Solution-Grown Aligned C_{60} Single-Crystals for Field-Effect Transistors

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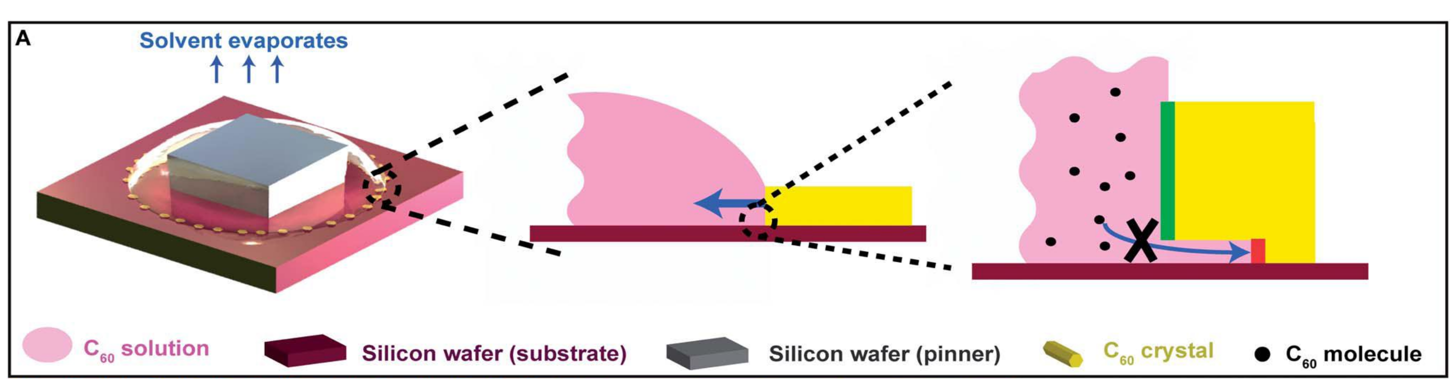
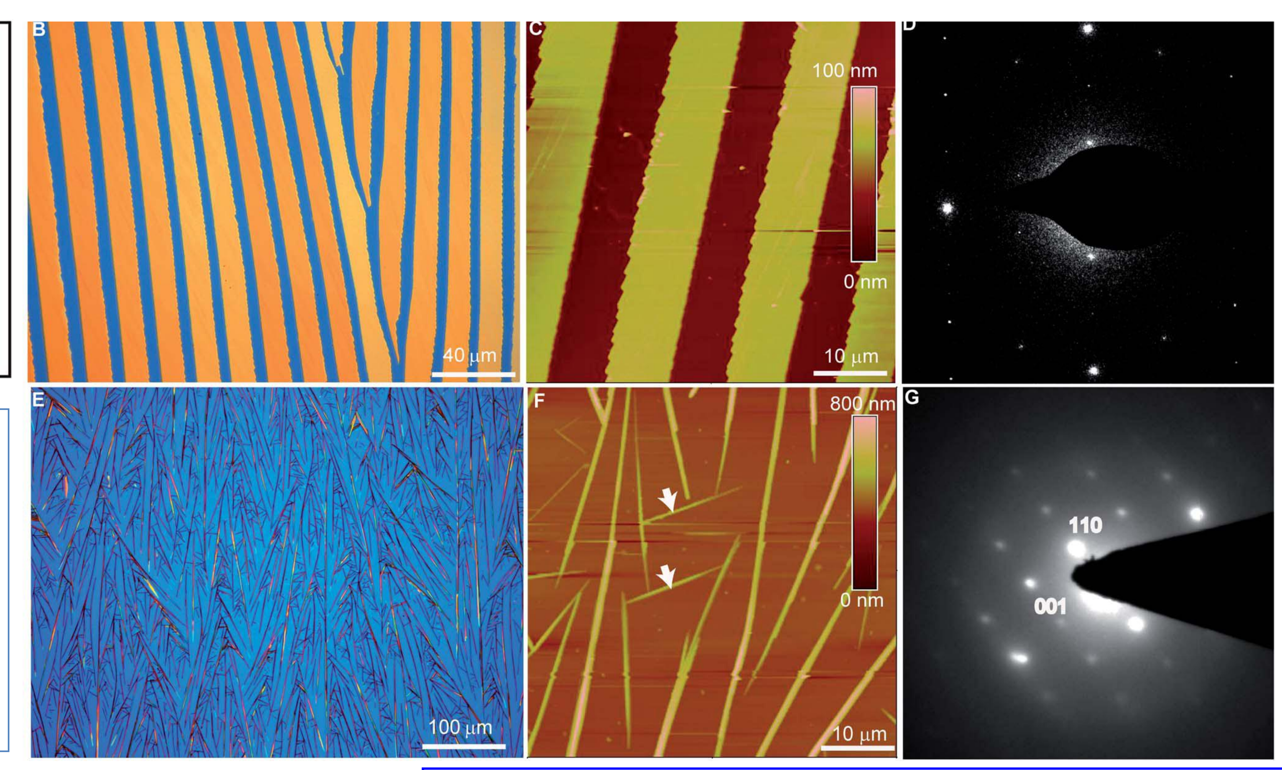
Introduction

