# 行政院國家科學委員會專題研究計畫 成果報告

## 光電高分子與矽奈米晶體複合材料於軟性太陽電池之應用 研究成果報告(精簡版)

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# 行政院國家科學委員會補助專題研究計畫成果報告

## 光電高分子與矽奈米晶體複合材料於軟性太陽電池之應用

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## 摘要

本研究探討矽奈米晶體與光電高分子複合材料於軟性太陽電池之應用，以改善軟性太陽電池效率與穩定度不足之問題。本年度研究之目標包括：製備高結晶度且尺寸精準之矽奈米晶體、研究界面改質方法使矽奈米晶體能有效分散並保持表面性質、以及開發可溶液成膜之多晶矽薄膜以利製備軟性太陽電池。本年度研究成果包括：(1)成功製備直徑小於 10 nm 之矽奈米晶體，並以 x-ray diffraction 與 electron diffraction 確定其為單晶；(2)利用 propionic acid (PA)進行矽奈米晶體之表面改質，使矽奈米晶體可在溶劑中完全分散；(3)分析改質後矽奈米晶體之 photoluminescence 現象，確認其 quantum confinement 效應；(4)以改質後之矽奈米晶體進行溶液成膜，達到品質良好之多晶矽薄膜；(5)利用所製備之多晶矽薄膜製成二極體，發現其二極體具低漏電流、低起始電壓、以及高導電率。在後續研究中，我們將從事下列工作：(1)將矽奈米晶體與 p 型高分子半導體如 poly(3-thiophene)(P3HT)等摻混，製備軟性太陽電池；(2)研究其他表面改質方法，以更有效操控矽奈米晶體之表面性質；(3)將溶液成膜之多晶矽薄膜製備成薄膜電晶體；(4)將矽奈米晶體與電致發光高分子摻混，以製備發光二極體。

**Abstract**

This work studies the film-forming property of surface-functionalized Si nanoparticles, with the goal of producing uniform, homogeneous Si films by solution casting for use as active material for flexible polymer solar cells. We adopted a simple, low-cost route of preparing Si nanoparticles, which involved annealling Si suboxide nanoparticles into highly crystalline Si cores enclosed in $SiO_2$ shells, followed by etching the $SiO_2$ shells in acids to obtain H-terminated Si nanoparicles (H-Si nps). The H-Si nps were characterized in terms of size, size distribution, degree of aggregation and crystallinity, and were tested for their film-forming property. The H-Si nps were then functionalized by propionic acid (PA) into PA-Si nps to improve the dispersion of the nanoparticles in tetrahydrofuran (THF). The PA-Si nps were mixed with H-Si nps, and the mixture was casted into films. The films were incorporated into diodes (Al/PA-Si:H-Si/ITO) to characterize their electrical properties. H-Si nps prepared by annealing and etching $SiO_x$ (x<2) nps were of high crystallinity and small size (<10 nm), but were prone to aggregate in solution, and thus could not be formed into continuous Si films. Functionalizing the H-Si nps into PA-Si nps significantly improved their dispersion in solution, allowing uniform, continuous films to be cast from blended solutions of PA-Si and H-Si nps, as confirmed by zetasizer, SEM, and AFM. Diodes with the H-Si/PA-Si films showed low leakage current with reasonably high conductance and low turn-on voltage, indicating good potential of the Si films for applications in optoelectronic and microelectronic devices such as thin film transistors (TFT) and solar cells.

# 光電高分子與矽奈米晶體複合材料於軟性太陽電池之應用

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## Introduction

Nano-structured silicon is a material of great interest during the past decade, owing to its attractive advantages such as efficient photoluminescence of visible lights and good compatibility with existing silicon technologies, and thus has many potential applications in optoelectronic and microelectronic devices. Among Si nanostructures, Si nanoparticles are particularly attractive because of their solution processibility to form Si films, which would offer low process cost and compatibility to organic electronics.

