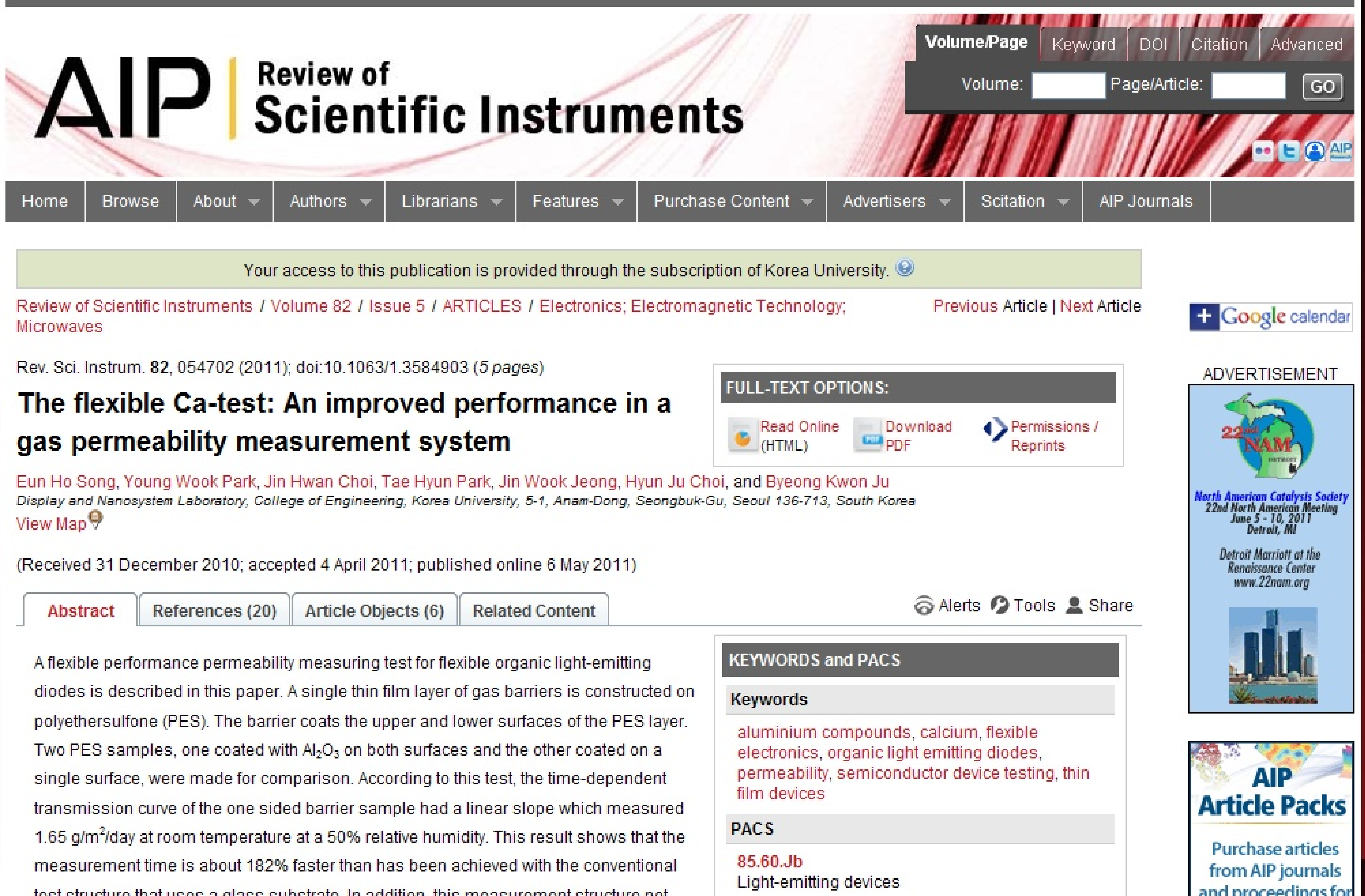

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The flexible Ca-test: An improved performance in a gas permeability measurement system