Single crystals of C_{60} have been widely prepared previously. However, their electronic properties are much less frequently studied, though C_{60} is known as an outstanding electronic material. Also, the reported electron mobility values (~10^{-2} $cm^2V^{-1}s^{-1}$) of C_{60} single-crystals are unexpenctedly low possibly due to the difficulties in the fabrication of single-crystal devices. We have recently reported a droplet receding method for the solution-grown C_{60} single-crystals with mobilities above 1 $cm^2V^{-1}s^{-1}$. Here we systematically investigate the effect of the solvent and surface properties of the substrate on the growth of the C_{60} single-crystals. On the well-wet FET substrates, well-aligned C_{60} needle-like and ribbon-like single-crystals were grown from suitable solvents (m-xylene or a mixed solvent of m-xylene and CCl_4). Besides, we also successfully prepared single crystalline p-n junctions with this solution method and ambipolar charge transport properties were investigated.



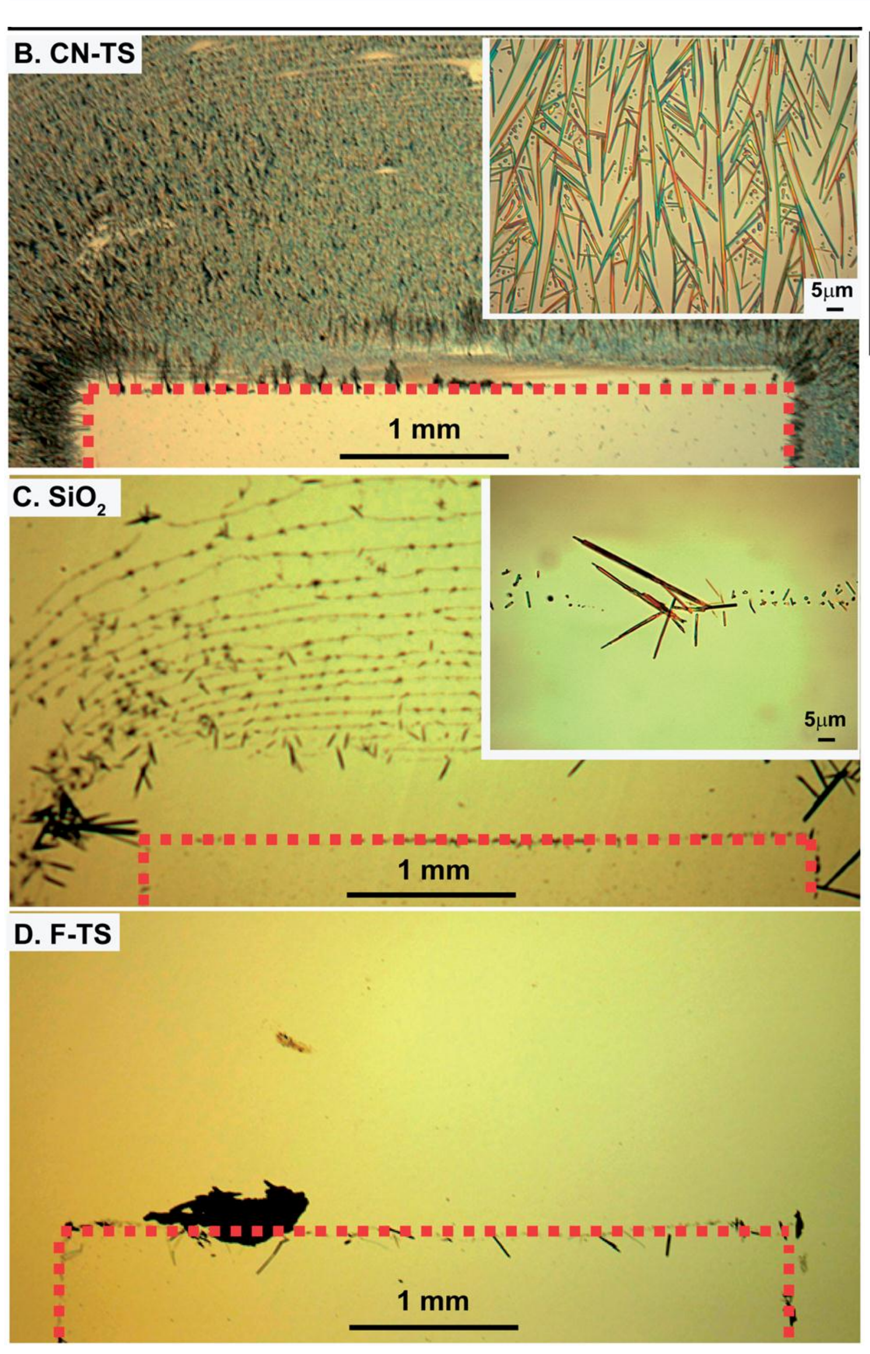
Schematic presentation of the droplet-pinned crystallization (DPC) method where a droplet of C_{60} solution is pinned by a silicon wafer. While the solvents evaporate, C_{60} crystals nucleate near the contact line of the droplet and grow along the receding direction towards the center, resulting in aligned crystals.

