行政院國家科學委員會專題研究計畫 成果報告

實用軟性太陽電池之研製:以原子層薄膜提高元件壽命、效率、面積、及製程實用性

研究成果報告(完整版)

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執行期間：95年01月01日至95年12月31日
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計畫主持人：蔡豐羽

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處理方式：本計畫涉及專利或其他智慧財產權，1年後可公開查詢

中華民國 96年03月30日

行政院國家科學委員會補助專題研究計畫 ■ 成果報告 □期中進度報告

（計畫名稱）

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中　華　民　國　九十六　年　三　月　三十　日

中文摘要

我們利用原子層沉積技術開發軟性太陽能電池之封裝材料與製程。我們在塑膠基板上製備之~100Å Al_2O_3 阻氣薄膜可將氧氣穿透率由 170 降至~1×10^{-3} std cc/m^2 day. 該阻氣薄膜可承受 1.5 cm 曲率直徑之彎曲而不影響其阻氣性。另外，我們將 polythiophene 與碳 60 衍生物混摻，在玻璃基板上製備成 bulk heterojunction 有機太陽能電池之標準元件，達到穩定元件特性，包括效率 > 3%、V_{oc} > 0.6 V、J_{sc} > 10 mA/cm^2 等。我們接著以傳統封裝方法封裝標準元件，亦即以玻璃蓋板搭配 UV 黏著劑封裝，並測得傳統封裝方法之封裝效能：在室溫大氣下，元件效率經 816 小時後下降達 45%。在下階段研究中，我們將利用原子層沉積技術封裝標準元件，以達到遠勝於傳統封裝方法之封裝效能。我們並將結合上述軟性阻氣基板與有機太陽能電池元件，開發具高穩定性之軟性太陽能電池。

關鍵詞：原子層沉積，有機太陽能電池，軟性電子，軟性顯示器，有機光電。

Abstract

This study utilized the technique of atomic layer deposition to develop an adequate and manufacture- friendly encapsulation process for flexible solar cells. The tasks for this first year of the project included developing flexible plastic substrates with a gas-permeation barrier and establishing reliable control devices of polymer solar cells. For the first task, we reduced the oxygen transmission rate of plastic substrates from 170 to ~1×10^{-3} std cc/m^2 day with a ~100Å Al_2O_3 film, which were bendable down to a 1.5-cm diameter of curvature without changing their barrier characteristics. For the second task, we established reproducible bulk heterojunction solar cells with poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61 butyric acid methyl ester that showed power conversion efficiency > 3%, V_{OC} > 0.6V, and J_{sc} > 10 mA/cm^2. Beyond the planned tasks, we proceeded to test the encapsulation effectiveness of the traditional encapsulation method, i.e., encapsulating with a glass lid and UV-curable adhesive, using our established standard solar cells. The encapsulated devices showed dismal lifetime in the ambience at room temperature: the efficiency decreased by 42% after 916 hours of storage. In the second year of our project, we will first develop thin-film encapsulation using the Al_2O_3 barrier films and the standard solar cell devices; secondly, we will combine the thin-film encapsulation process with the Al_2O_3–coated plastic substrates to realize highly reliable flexible solar cells.

Keywords: atomic layer deposition, organic solar cells, flexible electronics, flexible displays, organic electronics.

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I. INTRODUCTION

With the inevitable depletion of fossil fuels and the crisis of global warming looming as a result of excessive use of fossil fuels, development of renewable energy sources with low environmental impact has been on the top list of agenda for governments throughout the world. Among the many approaches toward renewable energy, solar energy is demonstrably the most matured technology, with solar panels based on the silicon technologies already a legitimate option in the commercial energy market. Silicon-based solar cells, however, though having been commercially available for several decades now, are still holding the status of a novelty that are not economically viable without government subsidies. The key factors undermining Si-based solar cells' commercial competitiveness are the high costs of the Si ingredient, the sophisticated batch-type manufacturing process, and the limited size that can be manufacture in a batch. Flexible organic solar cells are widely expected to address these commercializability issues of the Si-based solar cells, in that (1) they use organic semiconductors as the active material, which can be produced cheaply in a large scale; (2) they are compatible with continuous, roll-to-roll manufacturing process; (3) they can be made into large size and can explore applications requiring flexibility such as wearable solar cells, as shown in Fig. 1

Fig. 1. Demonstration of a wearable flexible display powered by a wearable flexible solar cell.