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A flexible performance permeability measuring test for flexible organic light-emitting diodes is described in this paper. A single thin film layer of gas barriers is constructed on polyethersulfone (PES). The barrier coats the upper and lower surfaces of the PES layer. Two PES samples, one coated with Al_2O_3 on both surfaces and the other coated on a single surface, were made for comparison. According to this test, the time-dependent transmission curve of the one sided barrier sample had a linear slope which measured 1.65 g/m^2/day at room temperature at a 50% relative humidity. This result shows that the measurement time is about 182% faster than has been achieved with the conventional test structure that uses a glass substrate. In addition, this measurement structure not

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Keywords

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I. INTRODUCTION

Organic light-emitting diodes (OLEDs) are one of the most promising future display devices, due to their high power efficiency, high luminous efficiency, large sight angle, and their potential for flexible displays.[1–3] However, the short life expectancy of OLEDs and various difficulties in their manufacture are critical weaknesses. In order to overcome these weaknesses, many studies have been performed over the last two decades.[4,5] As a result of this work, the drawbacks of OLEDs have become less pronounced. However, in the case of flexible organic light-emitting diodes (FOLEDs), there are still many challenges to overcome and much knowledge yet to be gained.[6–9] One significant problem that needs to be considered is the characteristics of flexible substrates. Most flexible substrates cannot protect a device from airborne water vapor. This is a serious problem, because permeated water causes organic material degradation. Furthermore, permeated water can cause electrochemical reductions at the cathode/organic interface, which generates a hydrogen evolution, creating bubbles at the cathode/organic interface layers. These bubbles delaminate the cathode materials and cause degradation to the device performance.[9,10] According to reports, a water vapor transmission rate (WVTR) below 10^{-6} g/m^2/day is critical in achieving an operational lifetime of over 10 000 h for an OLED device.[1] Another important consideration is the development of stable barriers which maintain a WVTR below 10^{-6} g/m^2/day when bending stress is applied. Therefore, many researchers have designed extremely impermeable barrier structures. Examples of these are laminated organic/inorganic layers, chemical vapor deposition, oil barriers, hydrophobic and hydrophilic nano structures, etc.[4,5,8,11,12]

It is important to be able to evaluate the barrier properties.[13–16] There are several methods used to check the barrier properties; each has specific advantages and disadvantages. A conventional WVTR measuring system (MOCON Inc., Minneapolis, MN) is limited to 5×10^{-4} g/m^2/day.[17] Newly designed test systems have been developed based on mass spectrometry and radioactivity, however these systems are not compatible with safety nor are they convenient.[14] Measurement techniques which use electrical property changes based on calcium (Ca) degradation have been designed.[13,15] Unfortunately, this method has some weakness in the fact that electrical noise occupies a relatively large portion of the data. In addition, the measurement time takes too long for an effective evaluation of the barrier performance. All of these measurement techniques have a critical drawback: changes in the characteristics cannot be detected when an external force is applied.

In this work, an advanced measurement method is reported which improves both the test reliability and reduces the measurement time by about half. In this paper, we call this approach the "flexible Ca-test" method. This newly designed test method can immediately detect barrier property changes induced by external stress. In addition, we consider the precise chemical reaction between water and calcium, so as to establish an accurate formula for the calculation of the WVTR and the oxygen transmission rate (OTR).

II. THE EXPERIMENTS

The flexible Ca-test structure is shown in Fig. 1. First, an electrode consisting of 250 nm thick silver and 2 × 2 cm^2, 100 nm thick Ca is deposited on a previously prepared barrier coated plastic substrate through a shadow mask, by the use of a thermal evaporation system. Ultraviolet (UV) resin glue is dispensed onto the border of the deposited Ca layer. Then, the lid (3 × 3 cm^2) which has an equivalent structure to