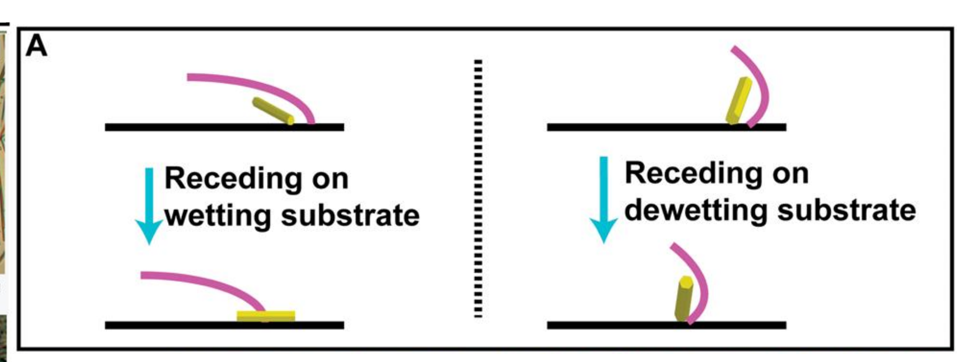


With a typical concentration of 0.4 mg/mL in different solvents, well-aligned ribbon-like (mix solvent of m-xylene and CCl_4) and needle-like (m-xylene) C_{60} crystals were obtained in-situ on the FET substrates.

Optical microscope and AFM images show the morphology of the crystals and the SAED patterns confirm the single crystallinity of the crystals. (from left to right)

