The Non-Fullerene Acceptor ITIC Induced the Morphology of Bulk Heterojunctions Through Thermal Annealing

The key component affecting the thermal stability of non-fullerene organic solar cells is explored.

The nanomorphology of bulk heterojunctions (BHJs) is a critical factor influencing the performance of non-fullerene organic solar cells (OSCs). Thermal annealing is widely used in enhancing device performance by reorganizing the donor and acceptor phases within BHJs. A team led by Tzu-Yen Huang (NSRRC) and Yan-Ling Yang (National Taiwan University of Science and Technology) systematically examined the vertical morphology of BHJ blend films, which utilized poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-alt-(3,3‴-di(2-octyldodecyl)-2,2′;5′,2″;5″,2‴-quaterthiophen-5,5‴-diyl)] (PffBT4T-2OD) polymer as the donor and 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2′,3′-d′]-s-indaceno[1,2-b:5,6-b′]dithiophene (ITIC) as the acceptor through thermal annealing.

The team made use of the neutron reflectometry (NR) instrument (**SPATZ**) at the Australian Nuclear Science and Technology Organisation (ANSTO) to study the blend morphology of BHJ thin films. **Figures 1(a) and 1(c)** illustrate the NR patterns and scattering length density (SLD) profiles of PffBT4T-2OD:ITIC BHJs with various blend ratios deposited on quartz-coated glass substrates. The SLD values of PffBT4T-2OD monomers and ITIC molecules were calculated to be 0.65 and 1.44×10^{-6} Å^{-2}, respectively. The NR curves of the 1:9 ratio revealed distinct Kiessig fringes spanning a Q-range of 0.02 to 0.10 Å^{-1}, indicating high-quality thin films. As the ratio of PffBT4T-2OD is increased, the clear fringes are preserved, demonstrating good film quality across different blend ratios. The fringes of the BHJ layer (9:1 ratio) became less defined due to the proximity of the SLD value of PffBT4T-2OD to that of the atmosphere, which reduced contrast. For all samples, the quartz layer on the glass substrate exhibited a consistent thickness of about 200 Å with a roughness of 13 Å. The SLD value of different BHJ layers ranged from 1.39×10^{-6} Å^{-2} (1:9 ratio) to 0.70×10^{-6} Å^{-2} (9:1 ratio). These findings suggest that the vertical morphology of the BHJ layers is well-mixed, without distinct phase segregation.

Thermal annealing is a common method for optimizing phase separation in a BHJ layer, facilitating the formation of the desired morphologies for efficient charge transport. To avoid surpassing the recrystallization temperature of ITIC at 170°C, the thermal treatment was carried out incrementally, with annealing temperatures reaching up to 150°C. **Figures 1(b) and 1(d)** present the NR patterns and the SLD profiles of the PffBT4T-2OD:ITIC BHJ layers (5:5 blend ratio) deposited on Si wafers, which were subjected to annealing at temperatures ranging from 90 to 150°C. The pristine PffBT4T-2OD:ITIC BHJ layers exhibit fringes in the Q-range of 0.010 to 0.040 Å^{-1}, indicating the formation of smooth and uniform thin films. At an annealing temperature of 130°C, the fringes remain intact, signifying that