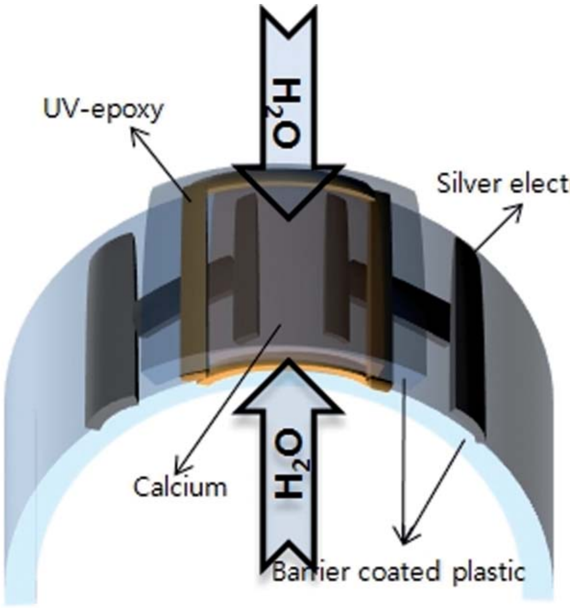

FIG. 1. (Color online) The structure of the flexible Ca-test cell.

the substrate is attached onto the dispensed UV resin. All of these processes are performed in a glove box system with an ambient nitrogen atmosphere.

Thin protective layers are deposited onto polyethersulfone (PES) (Cheil Industries[18]) in order to evaluate the water permeation properties. As shown in Fig. 2, the barrier samples use an Al_2O_3 inorganic layer. A radio-frequency (RF) magnetron sputtering system was used to make the Al_2O_3 barrier using Argon (Ar) plasma. The Ar gas flow rate was 5 sccm in the sputtering chamber using a RF power of 150 W. The barrier height was set to 300 nm, sufficient to show the barrier properties.[1] After making the barrier coated PES, we left the samples in ambient conditions for 2 days to eliminate the Ar plasma effect, in order to enable an objective evaluation of the barrier properties.

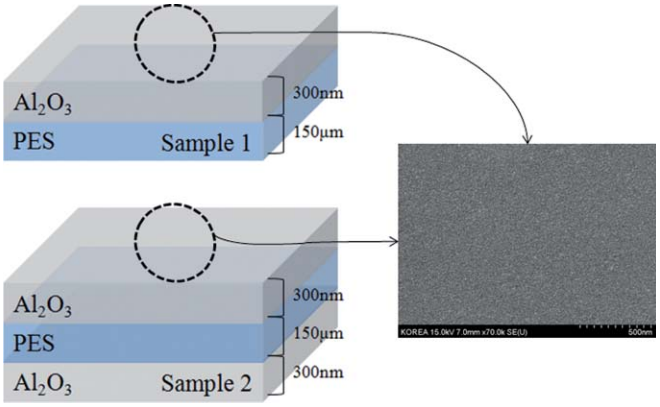

FIG. 2. (Color online) The test sample structure: the Al_2O_3 inorganic layer is deposited by the use of a RF-magnetron sputtering system. Sample 1 has an Al_2O_3 barrier coated PES deposited on one side; Sample 2 has an Al_2O_3 barrier coated PES deposited on both the upper and lower sides. The scanning electron microscope image of the Al_2O_3 layer is presented on the right side of the figure.

Calcium is a material which reacts with water and oxygen in air. The permeated water and oxygen react with the deposited Ca and form Ca oxide. Ca is a conductive metal; Ca oxide is a non-conductive insulator. For this reason, if we apply a constant voltage across calcium, the current flow through calcium decreases according to the amount of permeated water and oxygen reacting with it. We modified equations produced in previous research on Ca-testing using the electrical Ca property changes[15] in order to evaluate the barrier performance.

The modified performance equations are:

$$\mathrm{WVTR} = \frac{1}{2 - POE}\,\delta\,\frac{2M[\mathrm{H2O}]}{M[\mathrm{Ca}]}\left(1 - \frac{R_i}{R}\right) h_i \frac{24\mathrm{h}}{t},$$

$$\mathrm{OTR} = \frac{1}{2 - POE}\,\delta\,\frac{0.5M[\mathrm{O_2}]}{M[\mathrm{Ca}]}\left(1 - \frac{R_i}{R}\right) h_i \frac{24\mathrm{h}}{t},$$

where δ denotes the Ca density, is the molar mass of the indicated reagent, R is the resistance of Ca, and is the measurement time. R_i and h_i are the initial values of the Ca resistance and height, respectively. The POE denotes the "portion of the electrode" which describes a silver electrode on a substrate. It is difficult for water and oxygen to permeate through a silver electrode under the substrate, so we ignore the water permeation through the silver electrode. The POE has a value between 0 and 1. We performed an experiment under standard conditions (in an ordinary atmosphere) at 20 °C and 50% relative humidity (RH). When the flexible Ca-test is completed, an optical Ca-test is performed. The flexible Ca-test measurement value and the optical Ca-test measurement value are then compared in order to obtain the reliability of the flexible Ca-test.

