Development of standard gas barrier films to evaluate ultrahigh gas barrier properties

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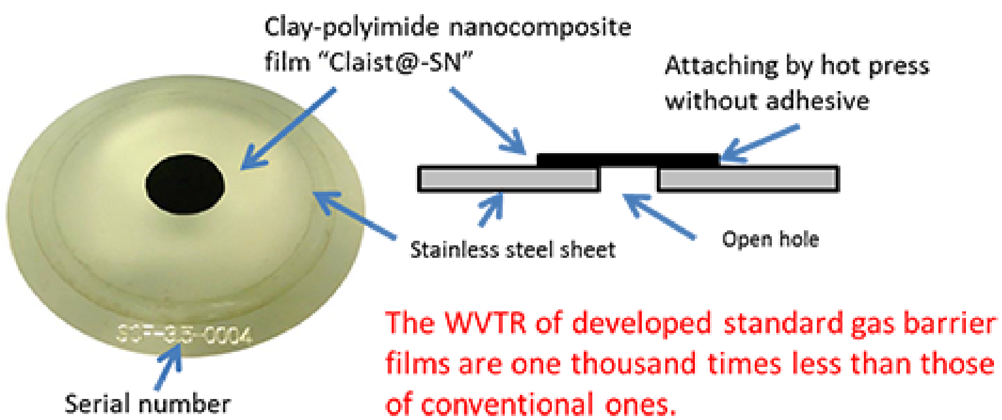

Photograph and schematic diagram of the developed standard gas barrier (SGB) film. Credit: Advanced Industrial Science and Technology

Hajime Yoshida (Senior Researcher), the Pressure and Vacuum Standards Group, the Research Institute for Engineering Measurement (Director: Toshiyuki Takatsuji), the National Institute of Advanced Industrial Science and Technology (AIST; President: Ryoji Chubachi), and Takeo Ebina (Prime Senior Researcher), the Research Institute for Chemical Process Technology (Director: Satoshi Hamakawa), AIST, have developed standard gas barrier films (SGB films) with a water vapor transmission rate of 10^{-6} g m^{-2} day^{-1} level. The SGB films are prepared using a barrier film with an ultralow gas transmission rate that is made from clay and polyimide.

The SGB films were fabricated by directly attaching the clay-based gas barrier film "Claist-SN" that has developed by AIST to a stainless steel sheet with an open hole by hot pressing. The water vapor transmission rate (WVTR) of the SGB film is controlled by two factors; the WVTR of Claist-SN itself and the area of the open hole. Three types of SGB films in the range of WVTR from 10^{-4} g m^{-2} day^{-1} to 10^{-6} g m^{-2} day^{-1} at the condition of 40 ℃ and 90 % R.H. were prepared. These values of WVTR are one thousand times less than those of conventional ones. The calibration of WVTR measuring devices by using these SGB films contributes the reliable evaluation of ultrahigh barrier films for organic electroluminescence devices (OLEDs) and organic photovoltaics cells, thereby contributing to the quality control and the long lifetime of these products.

These SGB films will be displayed at the 8th conference and exhibition of Japan Barrier Society to be held at Meiji University on May 3, 2016 and presented at the 63th Japan Society of Applied Physics spring meeting at the Tokyo Institute of Technology on May 21, 2016.

Figure 1: The reverse sides of three standard gas barrier (SGB) films developed WVTR 1.0×10^{-4} g m^{-2} day^{-1} (20 mm in diameter of the hole)(left), 1.1×10^{-5} g m^{-2} day-1(6.5 mm in diameter)(center), 3.1×10^{-6} g m^{-2} day^{-1} (3.5 mm in diameter)(right). Credit: Advanced Industrial Science and Technology

Flexible OLED displays and OLED lighting have many advantages such as thin, lightweight, being hardly broken when it is dropped, low energy consumption, and good compatibility with roll-to-roll processing. They are expected to contribute to realization of energy conservation and green innovation. When OLEDs are formed on a plastic film, however, the degradation of OLEDs due to water vapor and oxygen that transmitted through the film limits the lifetime of OLEDs. Other organic electronic devices such as organic photovoltaic cells also have the same problem.

Ultrahigh gas barrier layers for water vapor and oxygen are coated on the plastic film to prevent the degradation of organic electronic devices. The ultrahigh gas barrier layers are required to show a WVTR of 10^{-6} g m^{-2} day^{-1} level. Various WVTR measuring devices and methods have been proposed to measure such an extremely small WVTR. Most of such measuring devices need SGB films to calibrate them. However, the reliability of their measurement values was hard to evaluate because of the absence of SGB films with WVTRs of 10^{-6} g m^{-2} day^{-1} level.

The Research Institute for Engineering Measurement of AIST conducts research and development of a measuring device for gas barrier properties applying calibration techniques of a partial pressure analyzer, which has been cultivated through the development of pressure and vacuum standards. "Standard Conductance Element (SCE)" developed by AIST, which can be used to introduce various types of gases including water vapor with known, very small flow rate, enables the calibration of partial pressure analyzers.