Many techniques are available for efficiently producing Si nanoparticles, including laser ablation of, [1] thermal annealing of Si suboxides, and thermal decomposition of disilane and silane.[2] However, forming homogeneous Si films from solutions of Si nanoparticles is still difficult due in large part to the tendency of the nanoparticles to aggregate into heterogeneous morphology. The tendency to aggregate can be significantly decreased by functionalizing the surface of Si nanoparticles with organic ligands,[3,4] but no systematic study has been conducted to examine and optimize the film-forming property of such functionalized Si nanoparticles.

This work studies the film-forming property of surface-functionalized Si nanoparticles, with the goal of producing uniform, homogeneous Si films by solution casting. We adopted a simple, low-cost route of preparing Si nanoparticles, which involved annealling Si suboxide nanoparticles into highly crystalline Si cores enclosed in SiO2 shells, followed by etching the $SiO_2$ shells in acids to obtain H-terminated Si nanoparicles (H-Si nps).[5] The H-Si nps were characterized in terms of size, size distribution, degree of aggregation and crystallinity, and were tested for their film-forming property. The H-Si nps were then functionalized by propionic acid (PA) into PA-Si nps to improve the dispersion of the nanoparticles in tetrahydrofuran (THF). The PA-Si nps were mixed with H-Si nps, and the mixture was casted into films. The films were incorporated into diodes (Al/PA-Si:H-Si/ITO) to characterize their electrical properties.

## Experiment

The procedure of synthesizing H-Si nps was described as follows. First, $SiO_x$ (x < 2) nanopowder, supplied by DENKA Co., was annealed at $1000^{o}C$ for 2 hr using a high-temperature resistance furnace under a vacuum of ~$10^{-5}$ torr. After annealing, the powder was added to a mixture of methanol, HF (49%), and HNO3 (65%) and sonicated for 5 min to etch the outer oxide layer, hence yielding H-terminated Si nanoparticles. The H-Si nps were collected by filtering the solution through a PVDF membrane($0.45 \mu$m). The filtered H-Si nps were washed with a mixture of D.I water and methanol, and then dried in vacuum at $100^{o}C$.

The sizes of nanoparticles in solution before and after etching were measured by a PANalytical X'Pert PRO diffractometer operated at 45 kV and 40 mA. The H-Si nps were characterized by X-ray powder diffraction (XRD) and transmission electron microscope (TEM) (JEOL JEM-100CX 2 operated at 100 kV). To prepare the TEM samples, the H-Si nps were dispersed in THF and then dropped onto amorphous carbon-coated grid.

PA-Si nps were synthesized by dispersing H-Si nps in a mixture of hydrofluoric acid (HF) and acrylic acid (volume ratio = 1/4) with ultra-sonication, and then exposing, the solution with a UV light (254nm) under constant stirring for 48 hr.[6] The products were filtered

through a PTFE syringe filter before use. Photoluminescence (PL) specta of the PA-Si nps dispersed in THF were recorded by a FP-6300 Spectrofluorometer Fluorescence with an excitation wavelength of 360nm. The degree of dispersion of the H-Si and PA-Si THF solutions was evaluated by a Malvern Zetasizer 3000 HS (zetasizer).

Si nps films were prepared by spin-coating on Si wafers with suspension solutions of two formulations of Si nps. The first formulation contained only H-Si nps in TFF (10 mg H-Si nps in 5 mg THF, used after 5-min ultra-sonication). The second formulation was a mixture of PA-Si and H-Si (weight ratio = 25/1) in THF (2.88 wt %), which was spin coated at 2600 rpm. The films were characterized by optical microscopy (OM), scanning electron microscopy (SEM) (JOEL JSM-6700F Field Emission Scanning Electron Microscope), and Atomic force microscopy (AFM) (Digital MultiMode V).

Diodes containing the Si films were fabricated by spin-coating Si films on indium tin oxide (ITO) coated glass substrates, which were applied a 90-nm-thick Al film as the cathode by thermal evaporation through a shadow mask. The J-V characteristics of the diodes were measured using a Keithley 236 Source Measurement Unit.