This experiment is performed using a two-probe station connected to a Keithley 237 multimeter in order to measure the I-V characteristics. The measurement voltage is fixed at 5 mV in order to minimize the electrochemical corrosion at the contact interface and the unavoidable noise.

When performing the flexibility test for the barrier characteristics, the bending radius is maintained at 3 cm.

III. THE RESULTS AND DISCUSSIONS

In the flexible Ca-test, the main reactions of calcium with air are described as follows:[13]

$$\mathrm{Ca} + \mathrm{H_2O} \rightarrow \mathrm{CaO} + \mathrm{H_2},$$

$$2\mathrm{Ca} + \mathrm{O_2} \rightarrow 2\mathrm{CaO},$$

$$\mathrm{CaO} + \mathrm{H_2O} \rightarrow \mathrm{Ca(OH)_2}.$$

As can be seen, the oxygen and water vapor make CaO; CaO then reacts with the water vapor in the air to form $Ca(OH)_2$. Because the product CaO caused by the water vapor and oxygen is formed on the outside surface of the deposited calcium, consequently, after forming CaO, only water vapor can react with CaO to make $Ca(OH)_2$. Eventually, even if the water vapor and oxygen, both gas, could react with the deposited calcium, almost every reaction is related to the water vapor and not oxygen, meaning that the water vapor is the dominant oxidant in this test method. In addition, it is well known that the maximum allowable point of the WVTR is less than 10^{-6} g/m^2/day and that of the OTR is below 10^{-4} g/m^2/day.[1,4] In order to apply the barrier film to an OLED, it has to satisfy the WVTR condition which demands a 100 times harsher specification than the OTR.

The flexible Ca-test has two main advantages:

(i) First, it improves the data reliability and the measurement speed. In this model, in contrast to the conventional model, the water vapor permeates both sides of the test cell. Therefore, the initial Ca height is reduced on both sides simultaneously. In the past, there have been problems in the reliability of tests because the electrical Ca-test has a critical weakness involving unavoidable electrical signal noise. So we have sometimes found it hard to distinguish the noise from the data for barriers with an ultra low permeation. The reason for this difficulty is in the case of the ultra low water vapor permeated barriers, the test cell gathers little Ca degradation data. Therefore, the electrical signal noise accounts for a relatively large portion of the total data. In the flexible Ca-test, we solved this problem to some degree by expanding the water vapor permeation routine to both the front and back sides. This method increases the amount of data that can be attributed to the Ca degradation factor. Another consideration is that when we used the conventional Ca-test, we had to wait for a long time in order to obtain credible data in the case of the ultra low permeated barriers. In the flexible Ca-test, we achieve an incidental benefit, an improvement of the test speed by about 182%. This increase in the testing speed is because it reflects the electrode area of the flexible Ca-test cell.

Referring to the practical experiments, the WVTR of a 300 nm Al_2O_3 barrier on PES is 1.65 g/m^2/day, as can be seen in Fig. 3. The calculated WVTR of the barrier is equal in both test methods, however the required testing time for the WVTR is different for the conventional Ca-test and the flexible Ca-test. The WVTR measurement time for the flexible Ca-test is twice as fast as the time needed in the conventional Ca-test. Therefore, as mentioned earlier in this section, this reduced testing time increases the actual Ca degradation data relative to the noise data. This enhanced data selectivity leads to an improvement in the test reliability.