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Even though flexible organic solar cells are deemed highly promising, they are far from practical use because of their dismal efficiency and poor reliability/stability.[1] Most current efforts in developing flexible organic solar cells focus on optimizing the materials and device structure to improve their efficiency, but little attention has been paid to the issue of reliability/stability of the resulted devices, which arises from the high susceptibility of the organic materials to degradation by O_2 and H_2O in the ambience. [2] Previous studies estimated that for an organic light-emitting diode display, which uses similar materials as organic solar cells, the oxygen transmission rate (OTR) into the device must be below 1×10^{-3} - 1×10^{-5} std cc/m^2 day and the water vapor transmission rate (WVTR) below 1×10^{-6} g/m^2 day for the device to reach 10000 hours of lifetime. [2] Organic solar cells are expected to require the same OTR and WVTR values. Current method for achieving such low gas transmission rates is to encapsulate a solar cell device with a glass or metal cap with a getter that absorbs H_2O and O_2 entering through the rim of the cap, as illustrated in Fig. 2 (a). This method is not compatible with flexible solar cells and is size-limited and cost-prohibitive. In this study, we use the technique of atomic layer deposition (ALD) to develop defect-free thin films that serve as both a barrier on the plastic substrate and an encapsulation layer over the solar cell device, as illustrated in Fig. 2 (b) and (c). The objective is to achieve the required gas transmission rate for flexible organic solar cells with small thickness of barrier, such that the flexibility is not compromised by the addition of the inorganic barrier. The tasks of this stage of our project include (1) developing flexible plastic substrates with a gas-permeation barrier and (2) establishing reliable control devices of polymer solar cells.

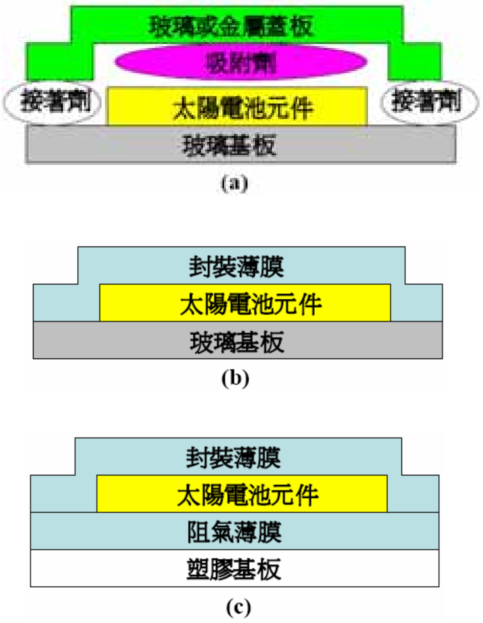

Fig. 2. Schematic drawings of (a) traditional encapsulation, (b) thin-film encapsulation of a device on a glass substrate, (c) thin-film encapsulation of a device on a plastic substrate.

II. EXPERIMENTAL SECTION

Fig. 3 shows the structure of the solar cell devices analyzed in study, whose preparation procedure is as follows. Poly(3,4-ethylenedioxythiophene) (PEDOT) with poly(styrenesulfonate) (PSS), Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61 butyric acid methyl ester (PCBM) were purchased from Sigma-Aldrich and used as received. P3HT and PCBM were dissolved separately in chlorobenzene, followed by mixing at a weight ratio of 1:1. PEDOT and the mixture of P3HT and PCBM were sequentially spin-coated onto an ITO glass (RiTdisplay Corp.) with a thickness of 70 nm and 100 nm, respectively. The cathode was formed by thermally evaporating a 250-nm layer of aluminum. The photovoltaic characteristics of the completed devices was measured using an AM 1.5G simulator of 100 mW/cm^2.