**Result and discussion**

The H-Si nanoparticles we prepared had the outer SiO2 layer completely removed after etching, as evidenced by the absence of the amorphous $SiO_2$ x-ray diffraction (XRD) peak at $2\theta = 21°$ (Fig. 1), which was predominant with the unetched nanoparticles. The 3 strong XRD peaks of the H-Si nanoparticles, which correspond to the (111), (220), and (311) orientations of cubic silicon, indicate that the H-Si nanoparticles were highly crystallized.

The H-Si nps were less than 10 nm in diameter individually, but were heavily aggregated when drop-cast into films on TEM sample grid, as shown in the TEM images in Fig. 2. Spin-coating also resulted in heavily aggregated films that were discontinuous (Fig 3). The

aggregation was already well developed in the solution phase, as the suspended H-Si nps showed an average size of 200 nm in the zetasizer results (Fig. 5). Moreover, the suspended H-Si nps did not show detectable photoluminescence. These results confirmed the poor film-forming property of H-Si nps and pointed to the need for surface functionalization.

Functionalizing the H-Si nps into PA-Si nps significantly improved the dispersion of the nanoparticles,[7] as can be seen in the appearance of the H-Si nps solutions undergoing functionalization, which changed from turbid to clear at the completion of the functionalization (Fig 4.). The complete dispersion of the PA-Si nps in THF was also confirmed by the zetasizer results (Fig. 5), which showed that the mean diameter of the suspended PA-Si nps was 10.3nm, in agreement with the individual particle diameter determined by TEM (Fig. 2). As a result of their complete dispersion, the suspended PA-Si nps showed strong photoluminescence with emission maximum at ~500nm (Fig 6.).

The film-forming property of the H-Si nps was improved by adding PA-Si nps (weight ratio = 1 H-Si/25 PA-Si) into the solutions of H-Si nps, as shown in the AFM images in Fig 7 a, where the surface of the spin-coated films was generally smooth with sparse spikes, which were attributed to aggregation of H-Si nps within the continuous PA-Si film. The segregation of PA-Si and H-Si can be more clearly seen in the AFM phase profile in Fig. 7 b, where the darker area represents the softer surface of PA-Si, which is continuous throughout the sample surface.

Having obtained continuous Si films from H-Si/PA-Si solutions, we incorporated the films in diodes (Al/PA-Si:H-Si/ITO) to study its electrical characteristics. The diodes showed low leakage current, which was manifestation of the good uniformity of the Si films, and reasonable conductance and turn-on voltage, as shown in Fig 9. Compared with reported diode characteristics with

nano-Si films produced by pulsed laser ablation, [8] the conductance was slightly lower and turn-on voltage smaller with the H-Si/PA-Si films.

## Conclusion

H-Si nps prepared by annealing and etching $SiO_x$ (x<2) nps were of high crystallinity and small size (<10 nm), but were prone to aggregate in solution, and thus could not be formed into continuous Si films. Functionalizing the H-Si nps into PA-Si nps significantly improved their dispersion in solution, allowing uniform, continuous films to be cast from blended solutions of PA-Si and H-Si nps, as confirmed by zetasizer, SEM, and AFM. Diodes with the H-Si/PA-Si films showed low leakage current with reasonably high conductance and low turn-on voltage, indicating good potential of the Si films for applications in optoelectronic and microelectronic devices such as thin film transistors (TFT) and solar cells.