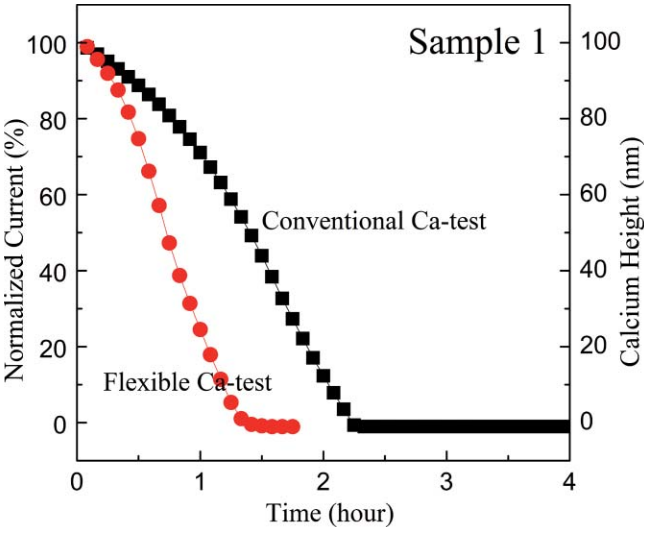

FIG. 3. (Color online) The actual WVTR measurements on Sample 1. We compare the measurement time for the conventional Ca-test and the flexible Ca-test.

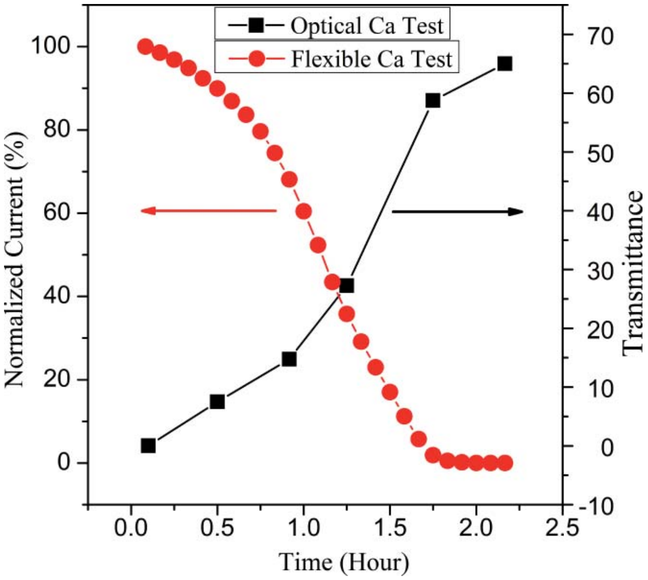

FIG. 4. (Color online) The comparison of the measured data performed by the flexible Ca-test and the optical Ca-test. The left y-axis represents the normalized current related to the flexible Ca-test. The right y-axis represents the transmittance related to the optical Ca-test.

In our previous research, the conventional Ca-test can measure the WVTR to below 10^{-6} g/m^2/day.[15] The flexible Ca-test uses the same principle to evaluate the barrier property, so it can also measure the WVTR to below 10^{-6} g/m^2/day, but also it provides a faster and a more accurate test than the conventional Ca-test.

In order to get more reliability data for the flexible Ca-test, we compared the flexible Ca-test to the optical Ca-test, which evaluates the permeability by the changing transmittance caused by calcium degradation. Figure 4 shows the rectangular line of the transmittance as it changes on the deposited calcium over time. The actual transmittance varies with wave length changes, as shown in Fig. 5(a). In Fig. 5(a), the upper black line, denoting the Al_2O_3 single layer coated plastic, presents the single barrier coated plastic transmittance. The red line, denoting the Al_2O_3 single layer coated plastic × 2, presents the two overlapped barriers coated plastic transmittance. Because the flexible Ca-test uses barrier coated plastic as the upper lid and the downside substrates, eventually the limit of the test cell transmittance becomes ~70% that is shown by the Al_2O_3 single layer coated plastic × 2 red line. We assume that the deposited calcium is totally oxidized after 100 min using the graph seen in Fig. 5(a). The WVTR value using the optical Ca-test is about 1.57 g/m^2/day determined by the WVTR formula denoted in Ref. 6. It is similar to the results obtained using the flexible Ca-test of 1.65 g/m^2/day. The two different experiments show the error of about 5% that is quite reasonable. Figure 5(b)