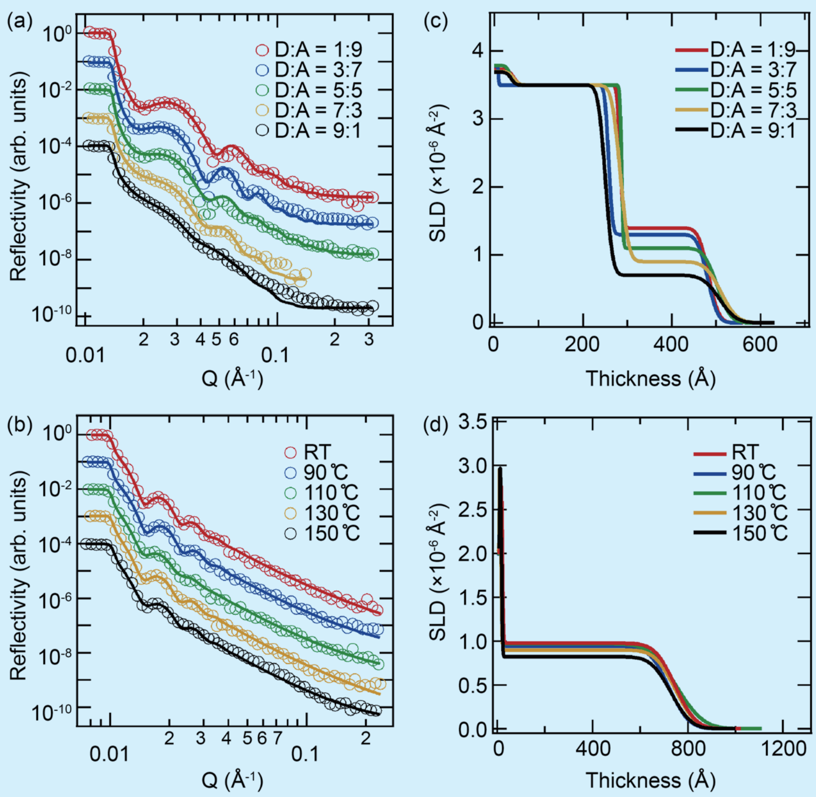

Fig. 1: (a) NR profiles and (c) corresponding SLD profiles of PffBT4T-2OD:ITIC BHJ films with different donor/acceptor ratios (1:9, 3:7, 5:5, 7:3, and 9:1) on the quartz-coated glass substrates. The individual data points and solid lines represent the experimental data and fitting results, respectively. The NR curves have been offset for clarity. (b) NR profiles and (d) corresponding SLD profiles of PffBT4T-2OD:ITIC (5:5) BHJ films on the Si wafers annealed from RT to 150°C. [Reproduced from Ref. 1]

the interface of the film is maintained. The corresponding SLD value ($0.96 \pm 0.05 \times 10^{-6}$ Å^{-2}) of the PffBT4T-2OD:ITIC BHJ layer also remains unchanged at this temperature. At 150°C, the fringes near Q = 0.025 Å^{-1} become indistinct, suggesting an increased diffusive interface between the air and the film, accompanied by a decrease in the SLD value to 0.81×10^{-6} Å^{-2}. These results indicate that interface diffusion of the PffBT4T-2OD:ITIC BHJ layers is initiated after annealing at 150°C.

To understand the phase behavior of BHJ blends, the individual donor and acceptor materials were examined under the same annealing conditions. The NR curves and SLD profiles of pristine PffBT4T-2OD films on the Si wafer with different annealing temperatures are shown in **Figs. 2(a) and 2(c)**. The fringes remain unchanged as the annealing temperature increases. The SLD profiles show that a thickness of 614 ± 9 Å and surface roughness of 30 ± 1 Å are retained after thermal treatment. These results suggest that even when the annealing temperature exceeds 90°C, the highly active side chains of PffBT4T-2OD do not induce significant vertical morphological changes in the films. On the other hand, **Figs. 2(b) and 2(d)** display the NR patterns and SLD profiles of pure ITIC thin films. The fringes are observed within the Q-range of 0.01 to 0.03 Å^{-1} for temperatures between 90 and 130°C. The corresponding film thickness and roughness are about 554 ± 10 and 106 ± 9 Å, respectively. The NR patterns become less distinct after thermal annealing at 150°C. In addition, there is little change in the position of the Kiessig fringes, indicating that there is little change in the ITIC film thickness. The thickness was set to 555 Å with limits of ±5 Å, and then the SLD value and interfacial roughness were fitted. The SLD value decreased to 0.75×10^{-6} Å^{-2} along with an increase in roughness to 139 Å. These results suggest that interface diffusion begins at 150°C, likely driven by intrinsic agglomeration of the ITIC molecules rather than by interactions with the substrate. Additionally, even brief annealing at this temperature appears to induce ITIC nanocrystal reorganization, leading to variations in the vertical morphology of the thin film.