Atomic layer deposition of Al_2O_3 was carried out in a stainless steel reactor with trimethylaluminum (TMA) (EpiChem Inc.) and H_2O as the precursors. The precursors were carried with a 20-sccm N_2 flow. The reactor pressure during deposition was maintained at ~ 1 torr. Various deposition temperatures, between 75 and 300º, were used. Polyimide substrates (Kapton HN), 50 μm in thickness, were purchased from GoodFellow Inc. and used as received. Poly(ethylene terephthalate) (PET) and poly(ethylene naphthalate) (PEN) substrates, both 125 μm in thickness, were provided by DuPont Teijin Films. OTR was measured with a MOCON 2/61 permeation tester. HeTR was measured with an in-house-built apparatus. [3] Temperature dependence of the HeTR was measured by heating the apparatus to temperatures between 25 and 200ºC with a heat tape. PECVD SiN_x barriers, 1000 Å in thickness, were prepared from SiH_4 and NH_3 at 250ºC. Sputtered SiN_x, 1000 Å in thickness, were prepared by RF sputtering a Si_3N_4 target in Ar without heating the substrates. Evaporated Al barriers, 1500 Å in thickness, were prepared by thermal evaporation in high vacuum of 1×10^{-6} torr.

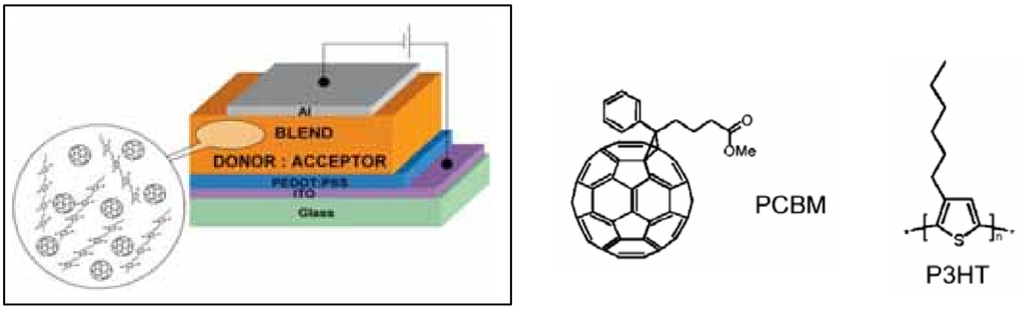

Fig. 3. Schematic representation of the structure of the solar cells analyzed in this study. The blend layer comprised the mixture of P3HT and PCBM.

III. RESULTS AND DISCUSSION

The ALD barriers were found to exceed the lower limit (0.1 std. cc/m^2 day) of the MOCON permeation tester at a thickness of 77 Å, while the PECVD (1000Å), sputtered (1000Å), and evaporated (1500Å) barriers had significantly higher OTRs of 2.2, 5.4, and 10.1 std. cc/m^2 day, respectively. Using our He permeation tester, the ALD barriers were measured to have a HeTR of 13 std. cc/m^2 day, which after calculation corresponds to OTR of 1×10^{-3} std. cc/m^2 day, as shown in the calibration curve in Figure 1. Given that the bare polyimide substrate' s OTR is 170 std. cc/m^2 day, the ALD barriers lowered the OTR by more than 5 orders of magnitude, achieving the barrier performance required by organic solar cells and OLEDs.

The activation energy for permeation (E_a), being 20 kJ/mol for the bare polyimide substrates, was reduced to 55 kJ/mol by the ALD barrier, but remained relatively unchanged by the other 3 barriers, as shown in Fig. 2. Note that E_a was determined by fitting the temperature dependence of HeTR to the Arrehnius relationship. The observation that E_a was unchanged by the 3 non-ALD barriers was consistent with previous results, [4] which indicates that the permeation was dominated by leaking through macroscopic defects, a mechanism that is not thermally activated. [5] The ALD barriers, on the other hand, caused significant increase in E_a to the polyimide substrates, which indicates that the gas transport mechanism was altered from leaking through macroscopic defects to permeation through the microstructure, a prerequisite for an effective barrier. The exceptional barrier performance of the ALD barriers compared with the other 3 types of barriers was attributed to the absence of macroscopic defects. In terms of WVTR, however, the ALD Al_2O_3 resulted in only small reduction from that of the bare plastic substrates. This was attributed to the ultra-thin thickness of the Al_2O_3 barrier and its solubility in water, which when coupled caused severe disintegration of the barrier, rendering it ineffective. A water-repellent coating over the Al_2O_3 barrier may be necessary to achieve low WVTR and will be one of the main tasks in the next phase of the project.