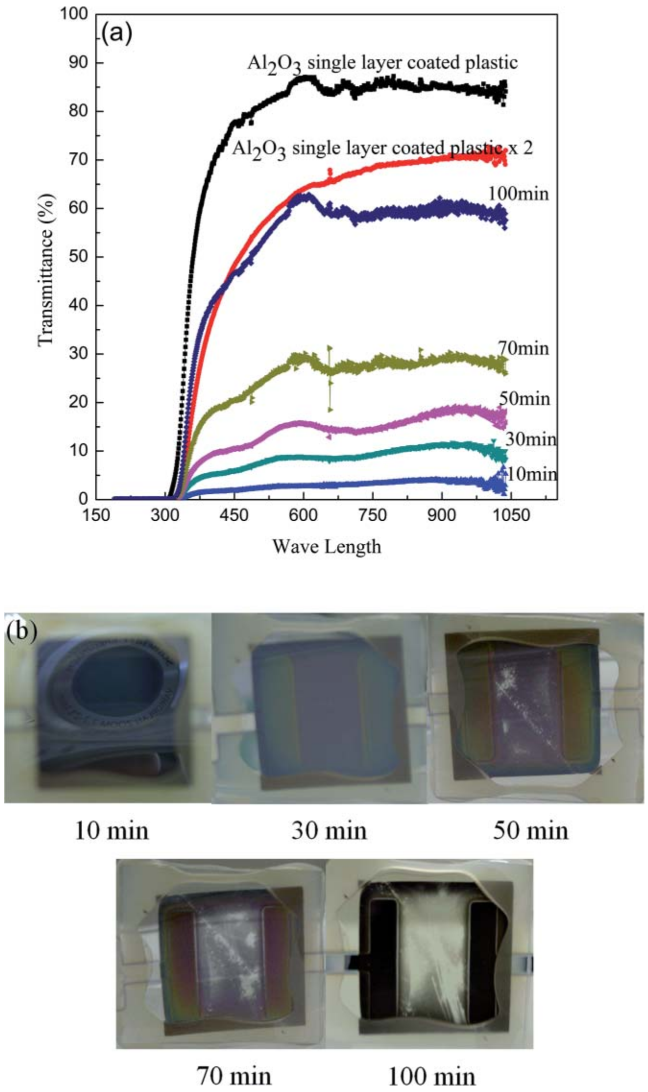

FIG. 5. (Color online) (a) Change in transmittance with wavelength and time. The upper two graphs show the bare substrate transmittance, which is just an Al_2O_3 coated single layer and two overlapped Al_2O_3 coated single layers, respectively. As the time increases the transmittance increases, caused by the calcium oxide formation. (b) Pictures of the calcium degradation over time; the center calcium is totally oxidized after 100 min, the cell is then seen as transparent.

shows the pictures of the calcium degradation over time. As the time increased to 30 min, the electrode became evident. When the time increased to 100 min center area of the test cell became totally oxidized, so it is seen as being transparent. The experiment focused on the center area of the test cell.

(ii) The other major advantage is in that the flexible Ca-test can measure the WVTR at the same time we apply the bending stress. The conventional WVTR measurement methods do not allow the application of a bending stress during measurement. So in the past, one has had to evaluate the barrier stability after applying the bending stress. However, this is not an appropriate approach to evaluate the barrier stability because the WVTR of the flexible barrier can change instantly when a bending stress is applied. For example, we might observe good flexibility properties in the barrier by the use of the conventional test method, after applying the bending stress. However, there was no guarantee that the barrier property did not degrade during the bending cycles. However, in the case of the flexible Ca-test, the substrate and the lid are constructed of plastic materials. This structure makes it possible to evaluate the flexible properties of the barriers. As shown in Figs. 6(a) and 6(b), we simultaneously performed a bending test on a 300 nm Al_2O_3 barrier on PES and the flexible Ca-test. (The actual picture illustrating the bending is shown in Fig. 4(a)). In Figs. 6(a) and 6(b), the red line shows the WVTR curve without bending. Figure 6(a) uses a single side coated Al_2O_3 single layer (Sample 1) that shows the WVTR to be 1.65 g/m^2/day. Figure 6(b) uses the double sided coated Al_2O_3 single layer (Sample 2) that shows the WVTR to be 2.85×10^{-1} g/m^2/day.