In summary, the study demonstrated the diffusive interfaces of the PffBT4T-2OD:ITIC BHJ thin films emerging when the annealing temperature exceeds 150°C primarily because of ITIC aggregation within the blends. Thermal annealing serves as a critical post-treatment process for removing residual solvent and optimizing phase distribution in BHJ thin films. Within a brief annealing period, the morphology of PffBT4T-2OD:ITIC BHJs are influenced by ITIC nanoclusters. The findings suggest that the initial unfavorable mixing contributes to the instability of ITIC molecules during annealing, adversely affecting power conversion efficiency and device stability. It is essential to consider thermal instability and processing conditions for the enhanced performance of OSCs for promising BHJs incorporating ITIC-based small molecules. (Reported by Tzu-Yen Huang)

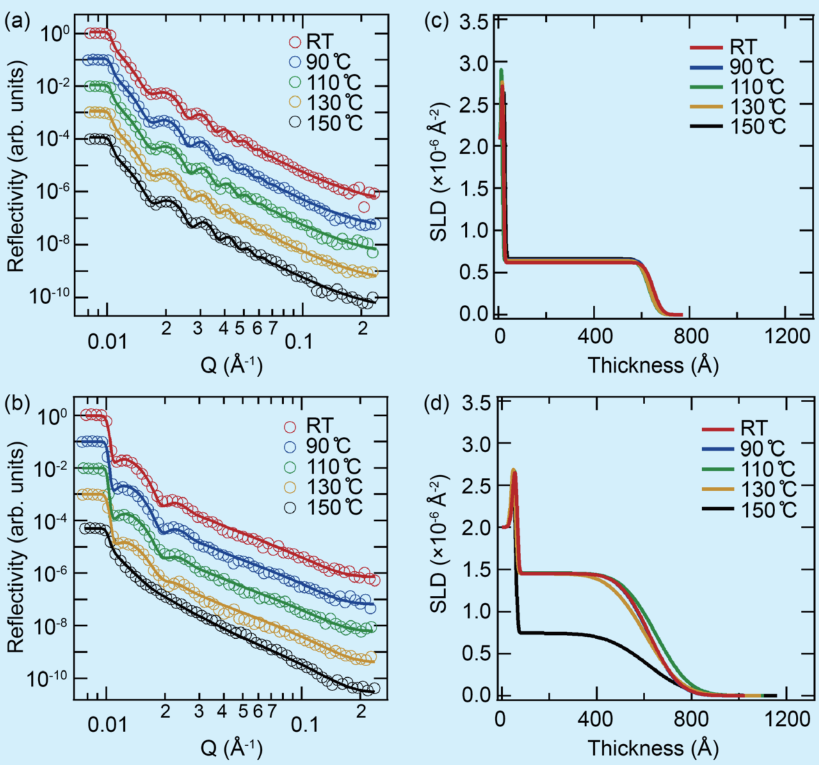

Fig. 2: NR curves and the corresponding SLD profiles for pristine (a,c) PffBT4T-2OD and (b,d) ITIC films on the Si wafers annealed from RT to 150°C. [Reproduced from Ref. 1]

This report features the work of Tzu-Yen Huang and his collaborators published in ACS Appl. Nano Mater. 7, 17588 (2024).

ANSTO SPATZ – Neutron Reflectometer

- NR
- Polymers, Morphology, Interfaces, Thin Films

Reference

1. T. Y. Huang, A. P. Le Brun, B. Sochor, C. M. Wu, Y. Bulut, P. Müller-Buschbaum, S. V. Roth, Y. L. Yang, ACS Appl. Nano Mater. **7**, 17588 (2024).