Effects of wettability on crystallization

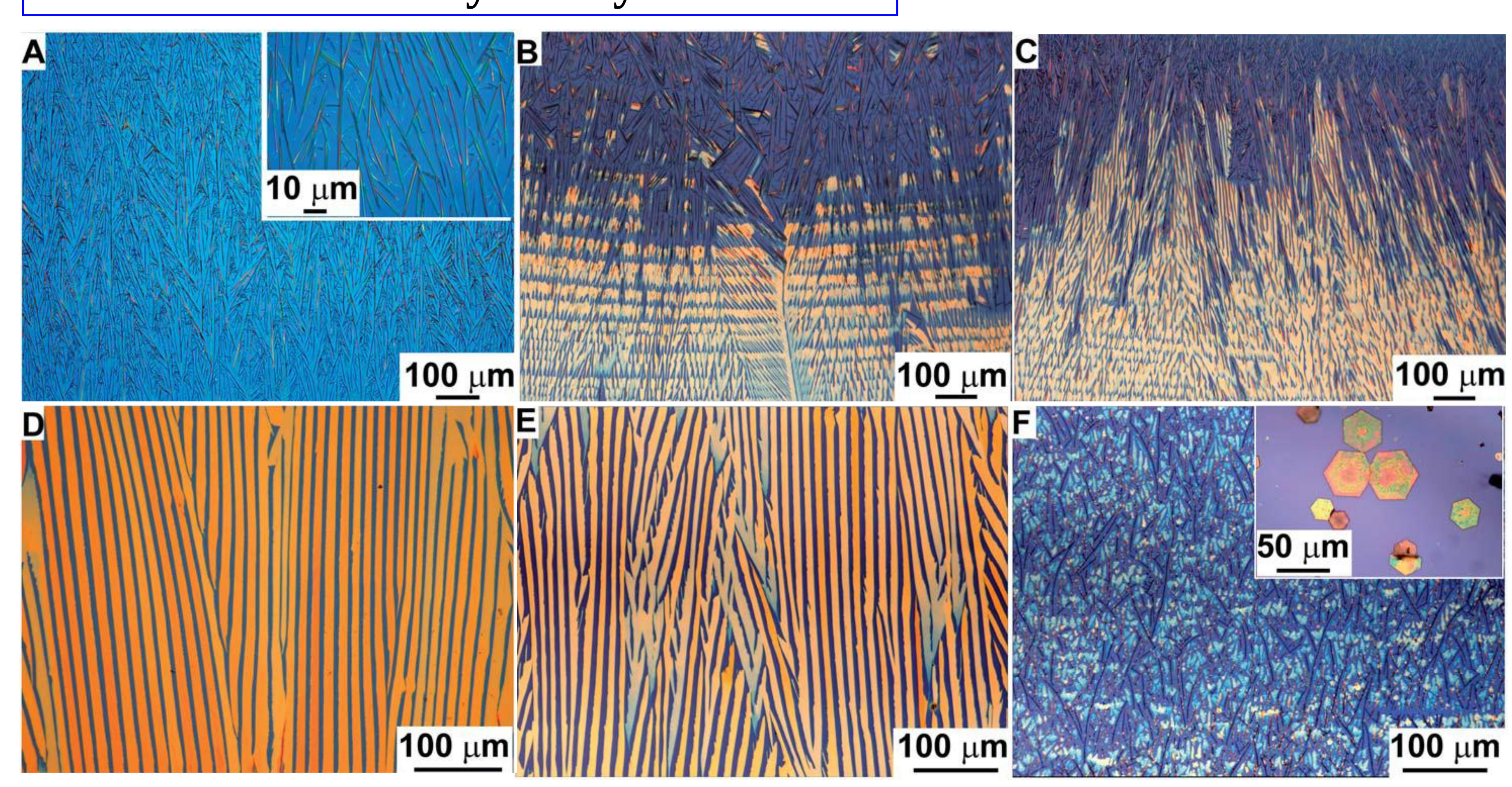




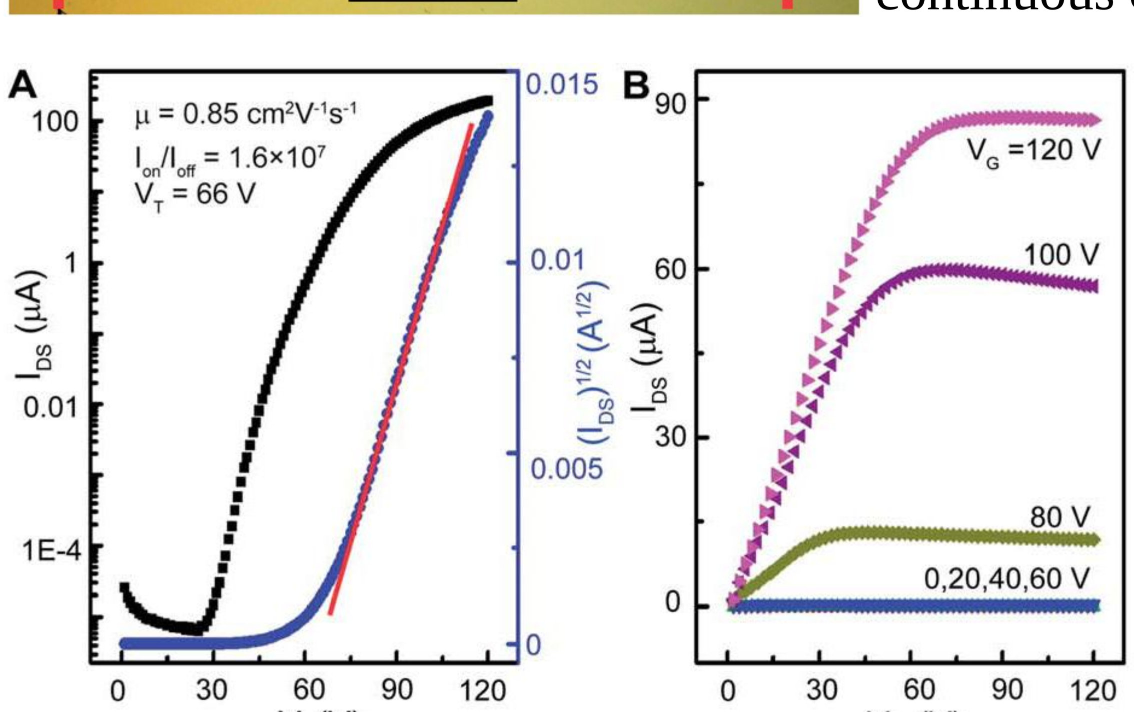
Substrates left are modified with CN-TS silane (B), bare SiO_2 (C), and modified with F-TS silane (D). CN-TS modified substrate has better wettability than the other two, thus better crystal attachment and alignment were obtained from 0.4 mg/mL C_{60} m-xylene solution.