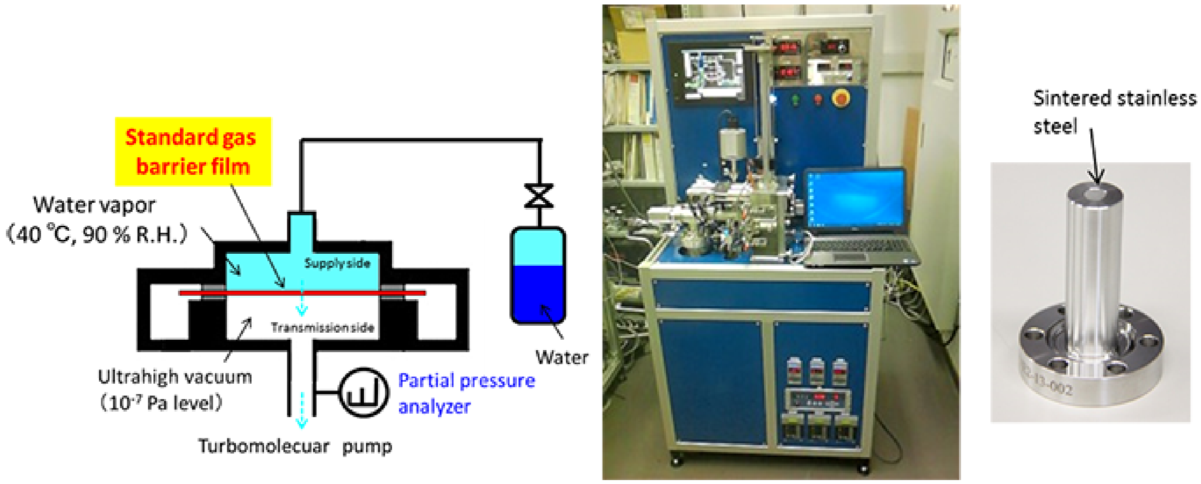

Figure 2: Schematic diagram (left) and photograph (center) of the WVTR measuring device used in this research and photograph of the SCE (right). Credit: Advanced Industrial Science and Technology

The Research Institute for Chemical Process Technology of AIST has been working to put Claist to practical use through collaborative research with research institutions such as universities and private enterprises since its development (AIST press release on August 11, 2004). Claist realizes high gas barrier properties due to its structure of compact lamination of clay crystals filling up their gaps by binder. It is also superior in thermal resistance and is applied to a wide variety of uses from food packaging to rocket development, including gaskets, flame resistant plastics, and gas barrier films. In May, 2010, an AIST consortium, Clayteam, was established to accelerate the development of Claist through industry-academia-government cooperation.

By integrating the measurement and calibration techniques of water vapor in ultrahigh vacuum of the Research Institute for Engineering Measurement and the Claist fabrication technique of the Research Institute for Chemical Process Technology, AIST pursued the development of high performance standard gas barrier films.

The WVTR of Claist can be controlled by adjusting parameters such as the mixing ratio between clay and binder. In this research, Claist-SN with WVTR of 2.0×10^{-3} g m^{-2} day^{-1} at the condition of 40 ℃ and 90 % R.H. was prepared using polyimide as the binder, where SN is the identification code which means polyimide was used as a binder. SGB films were prepared by directly attaching this prepared Claist-SN to stainless steel sheet with an open hole by hot pressing (Fig. 1). No adhesive is used to attach Claist-SN to stainless steel sheet, which means that no influence of water vapor transmitted through adhesive is appeared. When the effective measurement diameter of the sample film is 90 mm, the WVTRs of SGB films are designed to be 1.0×10^{-4} g m^{-2} day^{-1}, 1.1×10^{-5} g m-2 day^{-1}, and 3.1×10^{-6} g m^{-2} day-1 by using stainless steel sheets with a hole of 20 mm, 6.5 mm, and 3.5 mm, respectively, in diameter. A similar sample was also prepared by attaching a PET film to a stainless steel sheet with an open hole for comparison. Since the WVTR of the PET film (thickness of 80 μm) is 6.9 g m^{-2} day^{-1} at the condition of 40 ℃ and 90 % R.H., the WVTR of this PET sample is designed to be 3.4×10^{-3} g m^{-2} day^{-1} by using a stainless steel sheet with a hole of 2.0 mm in diameter.

