices by achieving the world’s smallest minimum bending radius (100 μm). With the feasibility shown with these sterilizable, flexible organic transistors, the contribution will accelerate the researches on the medical applications.

The paper will be published online in *Nature Communications* (UK) on March 6th, 2012 (GMT)

More information: Scientific Paper: Organic transistors with high thermal stability for medical applications

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