At the bending points (dashed circles) we applied a bending stress 500 times for each trial using short time intervals. As shown in Figs. 6(a) and 6(b), the result shows a drastic calcium oxide generation at each bending point on the graphs. This immediate absorption of water vapor is critical to a one side coating barrier as well as in a double sided coating barrier. This phenomenon can be explained by the

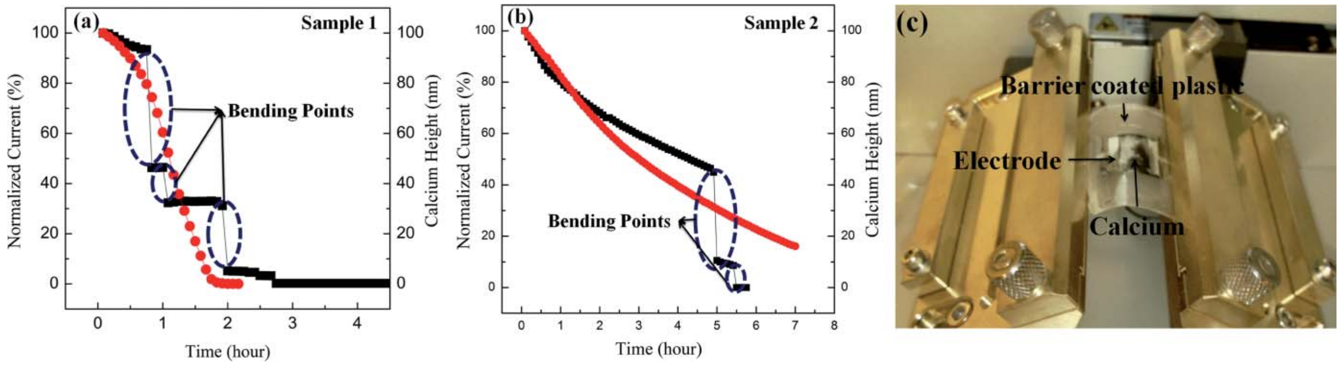

FIG. 6. (Color online) (a) The comparison of the WVTR curve without bending stress and with bending stress on Sample 1. (b) The comparison of the WVTR curve without bending stress and with bending stress on Sample 2. (c) The bending stress is applied to the flexible Ca-test cell. Each trial is repeated up to 500 times. In this test we found seriously degraded barrier properties.

pinhole and crack effects reported by many researchers. These reports claim that the water vapor permeates through barrier defects that are in the form of pinholes and cracks.[9,10,19,20] When bending stress is applied to the flexible Ca-test cell, the barrier Al_2O_3 materials split and the pinholes and the cracks are enlarged. The divided barrier surface allows the water vapor and oxygen to be absorbed more rapidly.

Unfortunately, flexible Ca-test cells cannot be completely bent like paper. In this case the flexibility of the epoxy is extremely important. The test limit for the bending radius depends on the flexibility of the epoxy. In our experiment, the maximum bending radius of the epoxy was about 2 cm. If an excessive bending force is applied the epoxy will fracture. Water vapor and oxygen are then transmitted through the cracks in the epoxy. Consequently, the flexibility and low water permeation characteristics of the epoxy are one of the major findings in the flexible Ca-test.

IV. CONCLUSIONS

In this work, we developed a quantitative WVTR measurement method applicable for flexible barrier technologies. The flexible Ca-test uses the principle of the Ca electrical properties changing through the permeation of water vapor and oxygen in air. In this system, a transmission rate in the range of 10^1–10^{-6} g/m^2/day can be measured. Furthermore, this flexible Ca-test can more precisely measure the WVTR than the conventional Ca-test, because the permeation of water vapor on both sides increases the useful Ca degradation data over the noise data. Using this flexible Ca-test, we can measure the change in the quantity of permeated water vapor through various kinds of barriers by applying a bending force. This application is the main advantage of the flexible Ca-test. Our results show that the tested barrier used in the flexible Ca-test responds well to external stresses. In this report, during the application of stress, the current flow through the Ca layer decreases extremely rapidly. We confirmed that the permeation of water vapor increased with time during the application of external stress when the barrier consists of an inorganic Al_2O_3 single or double layer. Therefore, we have designed a more accurate fast sensor using the Ca degradation principle. This sensor can also evaluate the flexibility of the barrier, which is needed for the achievement of stable flexible organic electronic devices.

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