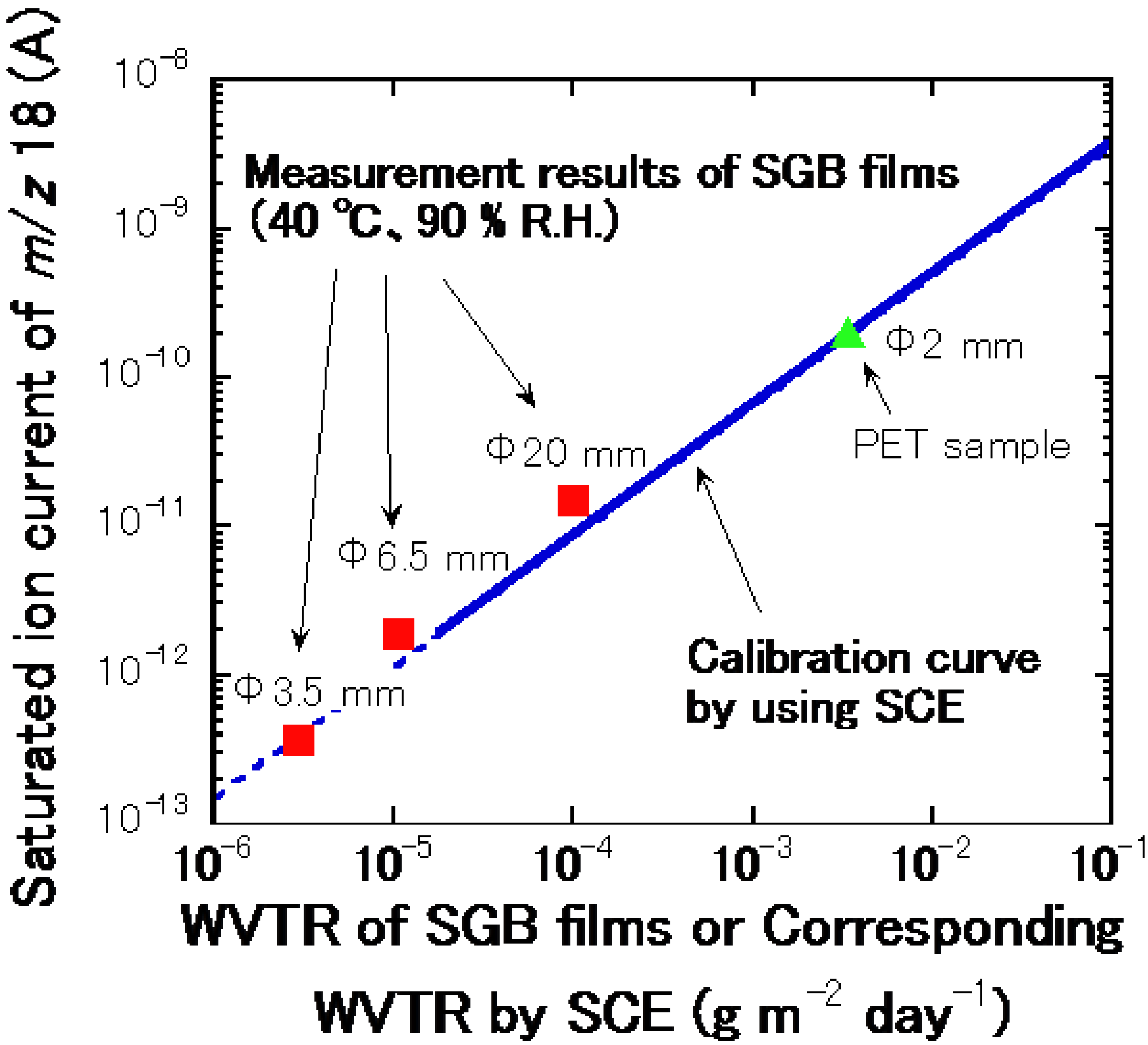

Figure 3: Measurement results of standard gas barrier (SGB) films using Claist-SN. Results of sample prepared using PET film (PET sample) is also shown for comparison. Credit: Advanced Industrial Science and Technology

The WVTR of prepared SGB films using Claist-SN and the comparison sample using PET film were measured by a WVTR measuring device of the differential pressure mass spectroscopy method (Fig. 2). After a film sample was located in this device, water vapor was introduced into the supply side (exposure side) of the film sample. The other side, which is the transmission side (detection side), was evacuated by a turbomolecular pump down to ultrahigh vacuum (10-7 Pa level). The WVTR of the film sample was measured by a partial pressure analyzer (quadrupole mass spectrometer). The differential pressure mass spectroscopy method has two advantages to measure small amount of WVTR. One is the low background pressure of water vapor before measurements due to evacuating the transmission side down to ultrahigh vacuum, and the other is that the water vapor only is measured excluding other residual gases like hydrogen by using a partial pressure analyzer as a detector. Calibration of the partial pressure analyzer is necessary to measure WVTR quantitatively. The measuring device includes the in-situ calibration system with a SCE. A calibration curve was obtained by measuring the relation between the flow rate of water vapor through the SCE and the ion current of the partial pressure analyzer, which were obtained by changing the water vapor pressure of the upstream side of the SCE step-wise.

The measurement results of the developed SGB films, including the film whose designed WVTR was 3.1×10^{-6} g m^{-2} day^{-1} (3.5 mm in diameter of the hole), at the condition of 40 ℃ and 90 % R.H. (Fig. 3) are on the line of the calibration curve prepared by using the SCE. These results indicate that the WVTRs of the developed SGB films accord with the design.

The developed standard gas barrier films are applicable to be equipped for various types of WVTR measuring devices. Comparison tests by different methods will be performed. The supplying system of standard gas barrier films with traceability to the national standard will be built.

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