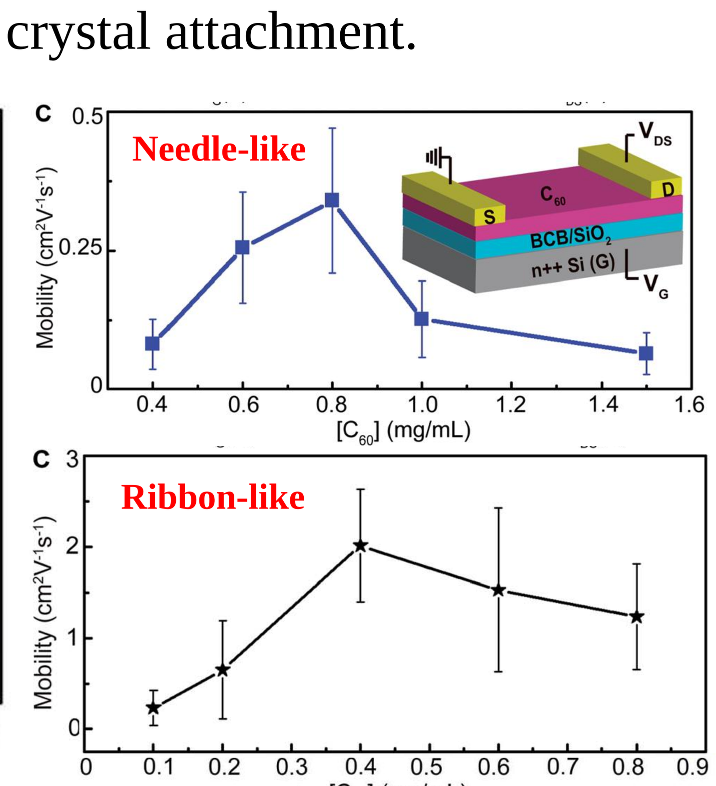
The effects of surface wettability on the DPC process can be explained by the schematic representation of the contact line on the wetting and dewetting surface above, in which a well-wetting droplet will increase the contact area between crystal and substrate thus favoring continuous crystal attachment.

Effects of wettability on crystallization



Different solvents result in different morphology of the C_{60} crystals. Needle-like (A) and disk-like (F) C_{60} crystals can be grown from pure m-xylene and CCl_4 respectively. When a mix of m-xylene and CCl_4 was applied, C_{60} crystals transform from needle-like to ribbon-like morphology from (B) to (E) with an increase of CCl_4 volume ratio in the mix solvent. Substrates used here are modified with BCB which ensures the good wettability and favors n-channel FETs.





FETs based on needle-like and ribbon-like C_{60} crystals were fabricated and tested in N_2 glovebox. With different C_{60} concentration, the electron mobilities are summarized in charts left. In needle-like crystal based FETs, mobility reached a peak value at 0.8mg/mL and decreased instead with higher concentration due to the steps formed on the bottom of the crystals. While in the ribbon-like case, with the increasing concentration, the increase in ribbon width and height result in decreasing and increasing contact resistance respectively. The interplay of these opposite effects resulted in the maximum mobility at the intermediate width (8.2 ± 3.4 mm) and height (57 ± 7 nm) of the ribbons.

Conclusions

We have demonstrated high-mobility FETs based on solution-grown C_{60} single-crystals using the DPC method. During crystallization, good wetting of C_{60} droplets on substrates, suitable solvents, and the intermediate crystal thickness were critical to induce well-aligned ribbon-shaped C_{60} single-crystals with an electron mobility as high as 2 $cm^2V^{-1}s^{-1}$, which is among the highest reported values for organic semiconductors. Besides, we also successfully prepared single crystalline p-n junctions with C8-BTBT (p-type) and C_{60} (n-type) from solution. FETs based on the junctions exhibit ambipolar charge transport property.

References

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[2] HY Li, CC Fan, HZ Chen, et al., *J. Mater. Chem. C*, **2014**, 2, 3617-3624