## References

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5. S. M. Liu, S. Sato, K. Kimura, *Langmuir*, **21***, 6324(2005).
6. S. Sato, M. T. Swihart, *Chem. Mater.*, **18**, 4083(2006)
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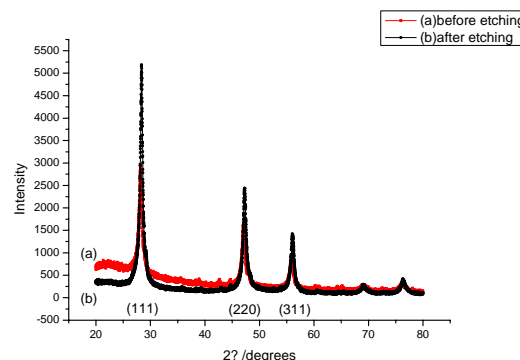
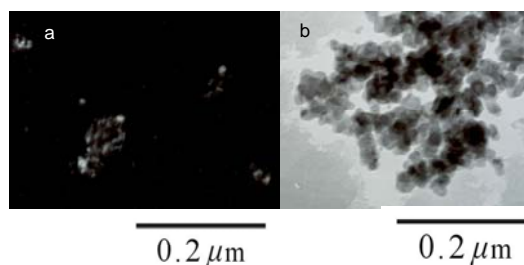Fig 1. XRD patterns of nanoparticles (a) before etching (b) after eching



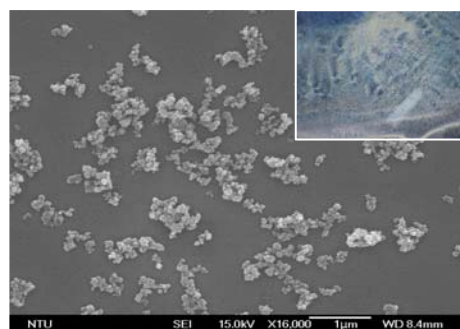Fig 2. (a) Dark field image (b) Bright filed image of H-Si nps THF solutions.



Fig 3. The SEM image of the H-Si nps films. The inset photograph is OM image of the H-Si nps films observed at 450x.
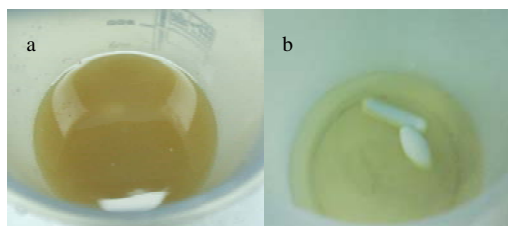


Fig 4. The Si nps HF/acrylic acid solution (a) before UV exposure (b) after exposure.
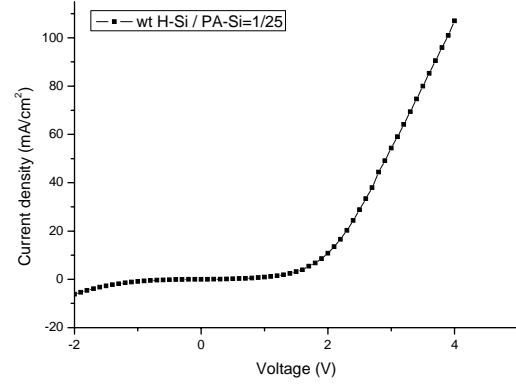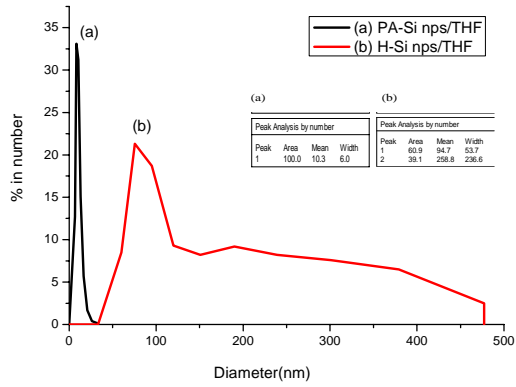
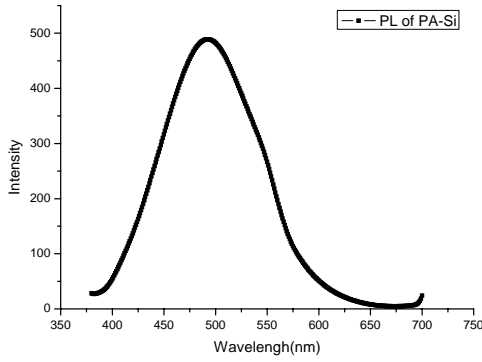Fig8 . The J-V characteristics of Al/PA-Si:H-Si/ITO heterostuctures
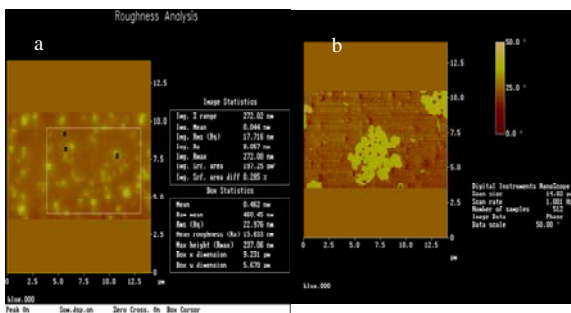