The ALD barriers showed good flexibility in that they could be repeated flexed to a curvature of 1.5-cm diameter without significantly increasing their gas transmission rates.

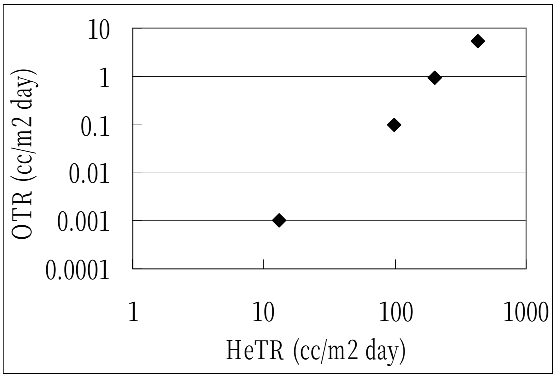

Fig. 4. Calibration curve for the HeTR values measured with our in-house-built He permeation tester against OTR values measured with the MOCON tester.

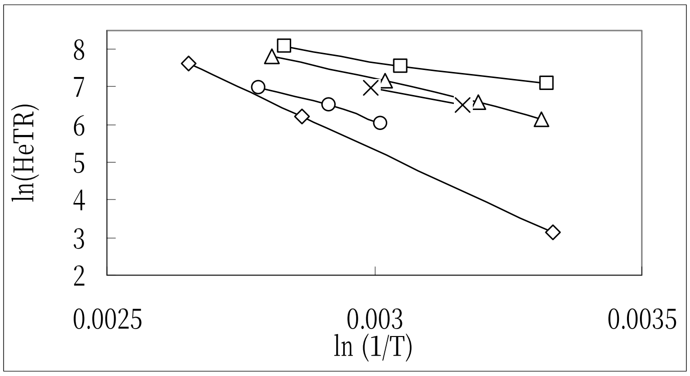

Figure 5. Temperature dependence of HeTR for bare polyimide (□), polyimide coated with 1000Å sputtered SiNx (Δ), polyimide coated with 1500Å evaporated Al (×), polyimide coated with 1000Å PECVD SiN_x (O), and polyimide coated with 77Å ALD Al_2O_3 (◊).

We established a fabrication process that yields polymer solar cells with reproducible performance that is on par with reported values based on similar structure and materials, [6, 7] as shown in Fig. 6. Typical values of the key performance metrics are as follows: power conversion efficiency (η) ~ 3%, V_{OC} ~ 0.6V, and J_{sc} ~ 10 mA/cm^2, and fill factor (FF) ~50. The performance of our solar cell devices is still inferior to the reported optimum of η ~ 5%, which may be attributed to the lower-than-optimum fill factor we have so far obtained. We have identified factors that may be responsible for the FF, including high series resistance and low shunt resistance. The problem of high series resistance may be resolved by (1) optimizing the thickness of the active layer, (2) applying proper annealing to the active layer to improve its morphology, (3) adequately prepping the ITO surface by using plasma cleaning or UV-ozone treatment, and (4) adding surfactants to the PEDOT:PSS layer to increase its conductivity.[8,9] The shunt resistance may be minimized by improving the quality of the spun-on films to eliminate pinholes and defects and by planarizing the asperity-prone ITO surface.[10,11] These measures will be explored in the next phase of the project.