Fig 6.The PL spectrum of PA-Si nps in acylic acid.



Fig 7.(a) The AFM height profile (b) The AFM phase profile of the H-Si

nps/PA-Si nps films.

# 出席國際學術會議心得報告

| 計畫編號 | NSC 95-2221-E-002-201 |
|---|---|
| 計畫名稱 | 光電高分子與矽奈米晶體複合材料於軟性太陽電池之應用 |
| 出國人員姓名<br>服務機關及職稱 | 蔡豐羽　台灣大學材料系　助理教授 |
| 會議時間地點 | Nov. 26 – Nov. 30 2007; Boston, MA, USA |
| 會議名稱 | MRS Fall Meeting |
| 發表論文題目 | **Photolithographic Patterning of Organic Light-Emitting Diode Displays Using an Electron-Injection-Enhancing Protecting Layer** |

一、參加會議經過

The electroluminescent (EL) material of an organic light-emitting diode (OLED) was patterned photolithographically under the protection of a thin (10 Å) atomic-layer-deposited (ALD) $Al_2O_3$ layer, and the resulted OLED device showed improved performance. ALD's characteristic low defect density and high conformality enabled the thin $Al_2O_3$ layer to protect the EL material from solvents throughout the patterning process and to serve as an effective buffer layer. An IPA pretreatment of the MEH-PPV surface prevented damages caused by the ALD precursors during the ALD process. The device characteristics of the patterned OLEDs were further improved by increasing the conductivity of the PEDOT:PSS layer, likely as a result of increased hole accumulation at the EL-buffer interface that enhanced electron injection. Our method renders photolithography compatible with OLED fabrication, promising to resolve the issue of patterning that has in part impeded OLED's commercialization.

二、與會心得

This meeting showcased the tremendous progress in the field of organic electronics including organic photovoltaics (OPV), organic thin-film transistors (OTFT), and organic light-emitting diodes (OLED). Interesting results related to my research topics include the following:

1. Si nanoparticles have been used with poly(3-hexylthiophene) (P3HT) to fabricate bulk-heterojunction solar cells, achieving power conversion efficiency (PCE) of 1%. Although the PCE value is impressive, considering the novelty of this approach, it is still much lower than the norm for OPVs. This deficiency may be due to the poor quality of the bulk-heterojunction films and to the impure surface of the Si nanoparticles. In light of the issues exposed by these results, we are developing film-forming methods to achieve good quality of bulk-heterojunction films as well as developing surface modification techniques to achieve desired functionality of the surface of Si nanoparticles.

2. Bulk Si has been used with a P3HT film to fabricate bilayer-heterojunction solar cells. The achieved PCE was quite low, but considering the simplicity of the bilayer structure, we see some value in this approach as a tool for investigating the photovoltaic mechanisms of the Si/polymer heterojunction solar cells.
3. Si nanoparticles can be produced in large quantity with high yield using a plasma enhanced decomposition process. This process may be useful to us when we commercialize our Si/polymer technology.