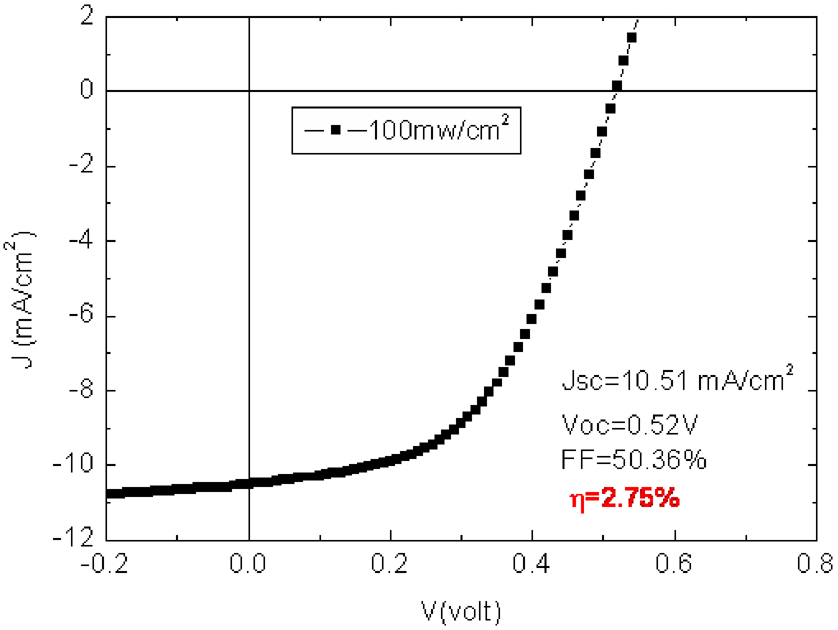

Fig. 6. J-V characteristics of two typical organic solar cell devices fabricated in this study.

To determine the baseline of the lifetime of our standard solar cells, we encapsulated the standard solar cells with a glass lid and UV-curable adhesive, as illustrated in Fig.2 (a) except for the absence of a getter. The encapsulated devices showed gradual degradation upon storage in the ambience at room temperatures, with the power conversion efficiency decreasing by up to 45% after 816 hours of storage, as shown in Fig. 7. The rapid degradation is attributed to photo-oxidation of the active materials that was permitted by the high O_2 and H_2O transmission rates of the UV-curable adhesive. The degradation is expected to be greatly decelerated on devices encapsulated with the ALD Al_2O_3 barriers, which will effectively lower O_2 and H_2O transmission rates. Encapsulation of polymer solar cells with ALD is the one of the tasks for the second year of our project.

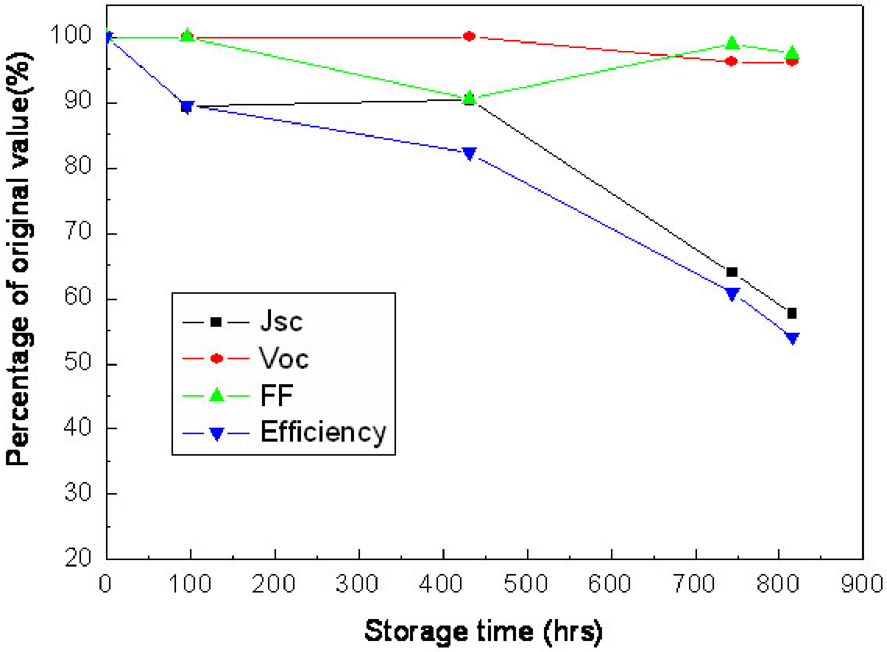

Fig. 7. Degradation of key characteristics of a polymer solar cell encapsulated with a glass lid and a UV-curable adhesive.

IV. CONCLUSION

This study utilized the technique of atomic layer deposition to develop an adequate and manufacture- friendly encapsulation process for flexible solar cells. The tasks for this first year of the project included developing flexible plastic substrates with a gas-permeation barrier and establishing reliable control devices of polymer solar cells. In the first task, we reduced the oxygen transmission rate of plastic substrates from 170 to ~1×10^{-3} std cc/m^2 day with a ~100Å Al_2O_3 film, which were bendable down to a 1.5-cm diameter of curvature without changing their barrier characteristics. In the second task, we established reproducible bulk heterojunction solar cells with Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61 butyric acid methyl ester that showed power conversion efficiency > 3%, V_{OC} > 0.6 V, and J_{sc} > 10 mA/cm^2. We proceeded to test the encapsulation effectiveness of the traditional encapsulation method, i.e., encapsulating with a glass lid and UV-curable adhesive, using our established standard solar cells. The encapsulated devices showed dismal lifetime in the ambience at room temperature: the efficiency decreased by 42% after 916 hours of storage. The coming stage of our project will combine the results above to realize high-reliability flexible solar cells.

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可供推廣之研發成果資料表

□ 可申請專利　　■ 可技術移轉　　日期：96 年 3 月 30 日

國科會補助計畫	計畫名稱：實用軟性太陽電池之研製: 以原子層薄膜提高元件壽命、效率、面積、及製程實用性 計畫主持人：蔡豐羽 計畫編號：NSC 95-2623-7-002-010-ET 學門領域：高分子
技術/創作名稱	**一種利用保護層形成光電元件的方法**
發明人/創作人	蔡豐羽、卓學照
技術說明	中文：本發明揭露一種利用保護層形成光電元件的方法。本發明在有機電激發光（Electroluminescent）材料上生成一層無反應性材料之超薄保護層，阻絕製程環境中溶劑或氣體與材料之直接接觸，使材料得以利用光微影技術形成圖樣，形成有機發光二極體(OLED)顯示器之像素。此保護層之厚度極小，在完成後不需由材料表面除去，可留存為顯示器之一部分。由於此保護層之超薄厚度，對顯示器性能並無負面影響，甚至有提升顯示器性能之功效。
	英文：his invention discloses that photolithography can be made compatible with the production of electronic devices containing sensitive materials, if the sensitive materials are over-coated with an ultra-thin layer of non-reactive materials (e.g. inorganic oxides) before undergoing photolithographic patterning. This protective layer isolates the sensitive materials from solvents and etching reactants used in photolithographic patterning, and does not need to be removed from the sensitive materials after patterning is completed. Because of its ultra-thin thickness (5-15Å), this integrated protective layer causes negligible adverse effect on the resulted devices. On an OLED device that was photolithographically patterned using a 12-Å Al_2O_3 protective layer, it was demonstrated that the electroluminescent efficiency significantly increased with the protective layer integrated in the device.
可利用之產業 及 可開發之產品	可利用之產業：顯示器產業與軟性電子產業。 可開發之產品：軟性電子產品，如軟性太陽電池、軟性顯示器、軟性 RFID 等

技術特點	低溫、大面積、大批次製程、低真空度需求、具高 flexibility
推廣及運用的價值	本技術可加速實現軟性電子產品之實用性，包括軟性太陽電池、軟性顯示器、軟性 RFID 等，且可推廣應用於所有使用敏感性光電材料之產品。本技術除用於增加材料與元件之穩定性外，也可用於敏感性光電材料之精準圖樣上(patterning)，同時解決軟性電子產品之兩大實用性問題。

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